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The GRIP deuterium-excess record

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Abstract

Ice cores from Greenland and Antarctica are ideal archives for retrieving long time series of deuterium-excess ($d = \delta D — 8 * \delta^{18}O$), a parameter influenced by conditions prevailing in the oceanic regions which provide moisture for polar snow. The central Greenland GRIP deuterium-excess record has recently been interpreted in terms of oceanic source temperatures both for the Holocene and for the last glacial period, this approach being less straightforward for the latter period because of changes in the precipitation seasonality between glacial and interglacial periods. This article examines why a conventional, or sea surface temperature, interpretation of the GRIP excess record seems inconsistent with inferred site and source temperature changes. In addition, the GRIP excess record is extended back into the penultimate glacial period and we assess its geographic significance through a comparison with existing Dye 3 and North GRIP data. We examine why low $\delta D/\delta^{18}O$ slopes observed during glacial times are associated with low deuterium-excess values. Similarities between the Greenland GRIP and Antarctic Vostok excess records are discussed in terms of potential links with insolation and insolation gradient changes. Finally, the isotope records in specific DO events are examined in light of intruiging differences between the isotope ratios (δD or $\delta^{18}O$) and the excess records that may result from a feedback mechanism linked with freshwater oceanic input.

1. Introduction

The deuterium-excess parameter, $d = \delta D - 8\delta^{18}O$, defined by Dansgaard (1964) and hereafter called the excess, characterizes the isotopic composition of precipitation in $\delta D/\delta^{18}O$ space (δD and $\delta^{18}O$ are the water isotopic compositions expressed in δ units per mill versus V-SMOW, the Vienna Standard Mean Ocean Water). The scaling factor of 8 is derived from the empirical Meteoric Water Line (MWL), $\delta D = 8\delta^{18}O + 10$, which describes very well present-day precipitation (Craig, 1961). Modern excess values in precipitation thus have an average value of 10, but vary both spatially and temporally at all timescales. Whereas the degree of moisture removal from a cloud, a process strongly controlled by temperature, is the key parameter for the distribution of either δD or $\delta^{18}O$ in precipitation (Dansgaard, 1964); excess values are largely influenced by conditions prevailing in the oceanic moisture source regions where this precipitation originates (Craig and Gordon, 1965; Merlivat and Jouzel, 1979). Reconstructing excess time series thus offers the potential of estimating how oceanic conditions prevailing in evaporative source areas have varied in the past.

Polar ice cores are ideal archives of excess time series. They can provide continuous and detailed records of δD and $\delta^{18}O$ at various timescales. Due to the relative simplicity of atmospheric processes in polar regions, they allow climatic information relating to the precipitation site and to the oceanic moisture sources to be disentangled. This co-isotopic approach has been quite successfully followed for Antarctic cores since the publication of the first Dome C excess record that extended back to the last glacial period (Jouzel et al., 1982). Longer time series are

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now available both for the Vostok (Vimeux et al., 1999, 2001a, b) and Dome F (Watanabe et al., 2003; Uemura et al., 2004) records, covering three and four glacial–interglacial cycles, respectively. The new EPICA Dome C core, for which the excess record (Stenni et al., 2001, 2004) currently covers the last 45 ka, now offers the possibility to extend this record back to 800 ka (EPICA Members, 2004). Numerous collections of excess values obtained from surface or Holocene samples have also been published (Jouzel et al., 1983; Petit et al., 1991; Qin et al., 1994; Delmotte et al., 2000; Vimeux et al., 2001b; Masson-Delmotte et al., 2004). For Greenland (Fig. 1), excess values were first determined for surface samples and for samples from the Late glacial and from the last climatic transition in the Dye 3 core (Dansgaard et al., 1989; Johnsen et al., 1989). Other published studies addressed surface samples (Fischer et al., 1998) as well as the GISP2 (White et al., 1997) and GRIP ice cores (Hoffmann et al., 1998a, 2001) extending through the last millenium. Limited GISP2 excess data are also available for the last climatic transition (Taylor et al., 1997). Studies are ongoing on the recently drilled North GRIP core with data currently available for the entire Holocene (Masson-Delmotte et al., 2005a) and for selected Dansgaard/Oeschger (hereafter DO) events (Landais et al., 2004a, 2006).

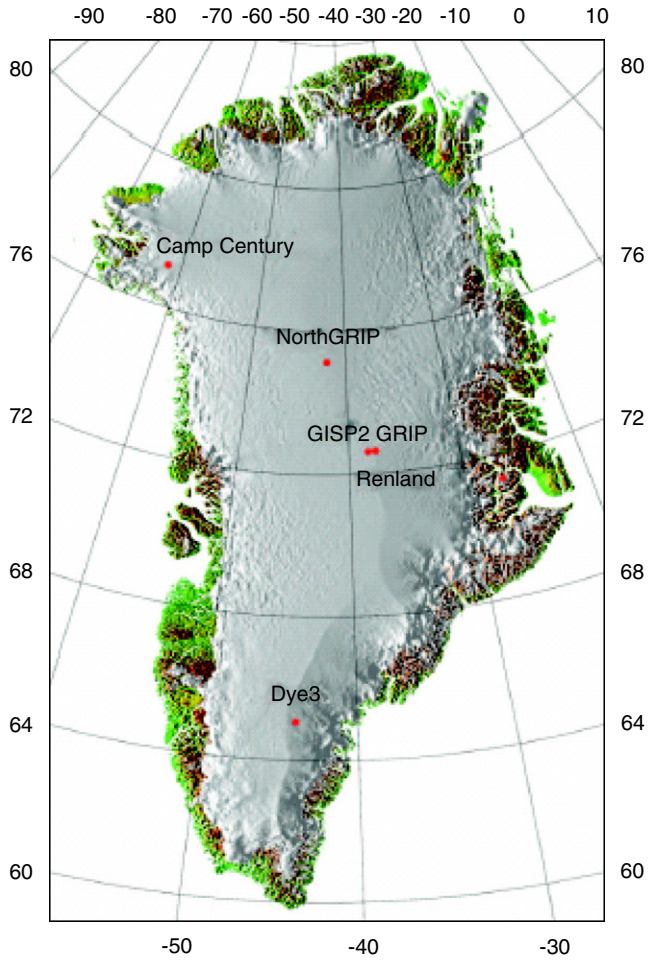

Fig. 1. Greenland sites.

In this article, we present and discuss the excess record available for the entire length (more than 3 km) of the ice core drilled for the European GRIP ice core project. We review previously published results dealing with the Holocene (Masson-Delmotte et al., 2005a) and with the last glacial parts of the record (Jouzel et al., 2005; Masson-Delmotte et al., 2005b), and extend these studies through a comparison with Dye 3 and North GRIP excess data. We then examine general characteristics of the GRIP excess record, pointing in particular to similarities between the GRIP and Vostok excess records and to possible links between these records and with insolation and insolation gradient changes. Finally, we focus on the nature of specific DO events that show intriguing differences between the isotopic (δD or δ^{18}O) and the excess records.

2. Deuterium-excess in precipitation: general principles

The basic reason for changes in the deuterium-excess of precipitation is that isotopic fractionation of HDO and $H_2^{18}O$ in the water cycle depends on differences in two physical properties: the water vapour saturation pressures and the molecular diffusivities of water species in air, properties which give rise, respectively, to the equilibrium and kinetic effects (Dansgaard, 1964; Merlivat and Jouzel, 1979). Incorporating these two types of fractionations into isotopic models of precipitation ranging from simple models (Dansgaard, 1964; Merlivat and Jouzel, 1979) to complex atmospheric General Circulation Models (GCMs) equipped with water isotope functions (Jouzel et al., 1987; Hoffmann et al., 1998b) results in a good match between present-day spatial and seasonal observations of isotopes and those predicted by the models. These models show that the large-scale δD and δ^{18}O variations are driven primarily by the equilibrium effect. This results from the fact that the equilibrium effect directly related to the saturation vapour pressure is 8–10 times more efficient for deuterium than for oxygen 18, giving rise to the global slope of 8. The observed MWL is remarkably linear. This linearity is aided, in part, by the use of δ values in expressing isotope ratios: a theoretically expected increase of the slope with decreasing temperature is partly compensated by a concurrent decrease of the value of $(1+\delta D)/(1+\delta^{18}O)$ as HDO is depleted to very low levels (Jouzel et al., 1991).

The relatively subtle differences of isotope ratios with respect to the MWL, which translate into a variability of the excess in a $\delta D/\delta^{18}O$ diagram, are largely governed by the kinetic effect. Unlike the equilibrium effect, the magnitude of the kinetic effect is nearly the same for HDO and $H_2^{18}O$, as the molecular diffusivities in air of these molecules are nearly equal. The kinetic effect must be taken into account for processes that take place out of thermodynamic equilibrium, e.g. when the water vapour pressure is under- or over-saturated over liquid water or over ice. Most important at the global scale is the kinetic

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effect associated with typical under-saturation of atmospheric water with respect to the oceanic surface. Two other processes for which this effect is at play during the atmospheric water cycle, namely evaporation of water drops under cloud base (Stewart, 1975) and snow formation (Jouzel and Merlivat, 1984), have important local influences. As a result, sea surface conditions (Merlivat and Jouzel, 1979) that define evaporation such as relative humidity, temperature and, to a lesser degree, wind speed (or the condition of the diffusional boundary layer), are key parameters for the deuterium-excess of atmospheric water vapour and precipitation. In turn, excess data contain information on the variations of these oceanic variables.

3. The deuterium-excess profile

Bedrock was reached in 1992 at the GRIP site (Fig. 1) and a continuous $\delta^{18}O$ ice record was published the following year (Dansgaard et al., 1993). Deuterium measurements were then performed at LSCE Saclay on the same samples (every 55 cm for a total 5495 of samples) providing a full deuterium-excess record in 1995. These δD and $\delta^{18}O$ records which, as expected, closely resemble each other, are reported in Fig. 2 along with the deuterium-excess parameter. At that time, we were unsuccessful in providing a quantitative interpretation of this excess profile. Our initial attempt to estimate site and source temperature changes from δD and $\delta^{18}O$ measurements led to obvious inconsistencies (see below), and thus we deferred its publication. It was only recently that Masson-Delmotte et al. (2005b) showed the importance of including seasonality in interpreting excess records, both for the accumulation of snow and for its isotopic composition, opening the way for a full interpretation of the GRIP excess record.

While a comparison between the $\delta^{18}O$ profiles measured along the two summit cores (GRIP and GISP2) shows that the records are basically undisturbed back to ~100 ka BP, there is now ample evidence for stratigraphic disturbance of the lowest part of the two cores (Bender et al., 1994; Fuchs and Leuenberger, 1996; Chappellaz et al., 1997; Landais et al., 2004b). Thus, the lowest part of the GRIP record (shaded area in Fig. 2) could not initially be exploited, because ice layers are clearly disturbed due to the proximity of the bedrock. We use here the reconstruction proposed by Landais et al. (2003) for the disturbed part of the GRIP ice core. These authors compared the composition of air bubbles (concentration in methane and isotopic composition of atmospheric oxygen) for these bottom sections with their counterpart in the Vostok Antarctic profiles. They identified ice from the penultimate glacial maximum corresponding to Marine Isotope Stage 6 (MIS 6) 190–130 ka BP (thousand of years Before Present) and provided a rough reconstruction of the Last Interglacial and glacial inception. Although this reconstruction is quite coarse (16 samples between 111 and 145 ka BP at GRIP), it allows us to extend the excess record back to MIS 6 (Fig. 3), albeit on a discontinuous basis.

Fig. 3 shows the GRIP excess record at a 200 yr resolution using the revised GRIP timescale (SS09sea) of Johnsen et al. (2001). Values range between 4.2‰ and 10.6‰ with the highest extreme values (not shown) for individual 55 cm samples being 12.6‰ during the Holocene and 2.1‰ during the Last Glacial Maximum (LGM, ~20 ka BP). A 55 cm sample corresponds to an average of 4 yr for the Holocene, and to about 25 and 100 yr for the LGM and the period around 100 ka BP, respectively. Once averaged over 200 yr (Fig. 3), the highest values (above 10‰) are found in the Holocene, the Younger Dryas (around 12 ka BP), around 40 ka BP (MIS 3), during most of the warm interstadials MIS 5a and 5c, and during the warmest part of the Eemian (MIS 5e). Lowest values (below 5‰) are observed between 42 and 51 ka BP. For the very bottom part of the ice core (below 2930 m), excess values vary around a mean value of 9‰, close to the average value of the last glacial–interglacial cycle. Together with average values also obtained for either δD or $\delta^{18}O$ profiles, this supports the idea that these very bottom layers resulted from a mixture of precipitation formed under different climates. The deepest 6 m of basal silty ice (below 3022.5 m) have an excess close to 8 (not shown), which is thought to originate from snow which precipitated at the ground surface in the absence of the ice sheet (Souchez et al., 1994).

4. A conventional interpretation of the GRIP δD and $\delta^{18}O$ records

The conventional interpretation of δD and $\delta^{18}O$ ice core time series is based on a Rayleigh-type model that approximates the processes that affect an isolated air mass. Such a model combines isotopic equations for evaporation at the sea surface, and for the formation of liquid and subsequently of solid precipitation, including the coexistence of liquid and solid phases (mixed cloud model developed by Ciais and Jouzel, 1994). This model enables the isotopic content of polar precipitation, δD_{ice} and $\delta^{18}O_{ice}$, to be estimated as a function of the conditions prevailing at the oceanic source (isotopic composition of the ocean, relative humidity, temperature and windspeed) and at the precipitation site (temperature of snow condensation, strength of the temperature inversion). Other model parameters account for the path followed by the air mass and microphysical aspects, namely the amount of condensate retained in the airmass, the temperature thresholds of mixed cloud formation, and the supersaturation of vapour with respect to ice which gives rise to a kinetic isotopic effect at snow formation (Jouzel and Merlivat, 1984).

This isotopic model can be used over a large range of microphysical parameters and atmospheric conditions, albeit with a number of simplifying assumptions. In particular, the parameterizations adopted for the

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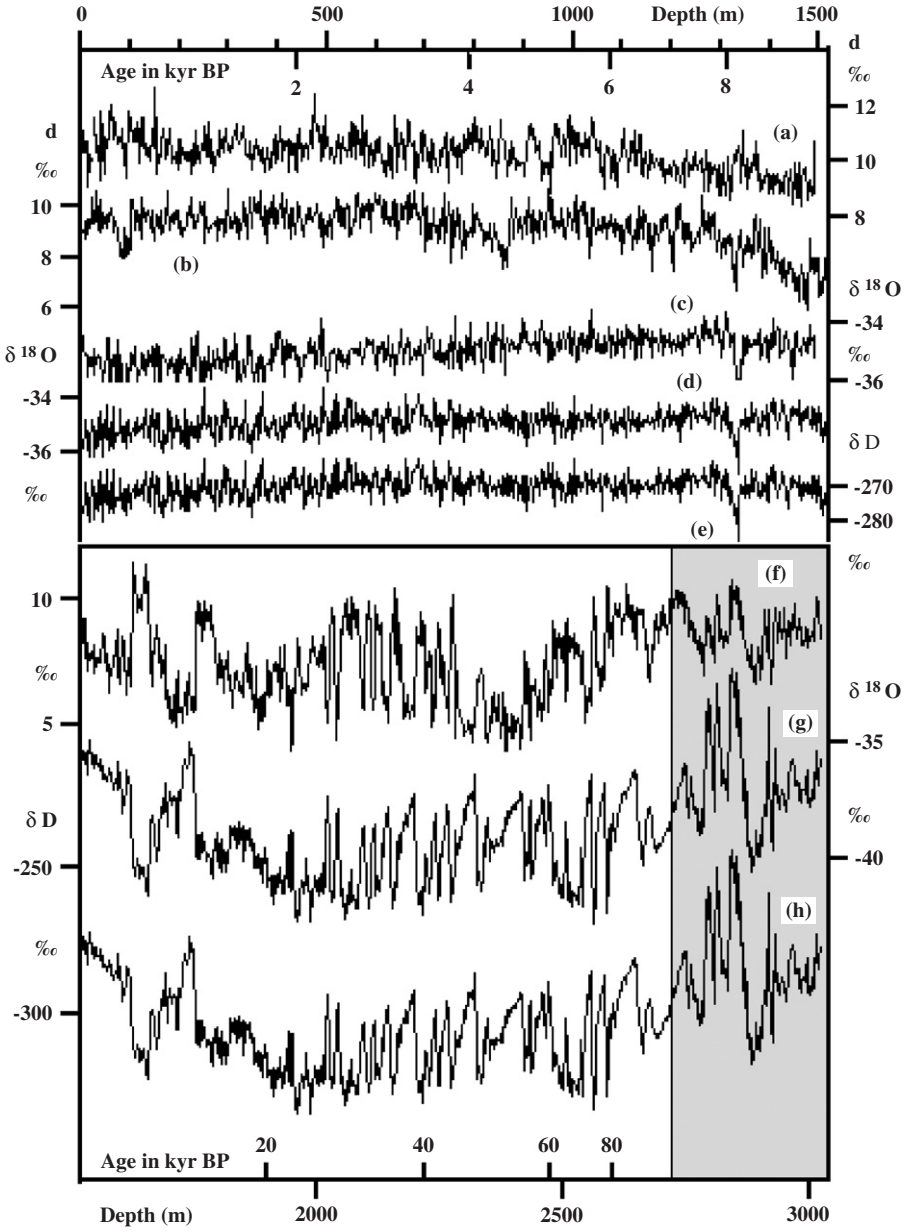

Fig. 2. Variation with respect to the GRIP depth (top and bottom linear scales with some ages indicated) of the isotopic profiles measured at: North GRIP (adapted from Masson-Delmotte et al., 2005a) with (a) the excess and (c) the oxygen 18 profiles (top scale). GRIP with the oxygen 18 record adapted from Dansgaard et al. (1993). Curves d and g correspond, respectively, to the upper (top scale) and lower (bottom scale) parts of the core. The same is done for the deuterium record (this work) with curves e (upper part) and g (lower part). The deuterium-excess, $d = \delta D - 8\delta^{18}O$, is derived from these two data sets with the North GRIP data (curve a reported on the GRIP timescale) and GRIP with curves e (upper part) and h (lower part). $\delta^{18}O$ and δD are expressed in ‰ with respect to V-SMOW (the Vienna Standard Mean Ocean water), d being expressed in ‰. Analytical accuracies (1σ) are of 0.5‰ and 0.07‰ for δD and $\delta^{18}O$, respectively, corresponding to an accuracy of 0.7‰ for the excess. The GRIP records are disturbed below a depth of ~2720 m (shaded area corresponding to an age of ~100 ka BP).

supersaturation of vapour during snow formation and for the strength of the temperature inversion are assumed to be valid for different climate states. It can be shown, however, that whereas δD_{ice} and $\delta^{18}O_{ice}$ depend primarily on the temperature of the site (T_{site}) and to a lesser degree on the temperature of the oceanic source (T_{source}), the reverse is the case for the excess, d_{ice}. The dependence on T_{source} largely arises from the fact that, in the simple model, T_{source} essentially determines the temperature at which cloud condensation starts and hence the degree of moisture removal experienced along a monotonically cooling trajectory. These two relationships observed in simple models have been supported by experiments performed using GCMs equipped with water isotope equations (Koster et al., 1992; Armengaud et al., 1998; Delaygue et al., 2000). Regardless of the complexity of the model used, it can be shown that the isotopic composition of polar snow, $\delta^{18}O_{ice}$ and δD_{ice} can be well expressed as a function of three main

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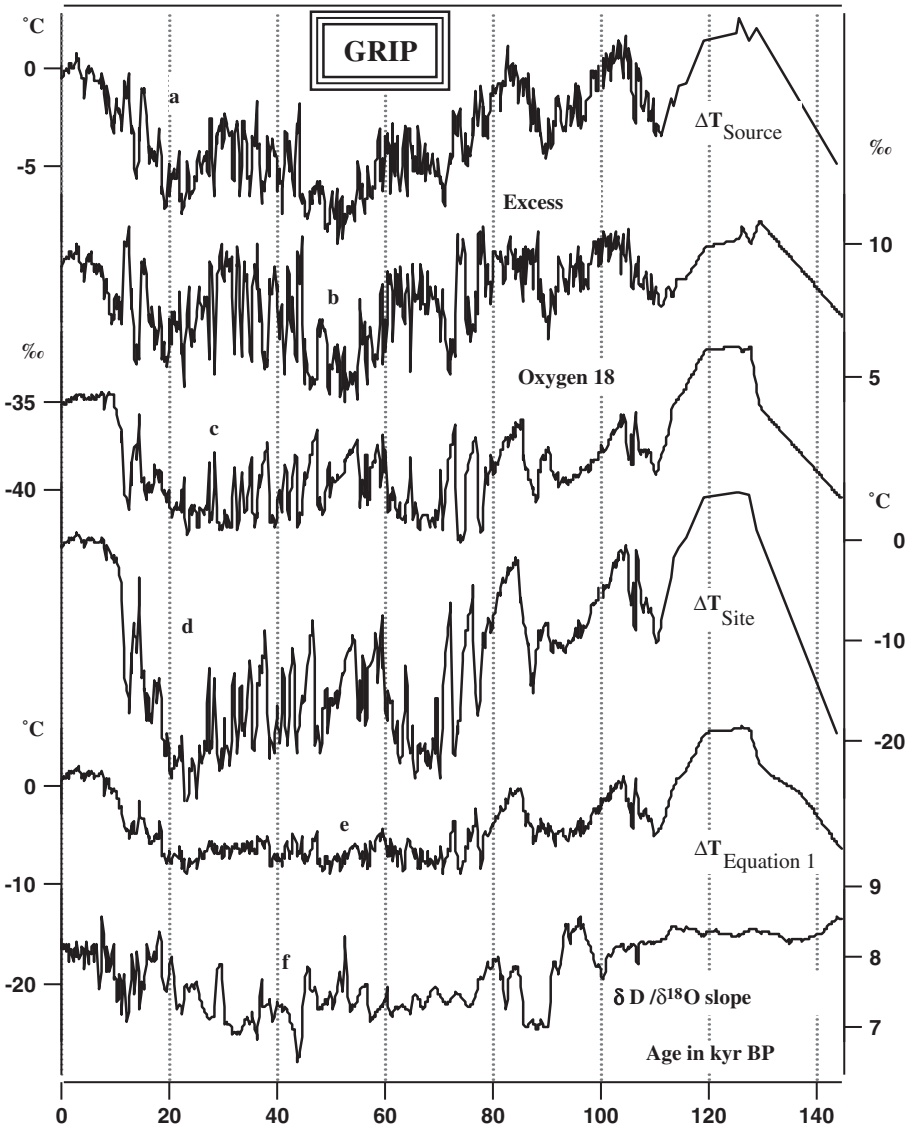


Fig. 3. Comparaison of time series (200 yr constant time step in all cases using the SS09sea timescale derived by Johnsen et al. (2001) with from top to bottom: (a) the source temperature change, ΔT_{Source}, as derived by Masson-Delmotte et al. (2005b), extended beyond 100 ka BP, (b) the GRIP deuterium-excess record with the bottom part (below 110 ka BP) reconstructed from gas measurements (Landais et al., 2003), (c) the GRIP oxygen 18 record (idem), (d) the site temperature change, ΔT_{Site}, as derived by Masson-Delmotte et al. (2005b) extended, as ΔT_{Source}, beyond 100 ka BP, (e) the site temperature change which would be derived applying Eq. (1), and (f) the $\delta D/\delta^{18}O$ slope along the GRIP ice core (running value over 50 successive samples).

parameters, T_{site}, T_{source}, and the starting isotopic composition, i.e., the isotopic composition of the oceanic source.

As far as the last parameter is concerned, it is worth noting that, even at constant excess values, any change in the isotopic composition of oceanic surface waters modifies the excess of water vapour above the ocean (Werner et al., 2000a) and thus that of precipitation worldwide (Delaygue, 2000). Again simple and complex models both show that a typical glacial to interglacial change of 1‰ in $\delta^{18}O$ results in an increase of the GRIP excess of about 2‰. Corrections for changes in the isotopic composition of the ocean over time caused by the formation of isotopically depleted ice sheets can be applied, and here we use the sea level record of Waelbroeck et al. (2002) for this purpose. However, no data are available to correct for an additional possible effect due to the local lowering of the surface water isotopic content as a result of massive iceberg discharge. Experiments conducted using an oceanic isotopic model (Roche and Paillard, 2005) suggest that this additional effect should be quite low, because the areas most isotopically influenced by iceberg discharge will also experience dramatically reduced evaporation.

It follows that, at least in the model world, both the site and source temperatures can be estimated using the combination of δD or $\delta^{18}O$ and excess. The coefficients of this regression are site dependent, with slightly different values for Antarctica and Greenland. In this latter case, Masson-Delmotte et al. (2005a) derived the following two equations in which the subscript corr indicates that changes in the isotopic composition of oceanic water are taken into

account (Δ refers to deviations from modern conditions):

$$\Delta T_{site} = 1.32\Delta\delta^{18}O_{corr} + 1.04\Delta d_{corr}, \quad (1)$$

$$\Delta T_{source} = 1.58\Delta d_{corr} + 0.29\Delta\delta^{18}O_{corr}. \quad (2)$$

In our initial approach to interpreting the δD and $\delta^{18}O$ GRIP data in the mid-1990s, we focused on the first aspect, correcting ΔT_{site} estimates for concurrent changes in source temperature, ΔT_{source}. However, this correction produced very small DO events in the derived temperature record, with some in the period from 20 to 60 ka BP completely eliminated (as illustrated in Fig. 3, curve e). This suggestion of feeble temperature changes associated with DO events contrasts sharply with drastic and abrupt changes observed in other core properties, such as in the calcium content, an indicator of concurrent changes in atmospheric circulation and in the hydrological cycle (Fuhrer et al., 1999), and one also identified in records from the North Atlantic (Bond et al., 1992, 1993). In addition, correction for changes in ΔT_{source} failed to explain the very pronounced ΔT_{site} increase associated with the last glacial–interglacial transition. Whereas studies based on paleothermometry measurements consistently provided estimates of temperature changes greater than 20 °C (Cuffey et al., 1995; Johnsen et al., 1995), our estimates were twice as low, as illustrated by comparison of curves e and d in Fig. 3.

Overall, therefore, we regarded the isotope-based reconstruction of T_{source} as erroneous. This conclusion was later fully supported by independent estimates of ΔT_{site} associated with DO events, derived from argon and nitrogen isotope measurements. Indeed, the latter approach (see Landais et al., 2005 for a recent review and references herein) systematically indicates large DO associated warmings, reaching up to 16±3 °C for DO 19 (see Fig. 4c for the results covering DO 18–20) and 24. Warmings in excess of 10 °C are inferred both for the rapid changes during the last deglaciation and for the DO events within MIS 3. For example, DO 12 warming is estimated to be 12±3 °C both at GRIP (Landais et al., 2004d) and North GRIP (Huber et al., 2006). By contrast, curve 3e suggests a corresponding warming of between only 3 and 4 °C for DO12, and about 5 °C for DO 19 and 24. Indeed, armed now with independent ΔT_{site} estimates we note that applying a simple source temperature correction deteriorates rather than improves the quality of the ΔT_{site} estimates with respect to those based on the $\delta^{18}O$ profile alone, when used without such correction. Using the present-day spatially derived temperature sensitivity for $\delta^{18}O$, for example, leads to estimates of ~7 °C for DO 12 and 24, and ~10 °C for DO 19 and 24, closer to currently accepted values.

5. The crucial role of seasonality in Greenland glacial isotopic records

This approach for deriving ΔT_{site} and ΔT_{source} from co-isotopic determinations (e.g., applying Eqs. (1) and (2)) has been successfully used for interpreting Antarctic data, providing quite consistent results for both parameters. It has also been applied to the last millenium data from Greenland (Hoffmann et al., 2001). As fully discussed by Masson-Delmotte et al. (2005b), the key for the glacial–interglacial scale is to account for changes in the seasonal distribution of precipitation. Such seasonality changes were probably moderate within Antarctica between modern and glacial conditions (Krinner et al., 1997; Delaygue et al., 2000; Krinner and Werner, 2003), as well as in Greenland during the last millenium and the Holocene, so they can be ignored in the interpretation of isotopic profiles at those locations and on those timescales; they cannot be ignored in Greenland when examining glacial–interglacial time periods.

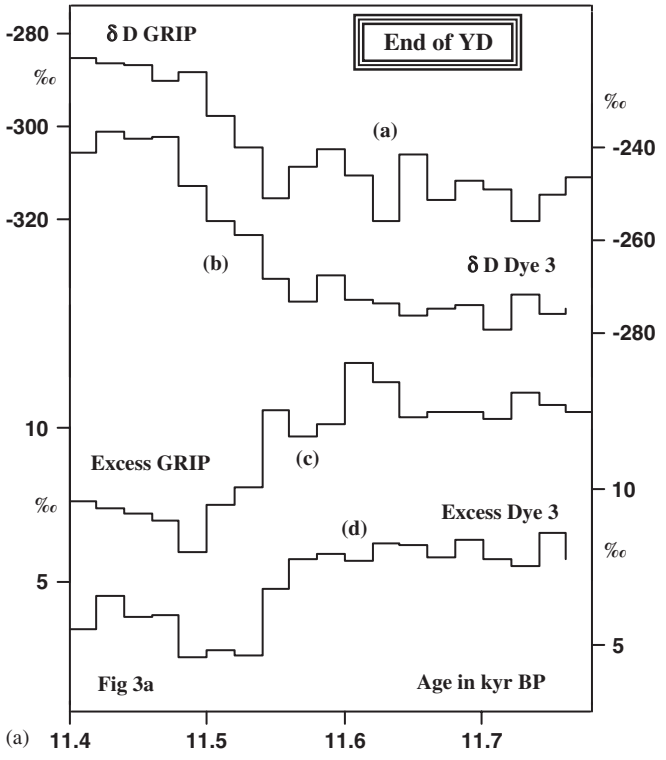
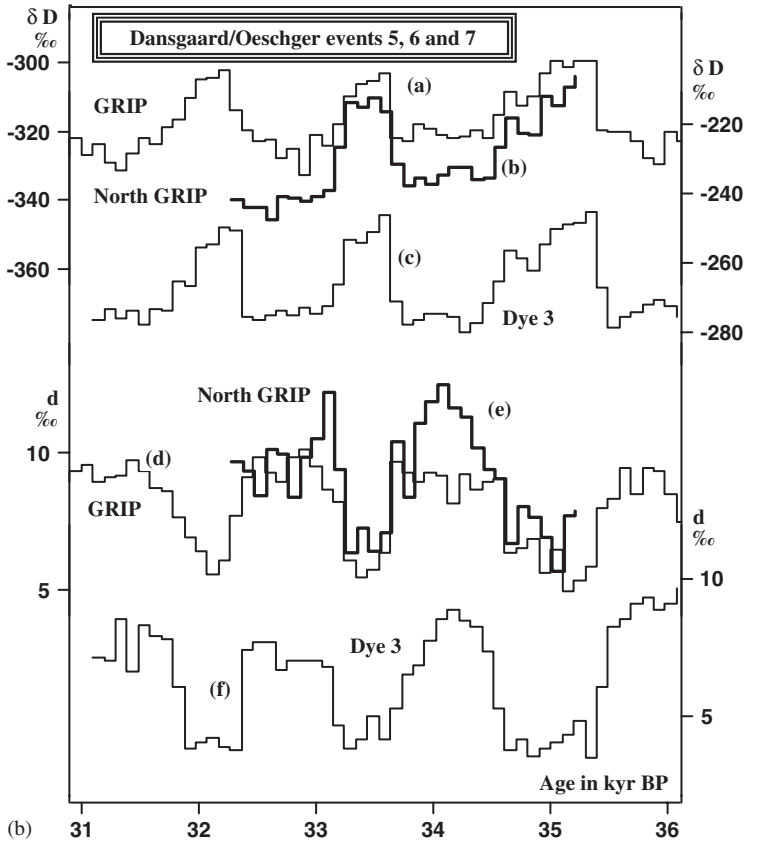


Fig. 4. (a) Comparison of the GRIP and Dye 3 (adapted from Dansgaard et al., 1989) isotopic data for the period corresponding to the end of the Younger Dryas from 11.8 to 11.4 ka BP (all reported on the GRIP timescale using a 20 yr time step) with the deuterium (a and b) and excess (c and d) being displayed in the upper and lower panels, respectively. (b) Comparison of the GRIP and Dye 3 (adapted from Johnsen et al., 1989) isotopic data for the period corresponding to DO events 6–8 (all reported on the GRIP timescale with a 100 yr time step) with the deuterium (curves a and c) and excess (curves d and f) being displayed in the upper and lower panels, respectively. Curves b and e correspond to the deuterium and deuterium-excess records for the period around DO 7. (c) Comparison of the GRIP and North GRIP (adapted from Landais et al., 2004a) isotopic data for the period corresponding to DO events 18–20 (all reported on the GRIP timescale with a 100 yr time step) with the deuterium (curves a and b) and excess (curves d and e) being displayed in the upper and lower panels, respectively. Curve c corresponds to the temperature record independently derived from nitrogen and argon isotopic measurements (adapted from Landais et al., 2004a).



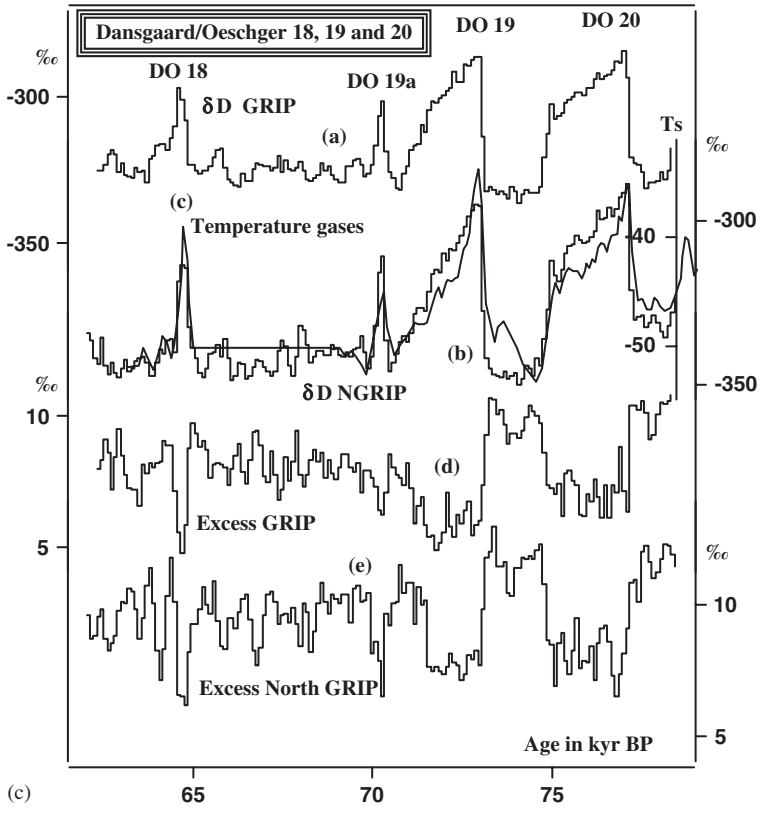


Fig. 4. (*Continued*)

It is thought that marked topographic and atmospheric circulation change occurred during the last glacial due to the presence of the Laurentide ice sheet. Combined with the extension of the sea-ice cover in the North Atlantic which makes Central Greenland a truly continental site, this promotes large changes in the seasonality of precipitation, with a shift towards a greater proportion of summer precipitation relative to winter (Fawcett et al., 1997; Krinner et al., 1997; Werner et al., 2000b). This seasonality shift convincingly explains why the conventional interpretations of the water isotope records underestimate temperature changes in Central Greenland by up to a factor of two (Cuffey et al., 1995; Johnsen et al., 1995; Dahl-Jensen et al., 1998). While Eqs. (1) and (2) are considered to be valid for individual precipitation events, they do not account for seasonality changes either in the distribution of snowfall (which in Greenland varies considerably between present-day and glacial climates) or its isotopic composition. This leads to reconstructed temperature records that substantially differ from those based on mean annual data. The large change in precipitation seasonality towards predominant summer accumulation during the glacial period coupled with enhanced seasonal temperature amplitude due to increased continentality are sufficient to explain the underestimation of ΔT_{site}. Correcting for these (Fig. 3) leads to a record that is by construction fully consistent with available independent Greenland temperature change estimates (Masson-Delmotte et al., 2005b).

The influence of the seasonal cycle on the excess record is more subtle. Because of its close link with sea-surface temperature (SST), and because ocean temperatures lag air temperatures due to the thermal inertia of the ocean, the excess record is shifted by 2–3 months with respect to the atmospheric seasonal cycle (White et al, 1988; Johnsen et al., 1989; Hoffmann et al., 1998a). As a result of this lag, the difference in excess between winter and summer is small (less than 1‰), and the main difference is between fall and spring. Thus summer–winter seasonality changes have a much weaker influence on reconstructions of ΔT_{source} dependent primarily on excess, than on ΔT_{site} dependent primarily on $\delta^{18}O$ or δD. Source temperature changes mimic the initial excess record (Fig. 3) with a glacial–interglacial amplitude of ~6 °C and rapid changes of 2–4 °C associated, but in antiphase, with the DO warmings (Masson-Delmotte et al., 2005b).

Following this method, we have extended the site and source temperature reconstructions, using now the entire GRIP isotope profile including the part from ~110 to 143.6 ka BP. Original data between 100 and 110 ka BP are presented, though the precise age of this section of the record is uncertain, due to the progressive deterioration of the comparison between GRIP and GISP2 isotopic profiles in this period (Grootes et al., 1993). Unlike for other parts of GRIP, δD and excess records are well correlated prior to 100 ka BP ($r^2 = 0.997$, $n = 108$). This results in reconstructed ΔT_{site} and ΔT_{source} that are in phase, a result that is not compromised by dating uncertainties. This reconstruction confirms that, at its maximum, the last interglacial was ~5 °C warmer than present day in Greenland, whereas temperatures during MIS 6 were probably similar to those of the LGM (curve 3d). It also indicates a ~2 °C warmer Last Interglacial maximum source temperature compared with the Holocene (see curve 3a). This last finding is an important constraint for those seeking to model and use the Last Interglacial period as an analogue for our future climate, warmed by enhanced levels of greenhouse gases.

It is possible that part of the excess changes associated with rapid warmings is due to particularly large local temperature changes (Severinghaus et al., 1998; Lang et al., 1999; Severinghaus and Brook, 1999; Landais et al., 2004a, 2005) rather than to remote moisture source effects. Running an isotopic model that incorporates a ΔT_{source} time series from which the rapid fluctuations have been smoothed out and with ΔT_{site} inferences of Masson-Delmotte et al. (2005a) leads to large and rapid variations in the predicted excess record at the Greenland site. Hence, the conclusion that there is a large contribution of ΔT_{site} to rapid excess changes cannot be ruled out, and this possibility should be kept in mind. Nevertheless, accounting only for rapid changes in ΔT_{site} does not explain the full amplitude and form of observed rapid excess fluctuations. Furthermore, the inversion method as applied by Masson-Delmotte et al. (2005a, b) provides an argument against such an interpretation, because it is based on a model approach with no a priori assumption. Although part of the excess variations could be explained by rapid ΔT_{site} changes, the fact that this procedure leads to a consistent interpretation in term of ΔT_{site} gives confidence to the ΔT_{source} record (the same set of model experiments are used to infer Eqs. (1) and (2)) and to its close link to the excess. In turn, the reconstructed oceanic source conditions, specifically the rapidity of changes and comparisons with other time series, can be assessed either from the excess data or from the reconstructed ΔT_{source}. It is with this in mind that we now address key attributes of the GRIP excess record as well as more general aspects of the δD and $\delta^{18}O$ co-isotopic measurements.

6. The GRIP excess record and its regional significance

With the assumption that the excess of Greenland snow is influenced by conditions prevailing in the oceanic moisture source regions, certain similarities, but also differences, between the GRIP excess record and those from Dye 3 (Southern Greenland) and North GRIP (~320 km North of GRIP) would be expected, as we expect some differences in their moisture source regions, Dye 3 being nearer to coastal waters, for example. Existing data allow an assessment of the regional significance of the GRIP excess variations with respect to (a) the Holocene fully measured at North GRIP (Masson-Delmotte et al., 2005a), (b) the end of the Younger Dryas available at Dye

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3 (Dansgaard et al., 1989), (c) for DO 5–7, for which co-isotopic measurements have been performed for Dye 3 (Johnsen et al., 1989) and North GRIP (DO 6: this work), and (d) for DO 18–20 (North GRIP Project Members, 2004 and Landais et al., 2004a). To facilitate these comparisons, the records have been placed on a common GRIP depth scale and then, on the SS09sea GRIP timescale, by correlating Dye 3 and North GRIP with GRIP using comparable events in the three $\delta^{18}O$ records.

Although characterized by variations of relatively small amplitudes, the Holocene part of the excess records (Fig. 2) shows distinctive features (Masson-Delmotte et al., 2005a). After an initial 2‰ increase, between 9.5 and 8 ka BP, the GRIP excess slowly increases towards its maximum around 3 ka BP and then slowly decreases towards its modern level, with a well marked and prolonged drop centred around 4.5 ka BP. North GRIP excess exhibits the same long term behaviour but with a smaller amplitude (by about a factor of two) and a significantly higher absolute value (by about 1–2‰). These characteristics have been discussed in Masson-Delmotte et al. (2005a) who draw three main conclusions: (i) the offset between the two sites is attributable to a different mix of moisture sources, (ii) the common long-term Holocene increasing trend is interpretable as a result of the increased relative contribution of low latitude moisture to Greenland snowfall, at least partly in response to the change in the Earth obliquity, and (iii) the abrupt excess declines, which punctuate the GRIP record, are suggested to be associated with reorganizations of the northern high latitude hydrological cycle.

Taken as a whole, the GRIP excess glacial and last transition record is characterized by a slowly oscillating trend over which are superimposed rapid changes (as illustrated in Fig. 2 of Masson-Delmotte et al., 2005b). These rapid excess changes are clearly associated with the DO events initially identified from the $\delta^{18}O$ record of ice (Dansgaard et al., 1993). In general (see more detailed discussion below) deuterium-excess and δD are anti-correlated with a decrease of the excess during rapid warmings (δD increases). From the comparison with Dye 3 and North GRIP data, displayed in Fig. 4a–c, this anti-correlation appears to be a general characteristic of the Greenland excess record for the last glacial period and the last climatic transition. Specifically:

- From very detailed measurements on the Dye 3 core (average resolution better than 3 yr), Dansgaard et al. (1989) first showed that the rapid warming at the end of the Younger Dryas was associated with a 5‰ excess drop occurring in no more than 20 yr, and probably in much a much shorter time (Fig. 4a). This figure points to a similar although less abrupt 5‰ shift at GRIP.
- In parallel, Johnsen et al. (1989) performed a detailed study of three successive rapid glacial oscillations (Fig. 4b) later identified as DO 5–7 (between 31 and 37 ka BP). They noted that highest excess values, again by ~5‰, were systematically obtained when comparing the cold and the mild phases of these DO events. A similar characteristic is evident in the corresponding GRIP record. This also holds true for North GRIP for which measurements were performed around DO 6 (Fig. 4b). Both GRIP and North GRIP show low excess values during mild phases and vice versa. The amplitudes are also quite similar at the three Greenland sites.
- In the NorthGRIP core, δD and $\delta^{18}O$ have also been determined on the sequence corresponding to DO 18–20 (Landais et al., 2004a), showing clear similarities between the GRIP and NorthGRIP excess profiles with again the highest values, by about 5‰, associated with the cold phases of the DO events (Fig. 4c). Also note that DO 19a (a short DO event not numbered in Dansgaard et al., 1993) has no excess counterpart at GRIP whereas it is clearly defined at North GRIP.

In summary, although there are site differences in the excess records of South (Dye 3), Central (GRIP) and North Greenland (North GRIP), their absolute excess values and the shape of specific excess events suggest concordance with a common regional signal over Greenland. With this in mind, some general properties of the GRIP δD and $\delta^{18}O$ co-isotopic measurements are examined with a focus on two specific aspects: variation in the $\delta D/\delta^{18}O$ slope, and comparison of the GRIP excess records with other paleoclimatic time series.

7. The GRIP excess record: overall characteristics

Analysing variations in the $\delta D/\delta^{18}O$ slope along the GRIP profile (Fig. 3) provides an alternative means of deriving δD and $\delta^{18}O$ co-isotopic measurements. Obviously, variations in excess and in $\delta D/\delta^{18}O$ slope are directly related. Relatively stable excess values result in a slope close to 8, whereas large excess changes reflect a divergence in this gradient: where excess values vary in the same direction as δD the slope is larger than 8, while if one of these two parameters increases and the other decreases the slope is lower than 8. Nevertheless, this $\delta D/\delta^{18}O$ slope contains useful complementary information with respect to the excess itself. While it remains close to 8 throughout the Holocene and is slightly higher before 90 ka BP, it is significantly lower during the glacial period with a minimum of 6.52 around 44 ka BP. Over the entire period from 80 to 20 ka BP, it equals 7.25, and if this value be used instead of 8 to calculate the excess, it would lead to a time series with decreased variability with respect to d over this period and to a partial smoothing of the associated rapid changes during DO events.

Hence the use of the coefficient of 8 to calculate the deuterium-excess is somewhat arbitrary. Had mass spectrometers been invented during a glacial period, we would likely be using the slope of 7.25 present at that time and not the slope of 8 observed today. However, a principal component analysis performed between the two isotopic

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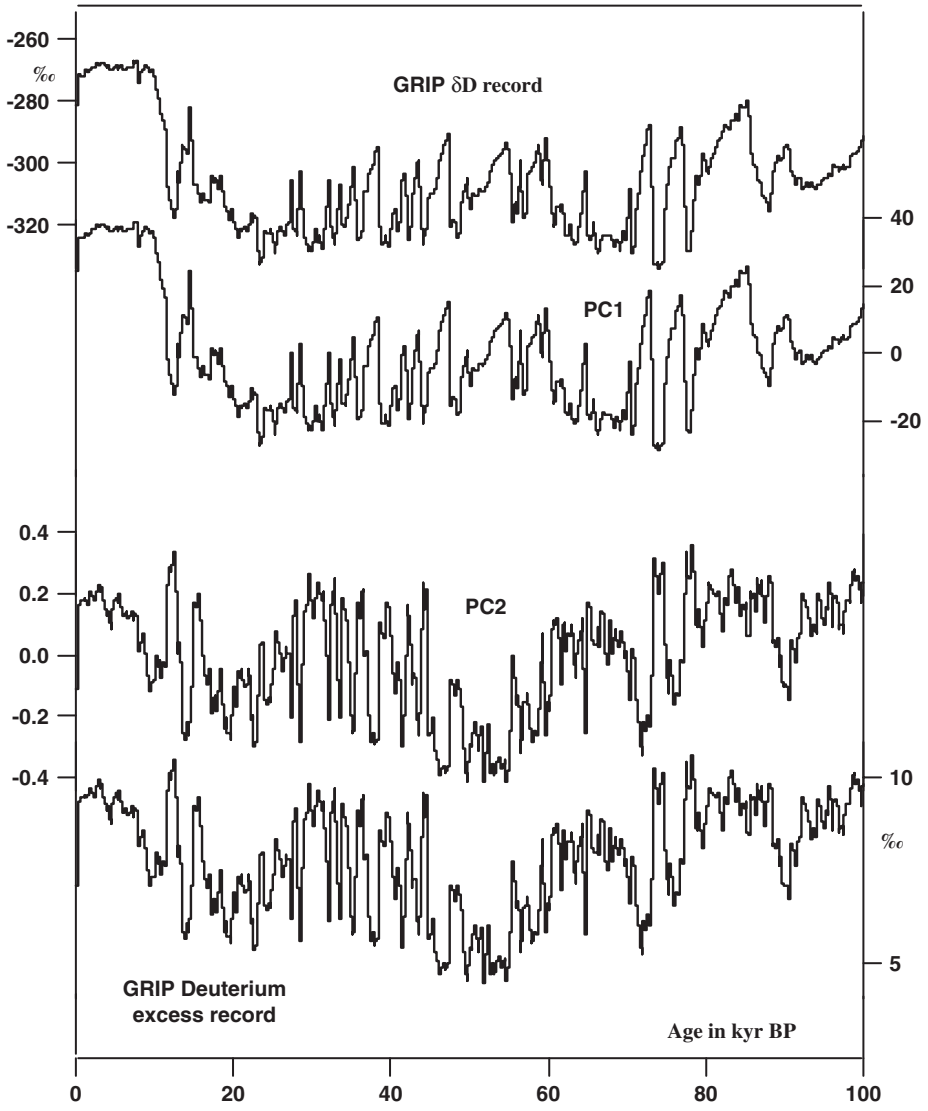

Fig. 5. This figure illustrates the similarities between the first principal component PC1 and δD (or δ^{18}O), and between the second component, PC2, and the deuterium-excess.

series (Fig. 5) indicates that the first component (PC1) is highly correlated with either δD or δ^{18}O ($r^2 = 0.999$) while the second component (PC2) is quite similar to the deuterium-excess ($r^2 = 0.960$). Interestingly, the ratio between PC1 and PC2 coefficients is of 8.04. This indicates that the deuterium-excess, defined with the value of 8, is an appropriate parameter for assessing second-order effects affecting the different fractionations between deuterium and oxygen 18 during kinetic processes, at least for the isotopic series as a whole.

At this point, it is interesting to examine from simple isotopic models how slopes as low as 6.5 could be explained (see also Johnsen et al., 1989). As noted earlier, from the Mixed Cloud Isotopic Model (Ciais and Jouzel, 1994), it can be shown that the δD/δ^{18}O slope increases linearly as a function of deuterium content (and thus site temperature) whereas it decreases when relative humidity increases. Glacial values around 7.5 could thus be explained by low Greenland temperatures during this period. This model shows that a glacial decrease in source temperature, such as the 5 °C inferred by Masson-Delmotte et al. (2005b), results in a further lowering of the δD/δ^{18}O slope. This approach has thus the merit of showing how individual parameters influence the slope, and to provide a reasonable explanation for, at first sight surprising, slope values as low as 6.5. This discussion additionally illustrates that deuterium-excess/slope changes are not simply influenced by changes in source conditions but also by the average temperature at the site.

8. Comparison of the GRIP excess record with Vostok excess and with other time series

Masson-Delmotte et al. (2005b) have pointed out an imprint of obliquity variations in the GRIP excess record, as previously noted for the longer Antarctic Vostok excess

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record (Vimeux et al., 1999). In this vein, it is interesting to compare the Vostok and GRIP excess records. To do so, we have placed the Vostok isotopic profiles on a GRIP time scale using the A1–A7 events (Bender et al., 1999; Blunier and Brook, 2001) to modify the GT4 timescale of Petit et al. (1999). For each of these events, we have assumed that the peak warmth in Antarctica is contemporaneous with the corresponding rapid warming in Greenland, and stretched the GT4 timescale accordingly. We have also used the synchronization later derived for Antarctic events A8 (Landais et al., 2006) and A9 (Caillon et al., 2001) corresponding to DO 23 and 24, respectively.

Fig. 6 displays the Vostok and GRIP excess records on a common age scale. The absolute excess levels are different, with higher excess values in the colder Vostok site. Each record has a specific variability on the short term. Nonetheless, the two excess records show some long-term similarities (Fig. 6). Both time series have lower glacial than interglacial values with relatively similar amplitudes of change. Both have relatively high values around 30 ka BP, and then lowest values around 45 ka BP corresponding to DO 12 and its Antarctic counterpart A2 (marine stage 3). However these similarities tend to disappear during marine stages 4 and 5 (e.g., before approximately 60 ky BP). In particular, excess values are high all along stage 5 at GRIP with successive maxima of relatively similar amplitude. Noticeably, there is a well marked maximum at Vostok around 110 ka BP at a time of a relative minimum at GRIP. Finally, whereas the warmest part of MIS 5e is characterized by low excess values at Vostok (around 130 ka BP), our data suggest high values at GRIP over a large part of this warm stage. Thus, unlike

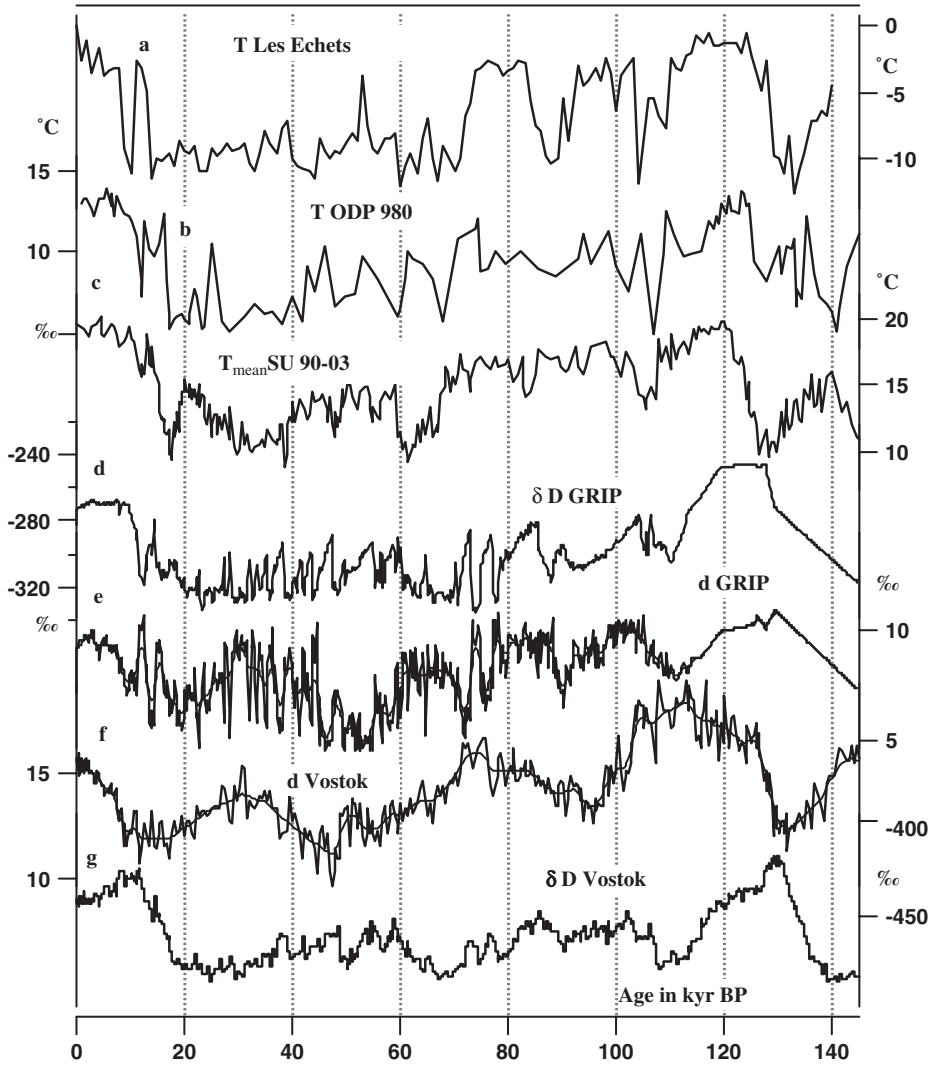

Fig. 6. Comparison of the GRIP deuterium-excess record (curve e with a superimposed smooth record) with other time series: (a) temperature record from les Echets (Guiot et al., 1993), (b) the North Atlantic ODP 980 temperature record of McManus et al. (1999), (c) the North Atlantic record (average of summer and winter temperatures) of Chapman and Shackleton (1998), (d) the GRIP deuterium record (this work), (e) the Vostok excess record along with a smooth record, (f) The Vostok deuterium record. The Vostok records are reported on a time scale established after correlation with the GRIP SS09sea (see text).

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for Vostok, where the correction due to changes in oceanic source conditions modifies the shape of the reconstructed temperature record (Cuffey and Vimeux, 2001; Vimeux et al., 2002), this source correction should be minimal at GRIP. However, the GRIP sequence is problematic between 100 and 110 ka BP and there are only few, poorly dated reconstructed data before 110 ka BP. A better possibility to look at the excess variation at the onset of the last glaciation should be offered by the North GRIP core. When completed, that record will extend undisturbed back to ~123 ka BP (North GRIP Project Members, 2004).

At GRIP, and NorthGRIP as well, warm temperatures are recorded in MIS 5e, with cooler temperatures in the later parts of MIS 5. In contrast, deuterium-excess levels remain high throughout MIS 5. Interestingly, temperature records from the North Atlantic and Western Europe also show high values throughout MIS 5. This is illustrated in Fig. 6 from the North Atlantic SST records derived by Chapman and Shackleton (1998) and McManus et al. (1999), and from the temperature record derived from the pollen record at Les Echets in France (Guiot et al., 1993). On orbital timescales, the GRIP excess record appears essentially in phase with the North Atlantic SST records, reinforcing the idea of a link between excess and moisture source temperatures. This is in contrast with the opposite rapid changes observed in Greenland deuterium-excess versus the North Atlantic (Masson-Delmotte et al., 2005b). This decoupling of temperatures between the North Atlantic and Western Europe from those observed in Central Greenland is also recorded during the Bølling/Allerød (BA). This decoupling mainly documented from the comparison between North Atlantic and continental records, now finds some counterpart in the GRIP excess record.

9. The GRIP excess record: nature of rapid changes

A key feature of the GRIP excess record is that each of the rapid warmings recorded by the δD or δ^{18}O records is characterized by a rapid decrease of deuterium-excess. From Dye 3 data (Fig. 4a), Dansgaard et al. (1989) noted that at the end of the Younger Dryas, the change in excess (e.g., in oceanic conditions) was more rapid (20 yr or less) than the temperature change at this site (50 yr). We have examined in a separate article (Jouzel et al., 2005) how fast the excess changes are in the GRIP record. For example, whereas deuterium and excess changes are both completed in 50 yr or less at the end of the YD, the δD at the transition between the LGM and the BA takes about 100 yr, although the excess decrease is still quite rapid (20 yr or less). As for DO events, for which the time resolution decreases going back in time, we note that the excess change can be more or less rapid from one event to the next (Jouzel et al., 2005). In this section, we focus on the nature of the events aiming to visualize some common features that characterize the relative behaviour of deuterium-excess and deuterium changes. To this end, we have selected the following four sequences for which the deuterium-excess changes are prominent: the last climatic transition, with a focus on the BA period that followed the very rapid change occurring around 14.5 ka BP, and DO events 5–8, 9–12, and 18–20. To illustrate the overall anti-correlation of excess with the deuterium record, we use an inverted scale to report the excess profile (Fig. 7).

One systematic feature that is observed for all of the large selected DO events (8, 12, 19 and 20) as well as for the BA period is that after rapid warmings, the δD record peaks and then decreases (saw-tooth shape), while the deuterium-excess tends to stay relatively flat and then decreases rapidly, giving to this latter record a more "step function" shape. For example, during the warm phase of the BA (from 14.5 to 13.2 ka BP), δD decreases by ~20‰ while the excess remains stable within 1‰. Noticeably, for those large events, this "step" shape is systematically shared by the GRIP calcium record, a proxy of dust fallout that thus reflects the strength of dust sources (mainly Chinese loess areas) and the efficiency of dust transport. As illustrated on Fig. 7a–d on which we have reported log(Ca), the relative stability of excess during the BA and the warm phases of DO 8, 12, 19 and 20 is paralleled by relatively stable (and low) dust fallout. We can speculate that the transient warm phase recorded in Greenland isotopes reflects a transient pulse in ocean and atmosphere heat transport towards the high northern latitudes, whereas the dust and deuterium-excess data reflects the greater stability of the mid-latitude atmospheric circulation, hydrological cycle and climate at other times.

Three of these large events, DO 12 (Landais et al., 2004d) and DO 19 and 20 (Landais et al., 2004a), have been the subject of studies combining isotopic studies in the ice and in the entrapped air bubbles (δ^{15}N and δ^{40}Ar), the latter study providing independent estimates of rapid Greenland temperature changes. Although their study was performed on the North GRIP ice core, we follow Landais et al. (2004a) in focusing on DO 19 and 20. These events have quite similar characteristics at GRIP and North GRIP sites, both concerning the estimated temperature warming (16 ± 3 °C at each site, Lang et al., 1999; Landais et al., 2004a) and the water isotope records (as illustrated on Fig. 4d). Based on the excess profile, Landais et al. (2004a) noted that when oceanic source conditions are included, the resulting site temperature decreases even more rapidly than suggested by δD alone, particularly during the warm phase of DO 19. This feature is convincingly supported by the temperature reconstruction derived from the δ^{15}N and δ^{40}Ar measurements (see Fig. 7d). In turn, this study reinforces our main conclusion inferred from this comparison between the deuterium and excess GRIP records, namely that source and site conditions are decoupled during the above-mentioned warm periods. Interestingly, during the cold phase preceding DO 19 (between 74.6 and 73.2 ka BP), the temperature estimated from isotopes in the gas phase shows a well-marked minimum whereas the deuterium profile is flat, an

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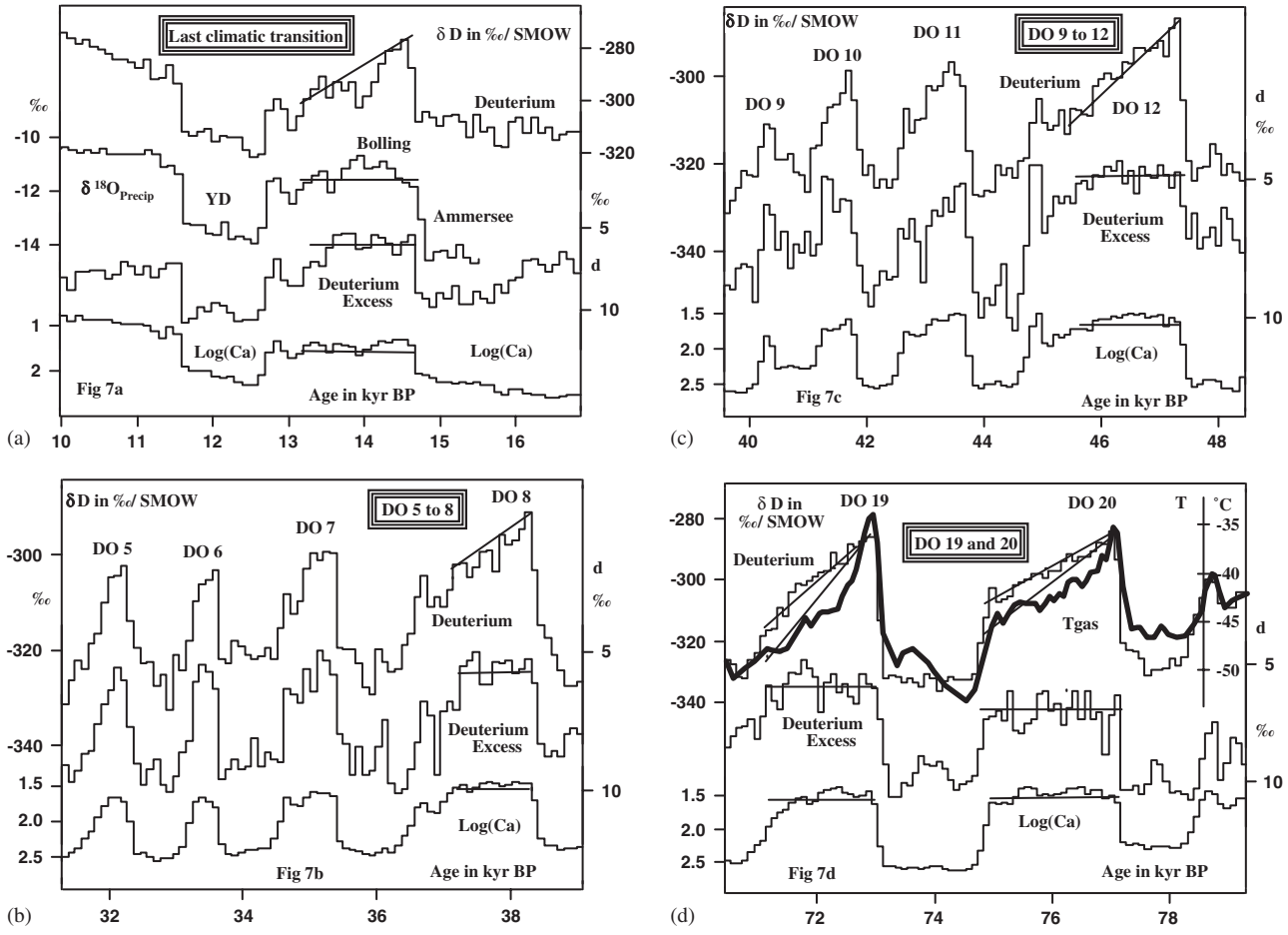

Fig. 7. Sequences of events illustrating the difference in shape between the GRIP deuterium record (a proxy of local temperature, top curve) and variations of the excess (this work; middle curve) and of log Ca (adapted from Fuhrer et al., 1999 ; bottom curve). For the last transition, we have added the isotopic record in European precipitation as derived from the Lake Ammersee record (adapted from von Grafenstein et al., 1999 and partly dated by correlation with the GRIP isotopic record). These four records have been evenly resampled at a 100 yr resolution. Straight lines illustrate the differences in shape between these records as observed for large events after a rapid warming has occurred (Last climatic transition and DO 8, 12, 19, and 20).

observation that points out the influence of parameters other than T_{site} on δD, including T_{source} as suggested by the excess, which shows a secondary minimum around 74 ka BP.

10. Concluding remarks

Although restricted to the last deglaciation, a comparison of the GRIP isotopes with the isotopic composition of European precipitation as inferred from deep-lake ostracods from Ammersee (Southern Germany) can shed some light on the mechanisms that could be at the origin of this difference between the deuterium and the excess Greenland records. Fig. 7a illustrates the remarkable correlation of decadal and longer variations of precipitation isotopes in Central Europe (von Grafenstein et al., 1999) and Greenland. But, it also highlights significant cross-North Atlantic differences during this period. As observed in the excess, the Ammersee isotopic record shows only a subtle (if any) long-term decrease after the rapid warming leading to the Bølling/Allerød (BA). This characteristic is shared by sea-surface temperature (SST) reconstructed time series from the North Sea and the Norwegian Sea (not shown). The resulting relative difference could be interpreted as an increasing cross-North Atlantic climate difference during the warm phase of the DO, driven possibly by the migration of the polar front from a position parallel and close to the East Greenland coast to a final southern and zonal position at the onset of the Younger Dryas. The consequence for the GRIP record would be a more active hydrological cycle at high latitudes and a stronger influence of moisture from a relatively cold but ice-free Greenland-Norwegian Sea during the Bölling, and thus lower excess values. The increasing excess starting around 13.5 ka BP would then argue that this climate gradient is progressively reduced during the subsequent Alleröd period.

A possible explanation for the progressive cooling of Greenland and the east–west migration of the polar front during the BA is a progressive decrease of the salinity of the Greenland-Norwegian Sea surface waters sustained by the surplus of fresh-water runoff from the Scandinavian Ice Sheet, which lost a considerable part of its volume during

this period. For example, exposure ages from ^{10}Be measurements indicate a ~600 km retreat of the ice limits from North East Poland (Rinterknecht et al., 2005) to at least Southern Finland (Rinterknecht et al., 2004) from ~15 to 12.5 ka BP. The resulting additional fresh-water runoff exclusively entered into the Greenland-Norwegian Sea and the Arctic Ocean and thus could have progressively increased the extent and seasonal duration of sea-ice, with preference along the East Greenland coast. We assume that the retreat of the Scandinavian Ice Sheet and the resulting additional fresh-water runoff continued during the whole interstadial, as long as Europe profited from high SSTs in the Norwegian Sea, and stopped with the beginning of the Younger Dryas. Slightly reduced freshwater runoff during the Younger Dryas could then have led to a gradual increase of surface salinities in the Greenland-Norwegian Sea, thus facilitating the resurgence of ocean heat transport, a rapid break-down of the permanent sea-ice cover and a rapid warming of both Greenland and Europe. Such a fresh-water feedback mechanism would be an attractive model for the explanation of all other large DO events, which almost all share common features in the deuterium, deuterium-excess and log(Ca) records with the BA Younger-Dryas sequence (Fig. 7b–d).

In a more general perspective, this article supports the conclusion that the interpretation of deuterium-excess from Greenland ice cores appears more somewhat more complex than for Antarctic ice cores. Accounting for changes in precipitation seasonality provides a consistent picture, however, in terms of Greenland site and oceanic source temperatures (Masson-Delmotte et al., 2005b) and is clearly a step forward in this interpretation. Further progress should result from the use of isotopic ocean-atmosphere General Circulation Models (GCMs). In principle, these models allow us to account for the complexity of topographic changes, source conditions and atmospheric circulation. They have, however, up to now, shown a very poor representation of the predicted characteristics of deuterium-excess in precipitation and clearly require additional work. Nonetheless, these models are our best hope to account for sources of complexity, such as the shifts of source location hypothesized in this article. In addition, one can use them to investigate some of the implicit but important assumptions embedded in the simple models. With significant improvements, isotopic GCMs would be ideal tools to examine the properties of stable isotopes, including excess, in regions such as Greenland. Particularly promising in this context are simulations based on regional isotopic models (Sturm et al., 2005) which should provide dynamical frameworks in which to place the regional isotopic fluctuations observed from south to north Greenland. With the growing recognition that the Last Interglacial period, which was significantly warmer than today, may be our most accessible analogue for a future, warmer climate, improving our understanding of the many clues that ice cores give us about past environments, particularly parameters such as excess that link land and ocean records, is a must.

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