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Climate of the Past
Discussions

Modelling the firn thickness evolution during the last deglaciation: constrains on sensitivity to temperature and impurities

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The transformation of snow into ice is a complex phenomenon difficult to model. Depending on surface temperature and accumulation rate, it may take several decades to millennia for air to be entrapped in ice. The air is thus always younger than the surrounding ice. The resulting gas-ice age difference is essential to document the phasing between CO_2 and temperature changes especially during deglaciations. The air trapping depth can be inferred in the past using a firn densification model, or using $\delta^{15}N$ of air measured in ice cores.

All firn densification models applied to deglaciations show a large disagreement with $\delta^{15}N$ measurements in several sites of East Antarctica, predicting larger firn thickness during the Last Glacial Maximum, whereas $\delta^{15}N$ suggests a reduced firn thickness compared to the Holocene. We present here modifications of the LGGE firn densification model, which significantly reduce the model-data mismatch for the gas trapping depth evolution over the last deglaciation, while preserving the good agreement between measured and modelled modern firn density profiles. In particular, we introduce a dependency of the activation energy to temperature and impurities in the firn densification rate calculation. The temperature influence reflects the existence of different mechanisms for firn compaction at different temperatures. We show that both the new temperature parameterization and the influence of impurities contribute to the increased agreement between modelled and measured $\delta^{15}N$ evolution during the last deglaciation at sites with low temperature and low accumulation rate, such as Dome C or Vostok. However, the inclusion of impurities effects deteriorates the agreement between modelled and measured $\delta^{15}N$ evolution in Greenland and Antarctic sites with high accumulation.

1. Introduction

Ice cores are important tools to decipher the influence of different forcings on climate evolution.

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They are particularly useful to depict the past variations of polar temperature and greenhouse gases. The longest record covers 8 last glacial – interglacial cycles (EPICA community members, 2004; Jouzel et al., 2007; Loulergue et al., 2008; Lüthi et al., 2008) and very high resolution climate records can be retrieved from ice cores drilled in high accumulation regions (Marcott et al., 2014; Rhodes et al., 2015; WAIS Divide Project Members, 2013, 2015).

Polar ice is a porous medium, and contains bubbles filled with ancient atmospheric air, allowing the reconstruction of the atmospheric composition in the past. The air is trapped at about 100 m under the ice sheet surface. Above that depth, the interstitial air in firn pores remains in contact with the atmosphere. Consequently, the air is always younger than the surrounding ice and this age difference, Δage, can reach several millennia at the low temperature and accumulation rate sites of East Antarctica.

A precise determination of Δage is essential to quantify the link between temperature changes recorded in the water isotopic measurements on the ice phase and greenhouse gas concentrations recorded in the gas phase. Still, quantifying the temporal relationship between changes in greenhouse gas concentrations in air bubbles and changes in polar temperature recorded in the isotopic composition of the ice is not straightforward. One way to address this question goes through the development of firn densification models that depict the progressive densification of snow to ice, and the associated decrease of porosity. Below a certain threshold density, the pores seal off and the air is trapped. The firn densification models thus calculate the Lock-in Depth (hereafter LID) according to surface climatic conditions. A higher temperature accelerates the firn metamorphism and leads to a lower LID. On the other hand, a higher snow accumulation at the surface will have the effect of increasing the firn sinking speed and hence the LID. In practice, accumulation usually increases when temperature increases, and both effects partially compensate each other, with the temperature effect being dominant in the current densification models for the LID simulation over glacial – interglacial transitions in deep drilling sites of the East Antarctic plateau. A first class of densification models is based on an empirical approach to link accumulation rate and temperature at different polar sites to densification rates (allowing the match between the modelled and the measured density profiles) (e.g. Herron and Langway, 1980). The Herron and Langway (1980) model assumes that the porosity (air space in the firn) directly relates to the stress induced by the overlying snow, hence the accumulation rate. A temperature dependence following an Arrhenius law is also implemented to account for a more rapid compaction at higher

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temperature. Finally, the exact model sensitivity to temperature and accumulation rate is adjusted empirically in order to simulate observed density profiles. Measured density profiles exhibit different densification rates above and below 550 kg/m^3 so that different empirical laws are used for densities above and below this threshold. Indeed, 550 kg/m^3 corresponds to the observed maximum packing density of snow (e. g. Anderson and Benson, 1963), hence to a change in the driving mechanism of firnification.

Despite its simple empirical description, and although more sophisticated empirical models have been developed (Arthern et al., 2010; Helsen et al., 2008; e.g. Li and Zwally, 2004; Ligtenberg et al., 2015), the Herron and Langway (1980) firn model often provides good quality results and is still used in a number of ice core studies (e.g. Buizert et al., 2015; Overly et al., 2015). However, its validity is questionable when used outside of its range of calibration, such as glacial periods at cold sites of the East Antarctic plateau for which no present-day analogue exists. As a consequence firn models including a more physical description of densification have been developed (e.g. Arnaud et al., 2000; Salamatin et al., 2009). The model developed over the past 30 years at LGGE (Arnaud et al., 2000; Barnola et al., 1991; Goujon et al., 2003; Pimienta, 1987) aims at using a physical approach which remains sufficiently simple to be used on very long time scales (covering the ice core record length). More complex models, explicitly representing the material micro-structure have been developed but require a lot more computing time (Hagenmuller et al., 2015; Miller et al., 2003).

In parallel to firn densification modelling, past firn LID can also be determined using the $\delta^{15}N$ measurements in the air trapped in ice cores. Indeed, in the absence of any abrupt temperature change at the ice-sheet surface, the $\delta^{15}N$ trapped at the bottom of the firn is directly related to the diffusive column height (DCH). This is due to gravitational settling in the firn following the steady state barometric equation (Craig et al., 1988; Schwander, 1989; Sowers et al., 1989):

$$\delta^{15}N_{grav} = \left[\exp\left(\frac{\Delta mgz}{RT_{mean}}\right) - 1\right] 1000 \approx \frac{gz}{RT_{mean}} \Delta m \times 1000\ (‰) \qquad (1)$$

Where Δm is the mass difference (kg/mol) between ^{15}N and ^{14}N, g is the gravitational acceleration (9.8 m/s^2), R is the gas constant (8.314 J/mol/K), T_{mean} is the mean firn temperature (K), and z is the diffusive column height (m) noted (DCH). In the absence of convection at the top of the firn, the firn LID is equal to the DCH.

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In Greenland ice cores, where abrupt surface temperature changes occurred during the last glacial period and deglaciation, $\delta^{15}N$ is also affected by thermal fractionation. An abrupt warming (on the order of 10°C in less than 50 years) indeed induces a transient temperature gradient in the firn of a few degrees (Severinghaus et al., 1998; Guillevic et al., 2013; Kindler et al., 2014). $\delta^{15}N$ is thus modified as $\delta^{15}N_{therm} = \Omega * \Delta T$ and this thermal signal is superimposed on the gravitational one ($\delta^{15}N_{therm}$ is at maximum 0.15‰).

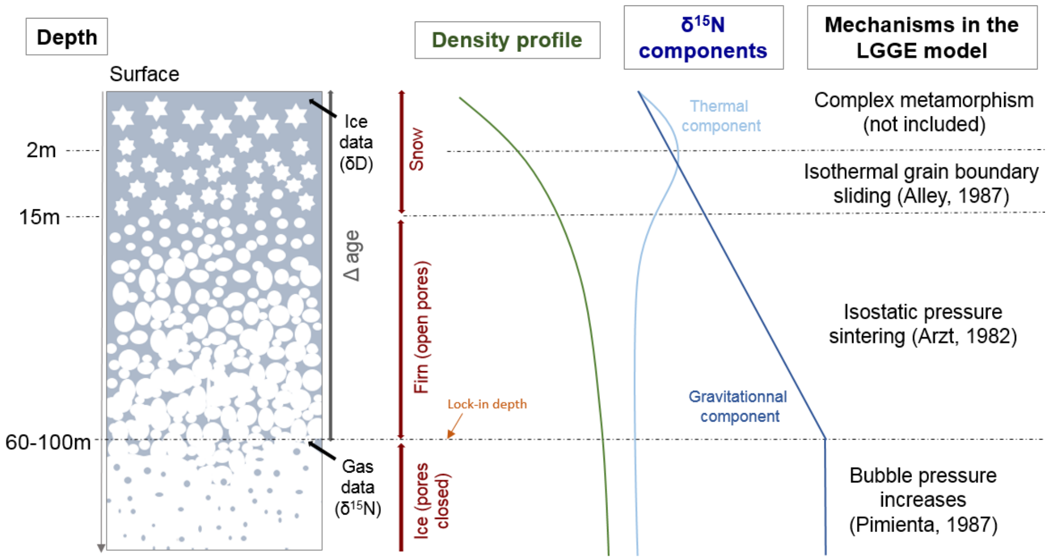

Figure 1: Overview of snow densification and influence on the $\delta^{15}N$ profile in the absence of any significant convective zone as observed in most present-day $\delta^{15}N$ profiles (Landais et al., 2006; Witrant et al., 2012).

While models can reproduce the observed $\delta^{15}N$ at Greenland sites over the last climatic cycle, a strong mismatch is observed for cold Antarctic sites, especially on the East-Antarctic plateau (Dreyfus et al., 2010). In particular, both the empirical and physical models predict a decrease of the LID during glacial to interglacial transitions (Goujon et al., 2003; Sowers et al., 1992) while the $\delta^{15}N$ evolution indicates an increase of the LID (Capron et al., 2013; Sowers et al., 1992). The decrease in the LID in the models is caused by the increase in temperature during the deglaciation, which has a stronger impact than the increase in the accumulation rate.

In this study, we test if simple modifications of the LGGE model can reduce the model-data mismatch for the LID evolution over the last deglaciation in sites on the East Antarctic plateau. In

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particular, we explore the underestimation of the firn densification rate at very low temperature evidenced over the glacial-interglacial transitions (Capron et al., 2013) and the possible influence of impurity concentration (Freitag et al., 2013; Hörhold et al., 2012). The manuscript is organized as follows: In the next (second) section we present the physical model with a focus on recent modifications. In a third section, we confront the model outputs to present-day observed firn density profiles and $\delta^{15}N$ data over the last deglaciation at different polar sites from Greenland and Antarctica. Section 4 summarizes our conclusions.

2. Densification model description and improvements

An in-depth description of the LGGE firn densification model is provided in Goujon et al. (2003). Here we first briefly summarize its content, and then detail the modifications introduced in this study. The main inputs to the model are temperature and snow accumulation rate. During climatic transitions occurring at similar or shorter time scales than firnification, the propagation of the atmospheric temperature signal into the firn has to be taken into account (Schwander et al., 1997). The thermo-mechanical model comprises four modules. A simple ice sheet flow module calculates the vertical speed in a 1D firn and ice column. This vertical speed is used in the thermal module to calculate heat advection. The thermal module solves the heat transfer equation, which combines heat advection and heat diffusion across the whole ice-sheet thickness. Using the resulting temperature profile in the firn, the mechanical module evaluates the densification rates resulting from three successive mechanisms detailed below. Finally, a gas-age module keeps track of snow layers sinking in a Lagrangian mode and uses a gas trapping criterion in order to evaluate the gas trapping depth and the ice age – gas age difference (Δage).

The model does not take into account the complex mechanisms associated with snow metamorphisms under the influence of strong temperature gradients, wind and sublimation/re-condensation (Colbeck, 1983; Kojima, 1967; Mellor, 1964). This kind of metamorphism affects the 1-3 meters at the top of the firn and has a minor role on the modelled LID.

Below this depth, the densification of snow into ice has been divided in three stages (e.g. Maeno and Ebinuma, 1983 and references therein; Figure 1). The first stage (from 2 to 15 m depth approximately), named “snow densification”, corresponds to a rearrangement and packing of snow grains until approaching the maximum compaction at a density of about 550 kg/m^3 (or 0.6 on a unitless scale relative to the density of pure ice) defined as the critical density. The second stage (from ~15 m to ~60-100 m depth) represents the firn densification by sintering associated with visco-

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plastic deformation. Finally, when the bubbles are closed, the ice densification is driven by the difference in pressure between air trapped in bubbles and the solid ice matrix subject to the weight of the overlying firn structure. In reality, the first stage densification mechanism (packing by boundary sliding) and the second stage mechanism (pressure sintering) likely coexist at intermediate densities. Below we further describe the mechanical structure of the model with a focus on recent modifications and refer to Arnaud et al. (2000) and Goujon et al. (2003) for more details.

The model uses macroscopic (simplified) mechanical laws, which link the densification speed (dD_{rel}/dt, in terms of relative density ($D_{rel} = \frac{\rho}{\rho_{ice}}$)) to its main driving force: the overburden pressure of overlying snow. It is important to note that in our model, the accumulation rate influences firn densification only through the overburden pressure:

$$P(h) = g \int_{o}^{h} \rho dz \qquad (2)$$

where g is the gravity constant and ρ is the density in kg/m^3. This differs from the Herron and Langway (1980) model where the effect of accumulation rate is adjusted and expressed with a different power law for snow and firn densification rates. In porous materials, the overburden pressure P is transmitted through contact areas between grains rather than the entire surface of the material. This is expressed by replacing P with an effective pressure P_{eff} in mechanical stress-strain laws. The relationship between P and P_{eff} depends on the material geometry (e.g. Equation A4 in Goujon et al., 2003). A higher temperature (T) facilitates the deformation of materials, and this effect is commonly represented by an Arrhenius law: $e^{\left(\frac{-Q}{RT}\right)}$ where R is the gas constant and Q an activation energy. The value of the activation energy depends on the underlying physical mechanism of deformation. We should note that Arrhenius expressions cannot represent deformation effects linked to ice melting. The relationships between densification speed and overburden pressure thus take the following general form:

$$\frac{dD_{rel}}{dt} = A_0 \times e^{\left(-\frac{Q}{RT}\right)} \times (P_{eff})^n \qquad (3)$$

where A_0 represents the dependency of the deformation speed on the material geometry change and n is the stress exponent. In the rest of the manuscript, we will refer to $A = A_0 \times e^{\left(-\frac{Q}{RT}\right)}$ as the

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creep parameter.

2.1 Densification of snow

During the first stage, the dominant snow densification mechanism is assumed to be isothermal boundary sliding and the model of Alley (1987) is used (Figure 1). The geometrical approximation used to build the model is to represent snow as equal size spheres with a number of contacts between neighbours increasing with density. In the LGGE model, the Alley mechanism is implemented as Equation A1 in Goujon et al. (2003):

$$\frac{dD_{rel}}{dt} = \gamma\left(\frac{P}{D_{rel}^2}\right)\left(1-\frac{5}{3}\times D_{rel}\right) \qquad (4)$$

It directly relates to Equation (5) in Alley (1987):

$$\frac{dD_{rel}}{dt} = \frac{2}{15}\times\frac{\lambda}{\nu}\times\frac{R}{r^2}\times\left(1-\frac{5}{3}*D_{rel}\right)\times\frac{P}{D_{rel}^2} \qquad (5)$$

where λ is the bond thickness, ν the bond viscosity, R the grain radius and r the bond radius. P is expressed as a function of accumulation and gravity (Equation 2).

The important simplification in the LGGE model is the replacement of geometry dependent parameters, not available for past conditions, with a variable γ, adjusted in order to obtain a continuous densification rate at the boundary between the first and the second stage of densification.

A first modification in this module consists of extending the Alley (1987) scheme to the upper two meters of the firn rather than using a constant density value. Indeed, since the model is not able to describe the metamorphism of the first two meters, we impose by continuity a constant densification rate equals to its value at 2 m depth.

The second modification concerns the transition between the snow and firn densification stages at the relative density of 0.6. In Equation (4), the term $\left(1-\frac{5}{3}\times D_{rel}\right)$ implies that the densification speed drops to zero at $D_{rel}=\frac{3}{5}$ (i.e. 0.6 the maximal compaction density). The second stage of densification (firn densification) is driven by an important overburden pressure on the contact area hence associated with a high densification speed. The transition between the sharp decrease of the densification speed for D_{rel} values close to 0.6 in the snow densification stage and the high

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densification speed at the beginning of the firn densification (i.e. in the same range of value for D_{rel}) causes some model instabilities especially at sites with high temperature and accumulation rate. In order to improve the model stability, we go back to the definition of the term $\left(1-\frac{5}{3}\times D_{rel}\right)$ in the initial formulation of Alley (1987). This term relies on a correlation between the coordination number (N) and relative density: $D_{rel}= 10\ N$. We slightly modified this relationship and imposes $D_{rel}= 10\ N - 0.5$ which better matches the data on Figure 1 of Alley (1987). This results in replacing the term $\left(1-\frac{5}{3}\times D_{rel}\right)$ in Equation (4) with $\left(1+\frac{0.5}{6}-\frac{5}{3}\times D_{rel}\right)$. This modification shifts the density at which the densification rate becomes relative zero from 0.6 to 0.65 and suppresses the model instability.

We also examine the effect of temperature on the first-stage densification mechanism and on the critical density. Alley (1987) calculated an activation energy of 41 kJ/mol, consistent with recommended values for grain-boundary diffusion (42 kJ/mol) or measured from grain growth rate (Alley, 1987 and references therein). In Goujon et al. (2003), no explicit temperature effect is used but the parameter γ varies by several orders of magnitude from site to site. The parameter γ is calculated to maintain a continuous densification rate between the first and second stages at a chosen critical density. We translate the variations of γ from site to site in to a mean activation energy using a classical logarithmic plot as a function of 1000/T (see e.g. Herron and Langway, 1980) and obtain a value of 48 kJ/mol. Using the revised temperature dependency for the firn densification mechanism (see next section), a slightly higher value of Q =49.5 kJ/mol is calculated (Supplementary Figure S1). This is fairly similar to the values in Alley (1987) but much higher than the value in the upper firn of the Herron and Langway (1980) model: 10.16 kJ/mol. Incorporating this explicit temperature dependency term, we obtain our new final expression for the upper firn densification rate:

$$\frac{dD_{rel}}{dt} = \gamma'\left(\frac{\max(P,0.1\ bar)}{D_{rel}^2}\right)\left(1+\frac{0.5}{6}-\frac{5}{3}\times D_{rel}\right)\times e^{\left(-\frac{Q}{RT}\right)} \qquad (6)$$

where $\gamma'\times e^{\left(-\frac{Q}{RT}\right)}$ is equivalent to γ in Equation (4). However γ varies by two orders of magnitude as a function of temperature whereas γ' remains in the range from $0.5.10^9$ to 2.10^9 bar^{-1}.

Finally, the temperature dependency of the critical density, which defines the boundary between the first and second stage densification mechanisms, is also re-evaluated. According to Benson (1960) and Arnaud (1997; 2000), this critical density increases with temperature. However the slope

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change in density profiles associated with the critical density may be difficult to locate and the Benson (1960) and Arnaud (1997) parameterizations are based on only few observation sites. We evaluate the critical density values which allow the best match of density data by our model results at 21 sites and do not find any correlation between critical density and temperature or accumulation rate (Supplementary Figure S2). We thus remove this dependency with temperature included in the old version of the LGGE model and use a mean relative critical density of 0.56 at the boundary between the first and second stage of densification in the new version of the model.

These modifications in the formulation of the Alley (1987) mechanism improve the LGGE model stability and consistency with measured density profiles. However, when the model is run on longer timescales, only small changes of the model behaviour on glacial-interglacial transitions are observed because the first stage of densification applies to a maximal 15 m depth interval compared to the second stage (Supplementary Figure S3).

2.2 Densification of firn

At this stage, the observation of density profiles with depth suggests that the densification rate is controlled by a classical power law creep as used for ice deformation (Arzt et al., 1983; Maeno and Ebinuma, 1983; Wilkinson and Ashby, 1975). Arzt (1982) proposed a pressure sintering mechanism for firn densification following a power law creep and taking into account the progressive increase of the coordination number. He solved the geometrical problem of compressing a random dense packing of monosized spheres with associated deformation of each sphere into irregular polyhedra. Equation (23) of Arzt (1982) is directly used in the firn densification model.

2.2.1 2.2.1 Revised temperature sensitivity of the firn densification rate

A strong assumption in the firn densification module is the constant activation energy corresponding to self-diffusion of ice (60 kJ/mol). This choice corresponds to a unique mechanism supposed to drive densification. Densification is thus assumed to be driven by dislocation creep (Ebinuma and Maeno, 1987) in which the associated mechanism is lattice diffusion or self-diffusion. At the grain scale, we can describe the lattice diffusion processes associated with dislocation as diffusion within the grain volume of a water molecule from a dislocation site in the ice lattice to the grain neck in order to decrease the energy associated with grain boundaries (Blackford, 2007). Typically, an

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activation energy of 60 to 70 kJ/mol is associated with this mechanism (Pimienta and Duval, 1987; Ramseier, 1967 and references therein).

However, multiple studies have already shown that several (6 or more) mechanisms can act together for firn or ceramic sintering (Bernache-Assollant and Bonnet, 2005; Blackford, 2007; Maeno and Ebinuma, 1983; Wilkinson and Ashby, 1975): lattice diffusion from dislocations, grain surfaces or grain boundaries; vapour transport; or surface and boundary diffusions. In order to properly take these different mechanisms into account, different activation energies (one activation energy per mechanism) should ideally be introduced in the firn densification model. Actually, it has been observed that, at warm temperature, an activation energy significantly higher than 60 kJ/mol should be favoured (up to 100-130 kJ/mol) in order to best fit density profiles with firn densification models (Arthern et al., 2010; Barnes et al., 1971; Jacka and Li, 1994). This suggests that a mechanism different from lattice diffusion is dominant for grain compaction at high temperature (i.e. higher than -10°C). At low temperature (-50°C), we are not aware of any ice sintering experiments aimed at determining the associated dominant mechanisms and activation energy. Still, by analogy with ceramic sintering, lattice diffusion from the surface of the grains should be favoured at low temperature (Bernache-Assollant and Bonnet, 2005).

Following these arguments, we propose a new parameterization of the activation energy in the LGGE firn densification model. We have thus introduced three different activation energies for the three different mechanisms highlighted above (Table 1, Figure 2). We have replaced the creep parameter in Equation (3) by:

$$A = A_0 \times \left(a_1 \times e^{\frac{-Q_1}{RT}} + a_2 \times e^{\frac{-Q_2}{RT}} + a_3 \times e^{\frac{-Q_3}{RT}} \right) \qquad (7)$$

The parameters Q_1, Q_2 and Q_3 are associated with three different firn sintering mechanisms (Figure 2). We have chosen a minimal number of mechanisms (3) for simplicity in the following but the conclusions of our work would not be affected by a choice of more mechanisms.

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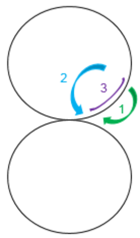

- Close to melting temperature: mass transfer by vapour diffusion
  (1) mechanism 1 associated with activation energy Q_1
- Low temperature: lattice diffusion (classical mechanism)
  (2) mechanism 2 associated with activation energy Q_2
- Very low temperature : superficial diffusion
  (3) mechanism 3 associated with activation energy Q_3

<u>Figure 2:</u> Sintering mechanisms of snow by analogy with the hot ceramic sintering (inspired by Figure 8 in Bernache-Assollant and Bonnet, 2005)

The determination of Q_1, Q_2 and Q_3 on the one side and a_1, a_2 and a_3 on the other side are not independent from each other. We first determine three temperature ranges corresponding to the dominant mechanisms: vapour diffusion close to melting temperature, volume lattice diffusion due to dislocation for low temperature and surface lattice diffusion for very low temperature. Then, we attribute values to the activation energies Q_1, Q_2 and Q_3. The coefficients a_1, a_2 and a_3 are then adjusted to produce the expected evolution of the creep parameter with temperature (Section 3.2) and respect the firn density profiles available (Section 3.1).
Our choice for the values of the different activation energies (Q_i) is based as much as possible on available data. For volume diffusion, several experimental determinations suggest a value for Q_2 between 60 and 75 kJ/mol (Arthern et al., 2010; Barnes et al., 1971; Pimienta and Duval, 1987). For vapour diffusion at warm temperature, empirical determinations of Q_1 lead to values of the order of 100-130 kJ/mol (Arthern et al., 2010; Barnes et al., 1971; Zwally and Li, 2002). For superficial diffusion dominant at very low temperature, the compaction rates are too slow to be tested in a laboratory setting, or observed in the field. As a result, we explored a large range of values for Q_3.
The optimal combination of Q_1, Q_2 and Q_3 values (Table 1) was chosen to 1) minimize the mismatch between modelled and measured modern density profiles, and 2) reproduce the change in LID obtained from the $\delta^{15}N$ data over the deglaciation at 4 Antarctic and Greenland sites (see Section 3.2 for the optimization and associated sensitivity experiments).
The resulting expression for the creep parameter A (Equation 7), does not significantly differ from using simply $A = A_0 \times e^{\left(-\frac{60000}{RT}\right)}$, as used in the original model. To illustrate this point, we calculated an equivalent activation energy, Q_{eq}, such that $A = A_0 \times e^{\left(-\frac{Q_{eq}(T)}{RT}\right)}$, and found Q_{eq} varying between 54 and 61 kJ/mol (Supplementary Figure S4). Thus only slight changes to the densification equation are needed to improve the behaviour of the model at cold temperature.

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Activation Energy (J/mol)	Coefficient
Q_1= 110000	a_1= 1.05*10^9
Q_2= 75000	a_2= 1400
Q_3= 1500	a_3= 6.0*10^{-15}

Table 1: Preferred set of values for the three activation energies and associated pre-exponential constants

2.2.2 2.2.2 Sensitivity of the firn densification rate to impurities

2.2.3

Firn densification can be influenced by impurity content in snow. Alley (1987) already suggested that grain growth is influenced by impurities dissolved in ice, and that impurities in the grain boundaries affect the relative movement of snow grains. More recently, Hörhold et al. (2012) observed a correlation between the small scale variability of density and calcium concentration in Greenland and Antarctic firn cores. Based on this observation, Freitag et al. (2013) proposed that the densification rate depends on the impurity content. They implemented an impurity parameterization in two widely used densification models (Herron and Langway, 1980; Barnola et al., 1991), and were able to reproduce the density variability in two firn cores from Greenland and Antarctica.

We have implemented this parameterization in our model assuming that the impurity effect is the same for all mechanisms. Concretely, we start again from the evolution of the creep parameter with respect to temperature given in Equation (7) and add a dependency to calcium concentration such as:

$$if\ [Ca^{2+}] > [Ca^{2+}]_{crit} :\ Q' = f1\left[1 - \beta \ln\left(\frac{[Ca^{2+}]}{[Ca^{2+}]_{crit}}\right)\right] \times Q \quad (8)$$

$$if\ [Ca^{2+}] < [Ca^{2+}]_{crit} :\ Q' = f1 \times Q \quad (9)$$

With, $[Ca^{2+}]_{crit}$ = 0.5 ng/g (the detection limit of continuous flow analysis). Q' represents the new activation energy calculated in function of the calcium concentration for each site. Our main simulations are performed with the f_1 and β calculated by Freitag et al. (2013) for application within the Herron and Langway model: f_1 = 1.025, β = 0.01. Using the values for application within the Pimienta-Barnola model (f_1 = 1.015, β = 0.0105) leads to similar results (section 3.2). For a first evaluation of the impurity effect in our model, both the temperature and impurity effects are

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combined through the application of Equations (8) and (9) to each of the three different activation energies Q_1, Q_2 and Q_3.

2.3 Densification of ice

The final stage begins at the close-off density ρ_{CO}, i.e. the density at which the average pressure in bubble starts to become higher than atmospheric pressure (Martinerie et al., 1992, Appendix 1). This density is calculated using the temperature dependent close-off pore volume given by Martinerie et al. (1994). Further densification of this bubbly ice is driven by the pressure difference between ice matrix and the air in bubbles (Maeno and Ebinuma, 1983; Pimienta, 1987). The densification rate strongly decreases with depth as these two opposite pressures tend to balance each other (Goujon et al., 2003). This stage is not essential for this study since $\delta^{15}N$ entrapped in air bubbles does not evolve anymore.

2.4 Lock-in depth

In the previous version of the model, the LID is computed as a defined steady closed to total porosity ratio. The ratio value used can be adjusted for each drilling site, for example it is 21% for Vostok and 13% at Summit in Goujon et al. (2003).

We revised the LID definition, taking into account recent advances in gas transport modelling (Witrant et al., 2012) that allowed correct simulation of the $\delta^{15}N$ behaviour in deep firn. Observations of modern firn air profiles show that the thickness of the lock-in zone (the zone in the deep firn with constant $\delta^{15}N$) increases when the snow accumulation rate increases (Witrant et al., 2012). Because $\delta^{15}N$ profiles are not available for all polar firn study, we propose a new definition of the LID based on the $\delta^{15}N$ modelling of Witrant et al. (2012). We estimate $\delta^{15}N$ in ice, i.e. after complete bubble closure, at 12 firn air pumping sites with the Witrant et al. (2012) model. For each site, the trapping density (ρ_{LID}) is then defined as the density at which the modelled $\delta^{15}N$ value in the open porosity of the firn equals the modelled $\delta^{15}N$ in ice. The resulting trapping density is strongly related to the accumulation rate (Supplementary Figure S5). As a result, we parameterized the trapping density (ρ_{LID}) as a function of the accumulation rate, following:

$$\rho_{LID} = 1.43 * 10^{-2} \times \ln\left(\frac{1}{A_c}\right) + 0.783 \quad (10)$$

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This parameterization leads to a much better agreement of the modelled LID with $\delta^{15}N$ measured at the available firn sampling sites than when using the outputs of the old model. However, when used for simulating the LID during glacial periods with extremely low accumulation rate, it can predict a trapping density that is higher than the close-off density, which is unrealistic. We thus also added a threshold in our new definition of the trapping density: when ρ_{LID} exceeds the close-off density (ρ_{CO}, Section 2.3), we impose ρ_{LID} to be equal to ρ_{CO}.

As mentioned above, this choice clearly improves the simulated $\delta^{15}N$ in ice, at least for present-day conditions. However, this modification does not solve the strong data – model mismatch over deglaciations (Supplementary Figure S6).

3. Results

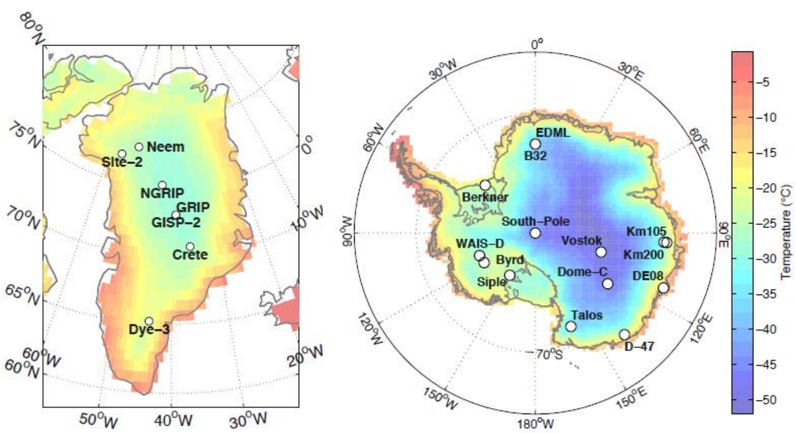

Figure 3: Maps of Greenland and Antarctica showing field sites and mean annual temperature from ERA interim (Dee et al., 2011)

3.1 Firn density profiles

We assessed the behaviour of the model by comparing measured and modelled firn density profiles from 21 sites from Greenland and Antarctica (Figure 3). Figure 4 shows this comparison at Byrd, NEEM, Dome C and Vostok, and other sites are displayed in the supplement (Supplementary Figure S7). A polynomial fit was adjusted to the density data in order to facilitate the comparison with

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model results. The data dispersion around the fit can be due natural density variations and/or measurement uncertainties.

A comparison of snow density measurement methodologies concluded that uncertainties are about 10 % (Proksch et al., 2016). Moreover, although firn density profiles are often used, the measurement technique is not always well documented. Efforts were made in this study to mention the methodology when available (Supplementary Table S1). At high densities (below bubble closure depth), the hydrostatic weighing technique is expected to be about 10 times more precise than simple volume and mass measurements (Gow, 1968) but rarely used, although it is important to correctly evaluate the fairly small density difference with pure ice density. We should note that the agreement between our model results and data is good at high densities for the three sites where hydrostatic weighing technique was used: Site 2 and D-47 (Supplementary Figure S7) as well as Byrd (Figure 4).

High-resolution measurements on small samples often aim at documenting the natural variability of density. Our model only simulates bulk density, and to illustrate a meaningful comparison, the highest resolution data (at DE08, B29, B32 and Dome C) were averaged over 0.25 m windows before being plotted. At some sites, a similar averaging was already performed before data publication (e.g. 1 m averaging at Byrd and Site 2, 0.5 m averaging at Mizuho). At a large number of sites, especially deep ice core drilling sites, measurements were performed on large volume samples. Still, it should be noted that at NEEM, although large volume samples were used, the data dispersion is higher than for Byrd (Figure 4) and part of the discrepancy between the model and data may be due to the uncertainty in the data.

For our study we have gathered density data covering the whole firn depth range, for which we had confidence in the data quality and the major site characteristics (temperature, accumulation). Although the effects of uncertainties on the data and natural density variability cannot be completely separated, we evaluate the data dispersion around the polynomial fit and use it as a rough indicator of data quality:

$$\sigma_{fit-data} = \sqrt{\left[\sum_{Nmax}^{i=1} \frac{\left(\rho_{fit}^{i} - \rho_{measured}^{i}\right)^{2}}{N_{max}}\right]} \quad (11)$$

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where N_{max} is the number of steps of data points, ρ_{fit} represents the regression of the density profile and $\rho_{measured}$ the measured density averaged on a 0.25 m window. $\sigma_{fit\text{-}data}$ generally lies below 10.0 kg/m^3 (Figure 5).

The modifications of the first densification stage described in Section 2.1 mainly reduce the slope change at the transition between the Alley (1987) and Arzt (1982) mechanisms and somewhat reduce the mismatches between the model results and polynomial fit to the data. The temperatures and accumulation rates at Dome C and Vostok being similar, model results at these sites are similar, but the density data have a clearly different shape. At Vostok, a high densification rate is observed well above the critical density of about 550 kg/m^3. One possible reason is the very different flow regimes of the two sites, one being at a Dome summit, and the other on a flow line and subject to a traction constraint (Lipenkov et al., 1989). This is not taken into account in our simplified 1D model. Some density data at other sites also show no densification rate change near the critical density, resulting in model-data mismatches (see Siple Dome, km 105, km 200, Mizuho on Supplementary Figure S7). However the new model still shows a tendency to overestimate the snow densification rate and then underestimate the densification rate in the firn, as shown for NEEM and Vostok on Figure 4.

The model result changes at high densities (above about 800 kg/m^3) are mostly due to the change in activation energies. The clearest improvement is obtained at South Pole, although the overall impact of using three activation energies remains small. No systematic improvement of the results was expected from adding the effect of dust as no specific tuning of the empirical parameterization of Freitag et al. (2013) was performed in our model, but the model results using the original parameterization of Freitag et al. (2013) always remain in reasonable agreement with the data. This is due to the fact that the impurity concentration remains small in modern climate, and consequently dust has a limited effect on the creep parameter (see also Supplementary Figure S4). In order to more quantitatively address and visualize the model data comparison with the different versions of the model on the 21 selected sites, we calculate the following deviation in parallel to the $\sigma_{fit\text{-}data}$ above (Equation 11):

$$\sigma_{model-fit} = \sqrt{\left[\sum_{Nmax}^{i=1} \frac{\left(\rho_{model}^{i} - \rho_{fit}^{i}\right)^2}{N_{max}}\right]} \quad (12)$$

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Figure 5 and Supplementary Table S1 display the $\sigma_{model\text{-}fit}$ for the 21 different sites before and after modifications detailed in Section 2. Overall, in terms of $\sigma_{model\text{-}fit}$, only a small improvement (about 3%) is obtained by using the modified model rather than the former Goujon et al. (2003) mechanical scheme. However a systematic improvement is obtained at the five coldest sites. On the other hand, the incorporation of the impurity effects following the Freitag et al. (2013) parameterization in our model most often deteriorates the model-data agreement.

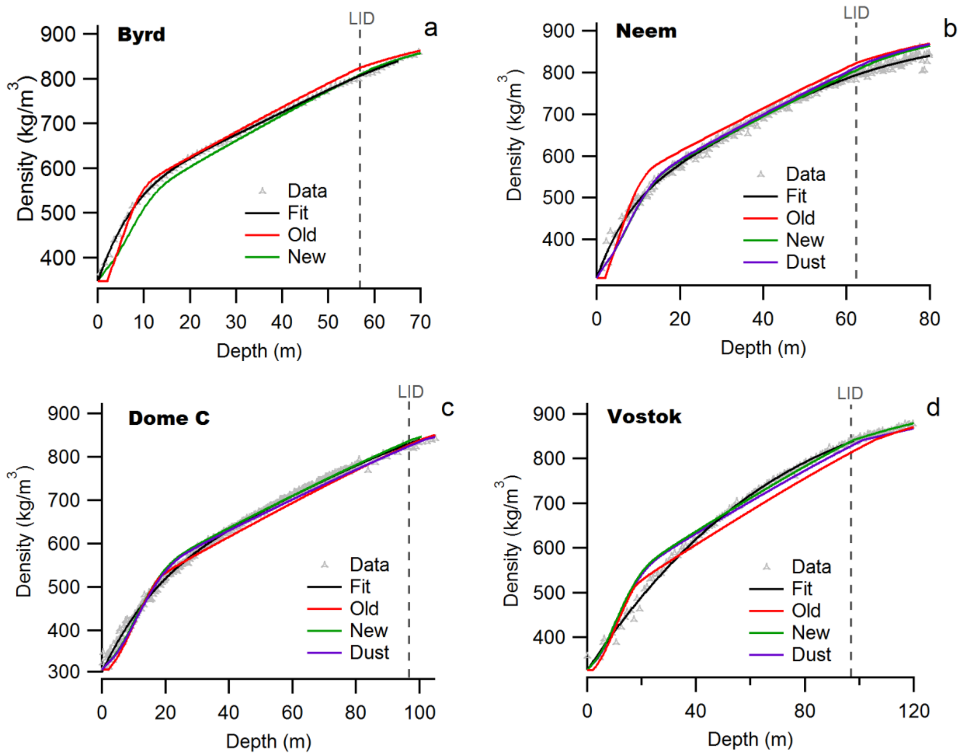

Figure 4: Density profiles of Byrd (a), NEEM (b), Dome C (c) and Vostok (d). The grey triangles correspond to the data. The black line corresponds to the polynomial fit, the red one to the old simulation, the green one to the new simulation and the purple one to the new simulation with impurity effect.

The comparison of the values of $\sigma_{model\text{-}fit}$ with $\sigma_{fit\text{-}data}$ shows that both are of the same order of magnitude. This means that our new model reproduces correctly the firn density profiles at different sites. The main disagreement between model and data is observed at the transition between the first and the second densification stage with too high modelled densities and an associated slope change in the density profile that is too strongly imprinted. This effect is due to a densification rate

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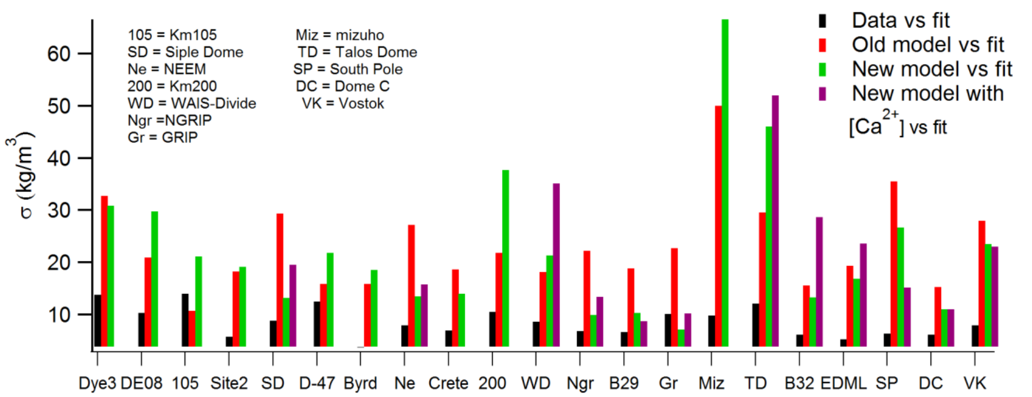
that is too high in the first stage, and this formulation is not affected by the new temperature sensitivity.

The first stage of densification is not crucial for our purpose here, which is to improve the agreement between the modelled LID and the evolution of $\delta^{15}N$ over deglaciations in Antarctica. In order to evaluate the ability of the model to predict the LID, we compared the depths at which the LID density, as defined by Equation (10), is reached in the polynomial fit to the data and in the new model results. In the old version of the model, the LID differences between the model and data range between -17.9 m (at South Pole) and +8.6 m (at km 200) with a small mean value of -1.9 m and a standard deviation of 6 m. In the new version, the LID differences between the model and data are comparable, ranging between -14.1 m (at South Pole) and +12.8 m (at Talos Dome) with a small mean value of -0.7 m and a standard deviation of 6 m. We thus conclude from this section that the LGGE new firn densification model preserves the good agreement between (1) modelled and measured firn density profiles and (2) modelled and measured LID. We explore in the next section the performances of the new model for coldest and driest conditions by looking at the modelled LID and hence $\delta^{15}N$ evolution over glacial – interglacial transitions.



<u>Figure 5</u>: Representation of the $\sigma_{fit\text{-}data}$ in black and the $\sigma_{model\text{-}fit}$ (in red for the old model, in green for the new model and in purple for the new model with the impurity effect) at 21 Greenland and Antarctic sites. The site characteristics are provided in Supplementary Table S1.

3.2 $\delta^{15}N$ glacial-interglacial profiles

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In order to test the validity of the densification model in a transient mode, we model the time evolution of $\delta^{15}N$ over the last deglaciation, and compare it to measurements at 4 Antarctic and Greenland deep ice-core sites: Dome C (cold and low accumulation site in Antarctica with a strong mismatch observed between data and the old model), EDML (intermediate temperature and accumulation rate in Antarctica with a significant mismatch between data and the old model), WAIS-Divide (high temperature and accumulation rate site in Antarctica with a good model-data agreement) and NGRIP (Greenland site with a good agreement between model and data) (Figure 3). The computation of $\delta^{15}N$ depends on the LID and on the firn temperature profile. The gravitational $\delta^{15}N$ signal is indeed calculated from the LID and mean firn temperature according to the barometric equation (Equation 1). The thermal $\delta^{15}N$ depends on the temperature gradient between the surface and the LID. The thermal $\delta^{15}N$ signal remains small in Antarctica because the temperature variations are slow (<2°C/1000 years), and is only important for abrupt climate changes in Greenland (e.g. NGRIP).

3.2.1

3.2.2 3.2.1 Input scenarios

For the simulation of the $\delta^{15}N$ evolution over the last deglaciation, the firn densification model is forced by a scenario of surface temperature and accumulation rate deduced from ice core data. In Greenland (NGRIP, GISP2), the temperature is reconstructed using the $\delta^{18}O_{ice}$ profiles together with indication from borehole temperature measurements (Dahl-Jensen, 1998) and $\delta^{15}N$ data for NGRIP (Kindler et al., 2014) for the quantitative amplitude of abrupt temperature changes. Greenland accumulation rate is deduced from layer counting over the last deglaciation (e.g. Rasmussen et al., 2006). The uncertainty in the temperature reconstructions can be estimated to ± 3°C over the last deglaciation in Greenland (Buizert et al., 2014). As for the Greenland accumulation rate, an uncertainty of 20% can be associated with the LGM value (Cuffey and Clow, 1997; Guillevic et al., 2013; Kapsner et al., 1995). In Antarctica, both temperature and accumulation rate are deduced from water isotopic records except for WAIS-Divide, where layer counting back to the last glacial period is possible (Buizert et al., 2015). Temperature uncertainty for the amplitude of the last deglaciation is estimated to -10% to +30% in Antarctica (Jouzel, 2003). In the construction of the AICC2012 chronology (Bazin et al., 2013; Veres et al., 2013), the first order estimate of accumulation rate from water isotopes for EDML, Talos Dome, Vostok and Dome C has been modified by incorporating dating constraints or stratigraphic tie points between ice cores (Bazin et al., 2013; Veres et al., 2013). The modification of the accumulation rate profiles over the last deglaciation for

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these 4 sites is less than 20% and the uncertainty of accumulation rate generated by the DATICE model used to build AICC 2012 from background errors (thinning history, accumulation rate, LID) and chronological constraints is 30% for the LGM (Bazin et al., 2013; Frieler et al., 2015; Veres et al., 2013). These values are consistent with previous estimates of accumulation rate uncertainties over the last deglaciation (± 10% for Dome C (Parrenin et al., 2007) and ± 30% in EDML (Loulergue et al., 2007)). The references of the scenarios for temperature and accumulation rate over the deglaciation used in this study are given in Supplementary Table S2.

We showed in Section 2.1 that surface density does not have a strong impact on the LID determination (Supplementary Figure S3). We do not have any indication of surface density in the past, so we impose a constant surface density of 0.35 for all sites at all times for transient runs. In order to convert the LID (deduced from density) to the diffusive column height measured by $\delta^{15}N$, we need an estimate of the convective zone in the past. We use a 2 m convective zone for all sites, except Vostok, where we use 13 m, in accordance with firn measurements (Bender et al., 2006). We assume that the convective zone did not evolve during the last deglaciation, consistently with dating constraints at Dome C and at Vostok during Termination 2 (Parrenin et al., 2012; Bazin et al., 2013; Veres et al., 2013; Landais et al., 2013).

3.2.2 Transient run with the old model

In this section, we focus on the $\delta^{15}N$ evolution over the deglaciation at different Greenland and Antarctic sites as obtained from the data and as modelled with the old version of the LGGE model. This comparison serves as a prerequisite for the comparison with outputs of the improved model over the same period for the same polar sites. The comparison between the old LGGE model and $\delta^{15}N$ data over the last deglaciation shows the same patterns as already discussed in Capron et al. (2013). At Greenland sites, there is an excellent agreement between model and data showing both the decrease in the mean $\delta^{15}N$ level between the LGM and the Holocene and the ~0.1 ‰ peaks in $\delta^{15}N$ associated with the abrupt temperature changes (end of the Younger Dryas, Bølling-Allerød, Dansgaard-Oeschger 2, 3 and 4, Figure 6 and Supplementary Figure S8). On the other hand, the modelled and measured $\delta^{15}N$ over the last deglaciation show significant dissimilarities in Antarctic $\delta^{15}N$ profiles displayed on Figure 6 and Supplementary Figure S8, except at the relatively high accumulation rate and temperature site of WAIS-Divide where the model simulates properly the $\delta^{15}N$ evolution in response to the change in accumulation and mean firn temperature estimated

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from water isotopic records and borehole temperature constraints (Buizert et al., 2015). Note that in Buizert et al. (2015), the modelled $\delta^{15}N$ was obtained from the Herron and Langway model. For the other Antarctic sites (Figure 6), we observe that model and data disagree on the $\delta^{15}N$ difference between the LGM and Holocene levels. At EDML, Dome C and Vostok, the model predicts a larger LID during the LGM, while $\delta^{15}N$ suggests a smaller LID compared to the Holocene (with the assumption of no change in convective zone during the deglaciation). In addition, the measured $\delta^{15}N$ profiles at Berkner Island, Dome C, EDML and Talos Dome display an additional short term variability, i.e. $\delta^{15}N$ variations of 0.05‰ in a few centuries during stable climatic periods. These variations can be explained by the ice quality (coexistence of bubbles and clathrates) at Dome C and EDML. Indeed, for pure clathrate ice from these two sites, such short term variability is not observed (e.g. Termination 2 at Dome C, Landais et al., 2013). At Berkner Island and Talos Dome, these variations cannot be explained by the quality of the measurements, by thermal effects nor by dust influence. They are also not present in the accumulation rate and temperature forcing scenarios deduced from water isotopes (Capron et al., 2013). This observation questions the possible presence of a convective zone and/or the accuracy of the reconstruction of past accumulation rate and temperature scenarios from water isotopes in Antarctica except at WAIS-Divide where layer counting is possible over the last deglaciation. We thus explore further the influence of accumulation rate and temperature uncertainties on the $\delta^{15}N$ modelling.

The uncertainties in the changes of temperature and accumulation rates over the deglaciation significantly influences the simulated $\delta^{15}N$, as already shown in previous studies and this sensitivity of $\delta^{15}N$ has even been used to adjust temperature and/or accumulation rate scenarios (Buizert et al., 2013; Guillevic et al., 2013; Kindler et al., 2014; Landais et al., 2006). We tested the influence of the accumulation rate and temperature scenarios on the simulated $\delta^{15}N$ profiles for the last deglaciation, but even with large uncertainties in the input scenarios, it is not possible to reproduce the measured Antarctic $\delta^{15}N$ increase at Dome C and EDML with the old version of the LGGE model.

This result is illustrated on Figure 7 where we display a comparison between the amplitude of the measured $\delta^{15}N$ change and the amplitude of the modelled $\delta^{15}N$ change with the Goujon version over the last deglaciation. For this comparison, we calculated the Last Glacial Maximum (LGM) $\delta^{15}N$ average over the period 18-23 ka and the Early Holocene (EH) $\delta^{15}N$ average over the period 6-10 ka (or smaller, depending on available data, cf blue boxes on Figure 6). We estimated the uncertainty in the measured $\delta^{15}N$ change by calculating first the standard deviation of the $\delta^{15}N$ data over each

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of the two periods, LGM and EH as $\sigma_{15N\_data\_EH}$ and $\sigma_{15N\_data\_LGM}$ and then the resulting uncertainty on the $\delta^{15}N$ change as:

$$\sigma_{15N\_EH-LGM} = \sqrt{\sigma^2_{15N\_data\_EH} + \sigma^2_{15N\_data\_LGM}}\,.$$

As for the modelled $\delta^{15}N$ change, associated error bars are deduced from the uncertainty on the temperature and accumulation input scenarios (shown on Supplementary Figure S9 for the improved model). The total error bar hence shows the difference between most extreme accumulation rate or temperature input scenarios. In these sensitivity tests, we assumed that it is not possible to have an underestimation of the temperature change with an overestimation of the accumulation rate (or the opposite) because changes in accumulation rate and temperature are linked, at least qualitatively.

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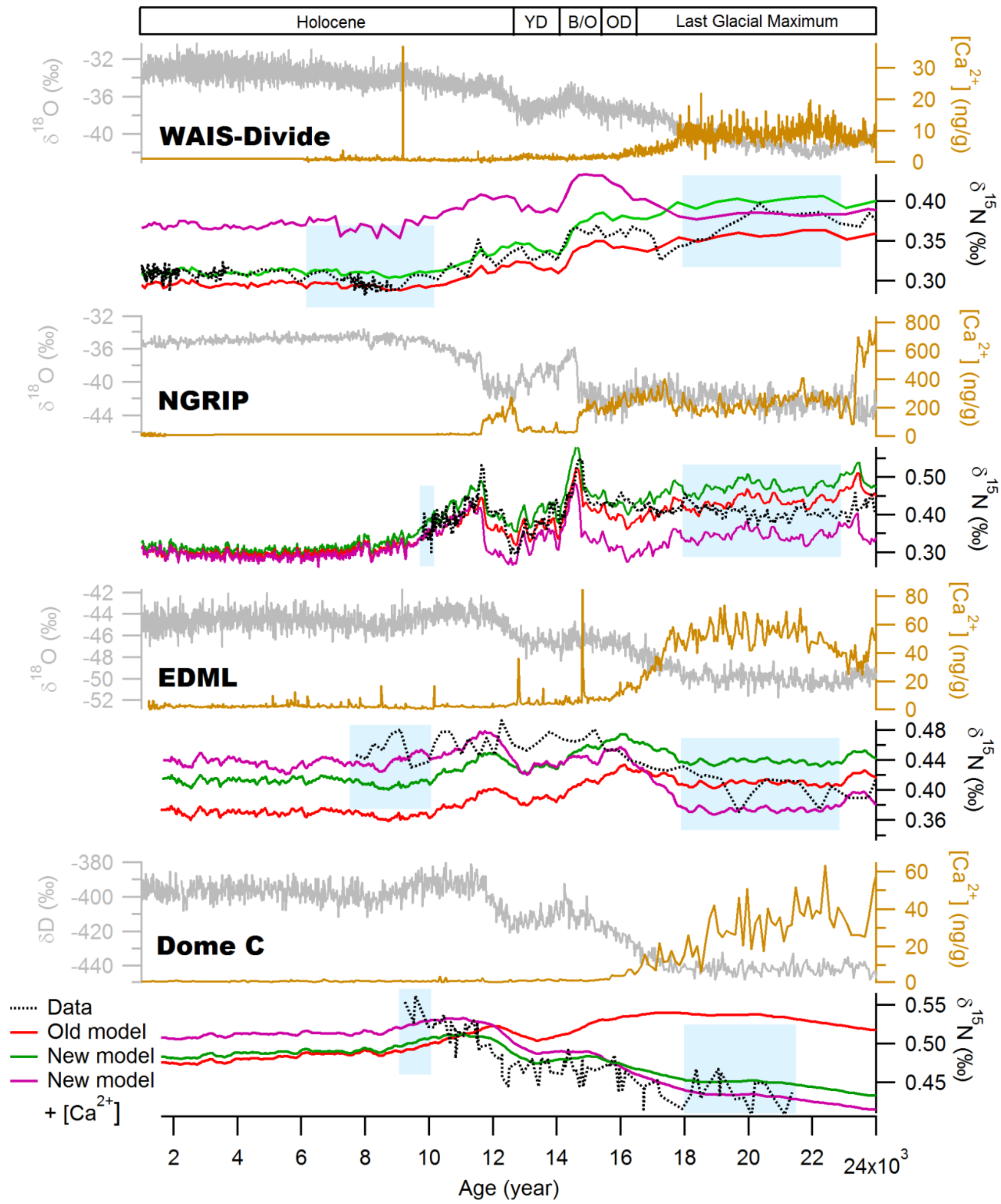

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646 *Figure 6: Comparison of the measured $\delta^{18}O$ or δD (grey), the calcium concentration (gold), the measured $\delta^{15}N$ (black)*
647 *and the modelled $\delta^{15}N$ (old (red), new version (green) and new version with impurity (purple)) of the LGGE model for*
648 *WAIS-Divide, NGRIP, EDML and Dome C. Blue boxes for each sites indicate the periods over which the $\delta^{15}N$ average for*
649 *the LGM and EH have been estimated for the calculation of the amplitude of the $\delta^{15}N$ change over the deglaciation.*

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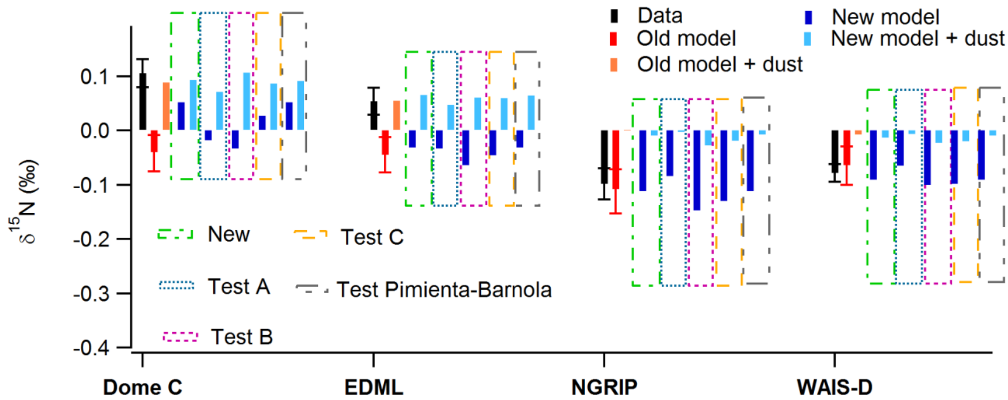

<u>Figure 7</u>: Difference between EH and LGM δ^{15}N at 4 different polar sites (raw data are given in Supplementary Table S3). The measured δ^{15}N difference is shown with a black bar. The modelled δ^{15}N difference is shown with colours: old version in red (orange with the impurity influence), new version in blue with different parameterizations. "New" corresponds to the parameterization of Table 1, sensitivity tests A, B and C are explained on Table 3. When "+ dust" is mentioned, it corresponds to the addition of the impurity influence as parameterized by Freitag et al., (2013) (Equations 8 and 9). Test Pimienta-Barnola corresponds to a test with the Freitag parameterization adapted to the Pimienta-Barnola model instead of the Herron and Langway model used for the other sensitivity tests. This test shows in light blue the result of the implementation of this parameterization combined with the "New" parameterization from Table 1. The same red error bars can be applied to all model outputs for each sites.

3.2.3 Results with updated temperature parameterization

By construction, the new LGGE firn model with the temperature dependency of the firn densification module depicted on Section 2.2.1 is expected to improve the agreement between model and data for cold sites of East Antarctica over the last deglaciation by increasing densification rate at low temperature. This new parameterization modifies the densification rate through the creep parameter given in Equation (7). Figure 8 shows the evolution of the creep parameter with temperature for different choices of the three activation energies Q_1, Q_2 and Q_3. Compared to the old model, the densification rate is higher at low temperature, below -55°C (i.e. for LGM at Dome C and Vostok, Table 1). At higher temperature (between -55°C and -28°C corresponding to present-day temperature in most polar sites), the creep parameter is slightly lower than in the old model. The difference between the 2 curves is however not large so that densification rate is not strongly modified over this range. This is in agreement with comparable firn density profiles obtained for the different polar sites using the old or the improved LGGE model (Section 3.1, Figure 4).

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In the improved model, the simulated profiles of $\delta^{15}N$ are comparable to $\delta^{15}N$ simulated with the old model at the sites that were already showing a good agreement between the old model outputs and data, for example NGRIP, GISP-2, Talos Dome and WAIS-Divide (Figure 6 and Supplementary Figure S8). This is expected since the corresponding densification rate is only slightly reduced in the temperature range of -55°C/-28°C which corresponds to the temperature range encompassed over the last deglaciation at these sites. This results in a deeper LID and hence higher $\delta^{15}N$ level, which is in general compatible with the data. At the coldest sites (Dome C, Vostok), the agreement between data and modelled profiles is largely improved with a modelled LGM $\delta^{15}N$ smaller than the modelled EH $\delta^{15}N$, but a perfect match cannot be found. At the intermediate EDML site, it is not possible to reproduce the sign of the slope during the deglaciation.

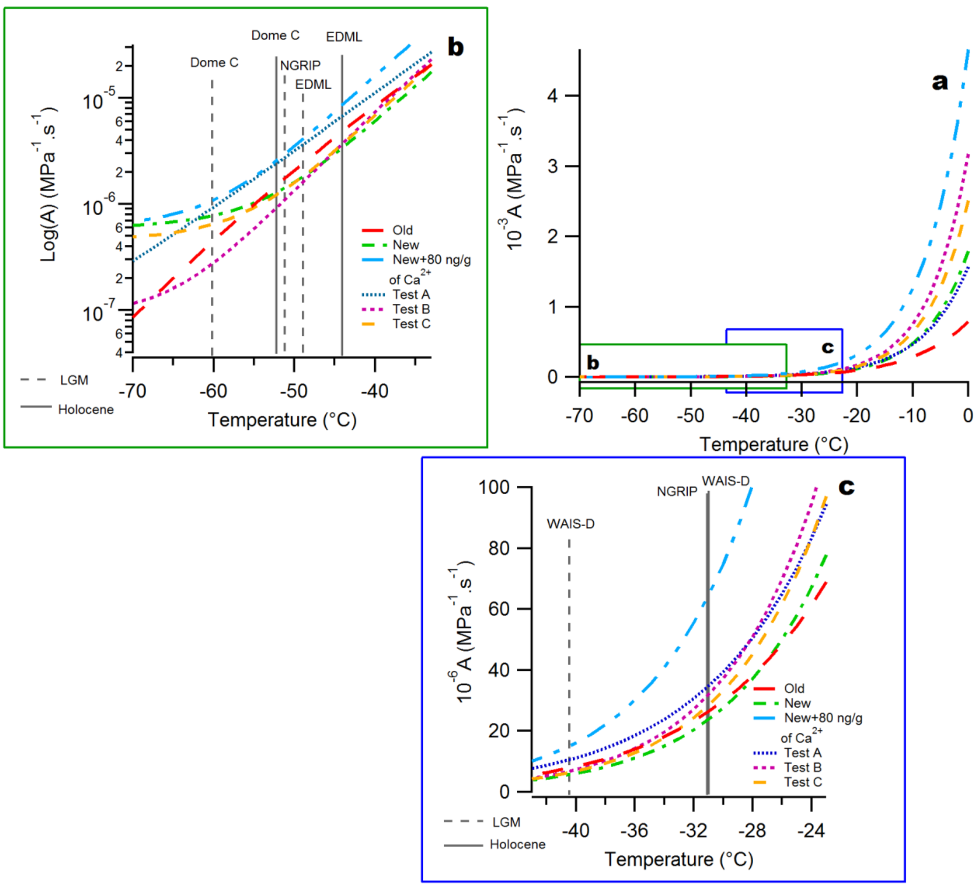

Figure 8: Evolution of the creep parameter (Equation 7) as a function of temperature for 6 different parameterizations. "Old" corresponds to the Goujon et al. (2003) version of the model; "New" corresponds to

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the improved LGGE model with parameterization described in Table 1; "New + 80 ng/g of Ca^{2+}" corresponds to the parameterization of Table 1 with the addition of the impurity effect following Equation (8) and a $[Ca^{2+}]$ value of 80 ng/g; Tests A, B and C are sensitivity tests run with the values presented on Table 3. Figure 8a shows the creep parameter evolution for the whole temperature range, Figure 8b is a focus at very low temperature and Figure 8c is a focus at intermediate temperature. The grey vertical lines indicates the temperature for Early Holocene (EH, solid line) and LGM (dotted line) at the 4 study sites presented in Figures 6 and 7.

Test	Activation energy (J/mol)	Coefficient
Test A	90000	$5.5*10^{5}$
	60000	1.0
	30000	$4.5*10^{-8}$
Test B	110000	$5.5*10^{9}$
	75000	1950.0
	1500	$9.0*10^{-16}$
Test C	100000	$4.5*10^{7}$
	75000	1670.0
	1500	$4.6*10^{-15}$

<u>Table 3:</u> Values used for the different sensitivity tests for three activation energies.

In order to more quantitatively assess the robustness of the proposed parameterization in Table 1, we confront in Figure 7 the measured and modelled $\delta^{15}N$ differences between the LGM and EH at the 4 Greenland and Antarctic sites selected above. For this comparison, we use not only the parameterization of Table 1 but also sensitivity tests performed with different parameterizations of the temperature dependency of activation energy and impurity effects (details on Table 3). When using the parameterization of Table 1 ("new model"), Figure 7 shows strong improvement of the agreement between measured versus modelled $\delta^{15}N$ difference between EH and LGM with, as mentioned above and shown on Figure 6, an inversion of the $\delta^{15}N$ difference for the very cold sites of East Antarctica (Figure 7).

The sensitivity tests illustrate the choice of our final parameterization. As displayed in Figure 8, test A has a higher creep parameter than the old model throughout the whole temperature range. Compared to the output of the old model, the LGM vs EH $\delta^{15}N$ change simulated with test A is slightly higher but the sign of the $\delta^{15}N$ change over the last deglaciation is still wrong at Dome C and EDML. This test shows that it is not the mean value of the creep parameter that needs to be changed, but the dependency to temperature. Test B has a higher creep parameter above -35°C, but a lower creep

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parameter than the old model below -35°C, which starts flattening and hence reaching values higher than the old model creep parameter below -65°C. The LGM vs EH $\delta^{15}N$ change simulated with test B is still comparable with data at WAIS-Divide. However, the model – data comparison deteriorates at NGRIP and EDML compared to the model-data comparison with the old version of the model. Moreover, it does not solve the model – data mismatch at Dome C. This shows that the change in the creep parameter at intermediate temperature is too steep. Test C is rather close to the "new model" over most of the temperature range. Strong differences occur at high temperature (above -30°C) but it does not affect the modelled $\delta^{15}N$ change between LGM and EH for our 4 sites. On the contrary, the slightly lower creep parameter at low temperature leads to a less good agreement between model and data for the Dome C deglaciation than when using the "new model".

Summarizing, the best agreement between data and model for Dome C is obtained for the parameters given on Table 1: the creep parameter of "new model" flattens below -50°C and is thus not very different for the LGM or the EH at Dome C. As a result, the modelled LID and hence $\delta^{15}N$ are less sensitive to temperature, and the sign of the EH-LGM difference can be inverted, and brought closer to the observations. It should be noted that despite many sensitivity tests we could not find a parameterization able to reproduce the EH-LGM $\delta^{15}N$ changes for all 4 sites. In the "new model" without impurity effect, it is not possible to reproduce the measured EDML $\delta^{15}N$ change over the last deglaciation even when taking into account the uncertainty in the input parameters (temperature and accumulation rate, Supplementary Figure S9).

3.2.4 Impurity softening

The dust content in LGM ice is much larger than in Holocene ice (Figure 6), and impurity inclusions in ice have an impact on the grain structure, allowing it to deform more easily (Alley, 1987; Fujita et al., 2014). We incorporated dust softening using the parameterization of Freitag et al (2013) as detailed in Section 2.2.2. We compared two expressions for the impurity softening (tuned to be applied to the Herron and Langway model, or Pimienta and Barnola model), but found that the differences between the two parameterisations were minor (Figure 7). We use the Herron and Langway parameters in the following.

Figure 8 shows the effect of impurities on the creep parameter: densification is enhanced over the whole temperature range. At all sites, incorporating impurity softening reduces the firn thickness

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during periods characterized by high impurity concentration in the ice (LGM). It thus leads to an increase of the EH-LGM LID difference (Figure 7).

This effect clearly helps to bring in agreement modelled and measured $\delta^{15}N$ at Dome C, Vostok and EDML (Figures 6, 7 and Supplementary Figure S8): for these sites, the model incorporating the parameterization of activation energy depicted in Table 1 and the impurity effects is able to reproduce the $\delta^{15}N$ increase over the last deglaciation. Note that short-lived peaks in impurities, likely triggered by volcanic events, have a limited effect on bulk firn thickness (Figure 6). Contrary to the improved situation in cold Antarctic sites, we observe that, at the warmer sites like NGRIP and WAIS-Divide, incorporating impurity softening deteriorates the model data fit, which was already good in the older version of the model, and also good with other firn densification models (Kindler et al, 2014; Buizert et al, 2015). It produces almost no change in firn thickness between the LGM and the EH at NGRIP, which contradicts $\delta^{15}N$ observations. The same mismatch is observed at WAIS-Divide using a different model, as already noted by Buizert et al. (2015). We tested the sensitivity to the dust parameterization by implementing the Freitag parameterization adapted to the Pimienta-Barnola model instead of the Herron and Langway model used with our improved model (cf section 2.2.2). The two different parameterizations of the impurity effect lead to very comparable LGM to EH $\delta^{15}N$ changes over the last deglaciation on the 4 sites discussed here.

The mismatch observed for the $\delta^{15}N$ simulations at WAIS-Divide and NGRIP when incorporating the impurity effect suggests that the parameterization presented in Equations (8) and (9) is not appropriate to be used on bulk [Ca^{2+}] concentration and/or for LGM simulation. Actually, the proposed parameterization by Freitag et al. (2013) was tuned to density variability in present-day firn, and may not be valid for LGM when [Ca^{2+}] concentrations were 10-100 times larger than present-day. It is also possible that the dust effect saturates at high concentration, and is no longer sensitive above a certain threshold.

It is also possible that impurity influence, like temperature, acts differently depending on the dominant mechanism for firn deformation, and that the impurity effect is more important at colder temperature. The mechanisms by which impurities influence firn deformation are still poorly understood. In particular, the solubility of dust particles, and their position inside or at the grain boundaries may act on deformation in opposite way. More work is thus needed before the correct "impurity effect" component and the mechanisms by which it acts on densification are identified

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(e.g. Fujita et al., 2014, 2016). Here, we have shown that a simple parameterization as a function of $[Ca^{2+}]$ concentration does not provide uniformly good results, and seems only suitable for sites on the Antarctic Plateau.

To sum up, the new parameterization of the creep parameter preserves good agreement between the old model outputs and data at sites that were already well simulated (WAIS-Divide, NGRIP, Talos Dome), and improves the simulation of the deglaciation at cold Antarctic Sites (Dome C, Vostok). However, the EH-LGM $\delta^{15}N$ change at Dome C and EDML cannot be reproduced using only the temperature dependency of activation energy. The inclusion of impurity effect improves the situation for cold sites but leads to inconsistent $\delta^{15}N$ evolutions over the deglaciation at WAIS-Divide and NGRIP.

4. Conclusion and perspectives

In this study, we have presented an up-to-date version of the LGGE firn densification model. We have summarized the physical basis and parameterization choices of this firn model that would explain the disagreement between model and data on both the firn density profiles and the $\delta^{15}N$ evolution over the last deglaciation. The mismatch was particularly strong in the extremely cold sites of East Antarctica where modelled $\delta^{15}N$ shows an increase over the deglaciation, contrary to the measured $\delta^{15}N$ decrease. Based on analogy with ceramic sintering at hot temperature and recent observations of the impurity effect on firn density, we have improved the LGGE densification model by incorporating new parameterizations for the evolution of the creep parameter with temperature and impurity contents within the firn densification module. We follow previous studies evidencing different dominant firn sintering mechanisms in different temperature ranges that support a temperature dependency of the creep activation energy. We showed that these new parameterizations improve the agreement between model and data at low temperature (below -30°C), and retain the good agreement at warmer temperature. In particular, the improved LGGE firn density model is now the first firnification model able to reproduce the $\delta^{15}N$ increase over deglaciations at cold sites such as Dome C and Vostok.

The new parameterization implies a more rapid firn densification at lower temperature and high impurity load than in classical firnification models. This leads to a significantly lower Δage in glacial period for deep polar ice cores such as Dome C, Vostok and Dome Fuji. This result is in agreement with the recent low Δage estimate by Parrenin et al. (2012) over the deglaciation at Dome C. This

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has important consequences for the study of the CO_2 vs Antarctic temperature lead or lag over deglaciation. Our new parameterization is hence in agreement with the recent study of Parrenin et al. (2013) showing that the increases in East Antarctic temperature and CO_2 are synchronous over the last deglaciation.

The new parameterization proposed here calls for further studies. First, laboratory or field studies of firn densification at very cold controlled conditions would ideally be needed to check the predominance of the surface lattice diffusion mechanism around -60°C; this is a real challenge because of the slow speed of deformation. Second, we have suggested that the current parameterization of impurity on firn softening should be revised for glacial conditions with low temperature (Greenland) and very high impurity load. Third, the separate effects of impurities and temperature on firn densification and hence $\delta^{15}N$ evolution should be tested on different periods than the last deglaciation. Sequences of events associated with non-synchronous changes in surface temperature, accumulation rate and impurity content would be particularly valuable for this objective.

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References

Alley, R. B.: Firn densification by grain-boundary sliding: a first model, J. Phys. Colloq., 48(C1), C1-249-C1-256, doi:10.1051/jphyscol:1987135, 1987.

Anderson, D. L. and Benson, C. S.: The densification and diagenesis of snow, in Ice and Snow: Properties, Processes and Applications, pp. 391–411, MIT Press., 1963.

Arnaud, L.: Modélisation de la transformation de la neige en glace à la surface des calottes polaires; Etude du transport des gaz dans ces milieux poreux, PhD Thesis, Université Joseph Fournier - Grenoble 1, 294 pp, 1997.

Arnaud, L., Barnola, J. M. and Duval, P.: Physical modeling of the densification of snow/firn and ice in, Phys. Ice Ore Rec., 26, 39–44, 2000.

Arthern, R. J., Vaughan, D. G., Rankin, A. M., Mulvaney, R. and Thomas, E. R.: In situ measurements of Antarctic snow compaction compared with predictions of models, J. Geophys. Res., 115(F3), doi:10.1029/2009JF001306, 2010.

Arzt, E.: The influence of an increasing particle coordination on the densification of spherical powders, Acta Metall., 30(10), 1883–1890, 1982.

Arzt, E., Ashby, M. F. and Easterling, K. E.: Practical applications of hot-isostatic pressing diagrams: four case studies, Metall. Trans. A, 14(1), 211–221, 1983.

Barnes, P., Tabor, D. and Walker, J. C. F.: The friction and creep of polycrystalline ice, in Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, vol. 324, pp. 127–155, The Royal Society, 1971.

Barnola, J.-M., Pimienta, P., Raynaud, D. and Korotkevich, Y. S.: CO2-climate relationship as deduced from the Vostok ice core: a re-examination based on new measurements and on a re-evaluation of the air dating, Tellus B, 43(2), 83–90, 1991.

Bazin, L., Landais, A., Lemieux-Dudon, B., Toyé Mahamadou Kele, H., Veres, D., Parrenin, F., Martinerie, P., Ritz, C., Capron, E., Lipenkov, V., Loutre, M-F., Vinther, B., Svensson, A., Rasmussen, S. O., Severi, M., Blunier, T., Leuenberger, M., Fischer, H., Masson-Delmotte, V., Chapellaz, J., and Wolff E.: An optimized multi-proxy, multi-site Antarctic ice and gas orbital chronology (AICC2012): 120-800 ka, Clim. Past, 9(4), 1715–1731, 2013.

Bender, M. L., Floch, G., Chappellaz, J., Suwa, M., Barnola, J.-M., Blunier, T., Dreyfus, G., Jouzel, J. and Parrenin, F.: Gas age–ice age differences and the chronology of the Vostok ice core, 0–100 ka, J. Geophys. Res., 111(D21), doi:10.1029/2005JD006488, 2006.

Benson, C. S.: Stratigraphic studies in the snow and firn of the Greenland ice sheet, PhD Thesis, California Institute of Technology, pp 228, 1960.

Bernache-Assollant, D. and Bonnet, J.-P.: Frittage: aspects physico-chimiques - Partie 1: frittage en phase solide, Ed. Techniques Ingénieur., 2005.

© Author(s) 2016. CC-BY 3.0 License.

Blackford, J. R.: Sintering and microstructure of ice: a review, J. Phys. Appl. Phys., 40(21), R355–R385, doi:10.1088/0022-3727/40/21/R02, 2007.

Buizert, C., Sowers, T. and Blunier, T.: Assessment of diffusive isotopic fractionation in polar firn, and application to ice core trace gas records, Earth Planet. Sci. Lett., 361, 110–119, doi:10.1016/j.epsl.2012.11.039, 2013.

Buizert, C., Gkinis, V., Severinghaus, J. P., He, F., Lecavalier, B. S., Kindler, P., Leuenberger, M., Carlson, A. E., Vinther, B., Masson-Delmotte, V., White, J. W. C., Liu, Z., Otto-Bliesner, B. and Brook, E. J.: Greenland temperature response to climate forcing during the last deglaciation, Science , 345(6201), 1177–1180, doi:10.1126/science.1254961, 2014.

Buizert, C., Cuffey, K. M., Severinghaus, J. P., Baggenstos, D., Fudge, T. J., Steig, E. J., Markle, B. R., Winstrup, M., Rhodes, R. H., Brook, E. J., Sowers, T. A., Clow, G. D., Cheng, H., Edwards, R. L., Sigl, M., McConnell, J. R. and Taylor, K. C.: The WAIS Divide deep ice core WD2014 chronology-Part 1: Methane synchronization (68–31 ka BP) and the gas age–ice age difference, Clim. Past, 11(2), 153–173, doi:10.5194/cp-11-153-2015, 2015.

Capron, E., Landais, A., Buiron, D., Cauquoin, A., Chappellaz, J., Debret, M., Jouzel, J., Leuenberger, M., Martinerie, P., Masson-Delmotte, V., Mulvaney, R., Parrenin, F. and Prié, F.: Glacial–interglacial dynamics of Antarctic firn columns: comparison between simulations and ice core air-δ15N measurements, Clim. Past, 9(3), 983–999, doi:10.5194/cp-9-983-2013, 2013.

Colbeck, S. C.: Theory of metamorphism of dry snow, J. Geophys. Res. Oceans, 88(C9), 5475–5482, 1983.

Craig, H., Horibe, Y. and Sowers, T.: Gravitational separation of gases and isotopes in polar ice caps, Science, 242(4886), 1675–1678, 1988.

Cuffey, K. M. and Clow, G. D.: Temperature, accumulation, and ice sheet elevation in central Greenland through the last deglacial transition, J. Geophys. Res. Oceans, 102(C12), 26383–26396, 1997.

Dahl-Jensen, D.: Past Temperatures Directly from the Greenland Ice Sheet, Science, 282(5387), 268–271, doi:10.1126/science.282.5387.268, 1998.

Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balmaseda, M. A., Balsamo, G., Bauer, P., Bechtold, P., Beljaars, A. C. M., van de Berg, L., Bidlot, J., Bormann, N., Delsol, C., Dragani, R., Fuentes, M., Geer, A. J., Haimberger, L., Healy, S. B., Hersbach, H., Hólm, E. V., Isaksen, L., Kållberg, P., Köhler, M., Matricardi, M., McNally, A. P., Monge-Sanz, B. M., Morcrette, J.-J., Park, B.-K., Peubey, C., de Rosnay, P., Tavolato, C., Thépaut, J.-N. and Vitart, F.: The ERA-Interim reanalysis: configuration and performance of the data assimilation system, Q. J. R. Meteorol. Soc., 137(656), 553–597, doi:10.1002/qj.828, 2011.

Dreyfus, G. B., Jouzel, J., Bender, M. L., Landais, A., Masson-Delmotte, V. and Leuenberger, M.: Firn processes and δ15N: potential for a gas-phase climate proxy, Quat. Sci. Rev., 29(1–2), 28–42, doi:10.1016/j.quascirev.2009.10.012, 2010.

Ebinuma, T. and Maeno, N.: Particle rearrangement and dislocation creep in a snow-densification process, J. Phys. Colloq., 48(C1), C1-263-C1-269, doi:10.1051/jphyscol:1987137, 1987.

© Author(s) 2016. CC-BY 3.0 License.

EPICA community members: Eight glacial cycles from an Antarctic ice core, Nature, 429(6992), 623–628, 2004.

Freitag, J., Kipfstuhl, S., Laepple, T. and Wilhelms, F.: Impurity-controlled densification: a new model for stratified polar firn, J. Glaciol., 59(218), 1163–1169, doi:10.3189/2013JoG13J042, 2013.

Frieler, K., Clark, P. U., He, F., Buizert, C., Reese, R., Ligtenberg, S. R. M., van den Broeke, M. R., Winkelmann, R. and Levermann, A.: Consistent evidence of increasing Antarctic accumulation with warming, Nat. Clim. Change, 5(4), 348–352, doi:10.1038/nclimate2574, 2015.

Fujita, S., Hirabayashi, M., Goto-Azuma, K., Dallmayr, R., Satow, K., Zheng, J. and Dahl-Jensen, D.: Densification of layered firn of the ice sheet at NEEM, Greenland, J. Glaciol., 60(223), 905–921, doi:10.3189/2014JoG14J006, 2014.

Fujita, S., Goto-Azuma, K., Hirabayashi, M., Hori, A., Iizuka, Y., Motizuki, Y., Motoyama, H. and Takahashi, K.: Densification of layered firn in the ice sheet at Dome Fuji, Antarctica, J. Glaciol., 62(231), 103–123, doi:10.1017/jog.2016.16, 2016.

Goujon, C., Barnola, J.-M. and Ritz, C.: Modeling the densification of polar firn including heat diffusion: Application to close-off characteristics and gas isotopic fractionation for Antarctica and Greenland sites, J. Geophys. Res. Atmospheres, 108(D24), 2003.

Gow, A. J.: Deep core studies of the accumulation and densification of snow at Byrd station and Little America V, Antarctica, CRREL Research Report 197, 1968.

Guillevic, M., Bazin, L., Landais, A., Kindler, P., Orsi, A., Masson-Delmotte, V., Blunier, T., Buchardt, S. L., Capron, E., Leuenberger, M., Martinerie, P., Prié, F. and Vinther, B. M.: Spatial gradients of temperature, accumulation and δ18O-ice in Greenland over a series of Dansgaard-Oeschger events, Clim. Past, 9(3), 1029–1051, doi:10.5194/cp-9-1029-2013, 2013.

Hagenmuller, P., Chambon, G. and Naaim, M.: Microstructure-based modeling of snow mechanics: a discrete element approach, The Cryosphere, 9(5), 1969–1982, doi:10.5194/tc-9-1969-2015, 2015.

Helsen, M. M., van den Broeke, M. R., van de Wal, R. S. W., van de Berg, W. J., van Meijgaard, E., Davis, C. H., Li, Y. and Goodwin, I.: Elevation Changes in Antarctica Mainly Determined by Accumulation Variability, Science, 320(5883), 1626–1629, doi:10.1126/science.1153894, 2008.

Herron, M. M. and Langway, C. C.: Firn densification: an empirical model, J. Glaciol., 25(93), 373–385, 1980.

Hörhold, M. W., Laepple, T., Freitag, J., Bigler, M., Fischer, H. and Kipfstuhl, S.: On the impact of impurities on the densification of polar firn, Earth Planet. Sci. Lett., 325, 93–99, 2012.

Jacka, T. H. and Li, J.: The steady-state crystal size of deforming ice, Ann. Glaciol., 20(1), 13–18, 1994.

Jouzel, J.: Magnitude of isotope/temperature scaling for interpretation of central Antarctic ice cores, J. Geophys. Res., 108(D12), doi:10.1029/2002JD002677, 2003.

Jouzel, J., Masson-Delmotte, V., Cattani, O., Dreyfus, G., Falourd, S., Hoffmann, G., Minster, B., Nouet, J., Barnola, J. M., Chappellaz, J., Fischer, H., Gallet, J. C., Johnsen, S., Leuenberger, M., Loulergue, L., Luethi, D., Oerter, H., Parrenin, F., Raisbeck, G., Raynaud, D., Schilt, A., Schwander, J., Selmo, E., Souchez, R., Spahni, R., Stauffer, B., Steffensen, J. P., Stenni, B., Stocker, T. F., Tison, J. L.,

© Author(s) 2016. CC-BY 3.0 License.

Werner, M. and Wolff, E. W.: Orbital and Millennial Antarctic Climate Variability over the Past 800,000 Years, Science, 317(5839), 793–796, doi:10.1126/science.1141038, 2007.

Kapsner, W. R., Alley, R. B., Shuman, C. A., Anandakrishnan, S. and Grootes, P. M.: Dominant influence of atmospheric circulation on snow accumulation in Greenland over the past 18,000 years, Nature, 373(6509), 52–54, 1995.

Kindler, P., Guillevic, M., Baumgartner, M., Schwander, J., Landais, A., Leuenberger, M., Spahni, R., Capron, E. and Chappellaz, J.: Temperature reconstruction from 10 to 120 kyr b2k from the NGRIP ice core, Clim. Past, 10(2), 887–902, doi:10.5194/cp-10-887-2014, 2014.

Kojima, K.: Densification of seasonal snow cover, Phys. Snow Ice Proc. HUSCAP, 1(2), 929–952, 1967.

Landais, A., Barnola, J. M., Kawamura, K., Caillon, N., Delmotte, M., Van Ommen, T., Dreyfus, G., Jouzel, J., Masson-Delmotte, V., Minster, B., Freitag, J., Leuenberger, M., Schwander, J., Huber, C., Etheridge, D. and Morgan, V.: Firn-air δ15N in modern polar sites and glacial–interglacial ice: a model-data mismatch during glacial periods in Antarctica?, Quat. Sci. Rev., 25(1–2), 49–62, doi:10.1016/j.quascirev.2005.06.007, 2006.

Landais, A., Dreyfus, G., Capron, E., Jouzel, J., Masson-Delmotte, V., Roche, D. M., Prié, F., Caillon, N., Chappellaz, J., Leuenberger, M., Lourantou, A., Parrenin, F., Raynaud, D. and Teste, G.: Two-phase change in CO2, Antarctic temperature and global climate during Termination II, Nat. Geosci., 6(12), 1062–1065, doi:10.1038/ngeo1985, 2013.

Li, J. and Zwally, H. J.: Modeling the density variation in the shallow firn layer, Ann. Glaciol., 38(1), 309–313, 2004.

Ligtenberg, S. R. M., Medley, B., Van Den Broeke, M. R. and Munneke, P. K.: Antarctic firn compaction rates from repeat-track airborne radar data: II. Firn model evaluation, Ann. Glaciol., 56(70), 167–174, doi:10.3189/2015AoG70A204, 2015.

Lipenkov, V. Y., Barkov, N. I., Duval, P. and Pimienta, P.: Crystalline texture of the 2083 m ice core at Vostok Station, Antarctica, J. Glaciol., 35(121), 392–398, 1989.

Loulergue, L., Parrenin, F., Blunier, T., Barnola, J.-M., Spahni, R., Schilt, A., Raisbeck, G. and Chappellaz, J.: New constraints on the gas age-ice age difference along the EPICA ice cores, 0-50 kyr, Clim. Past, 3, 527–540, 2007.

Loulergue, L., Schilt, A., Spahni, R., Masson-Delmotte, V., Blunier, T., Lemieux, B., Barnola, J.-M., Raynaud, D., Stocker, T. F. and Chappellaz, J.: Orbital and millennial-scale features of atmospheric CH4 over the past 800,000 years, Nature, 453(7193), 383–386, doi:10.1038/nature06950, 2008.

Lüthi, D., Le Floch, M., Bereiter, B., Blunier, T., Barnola, J.-M., Siegenthaler, U., Raynaud, D., Jouzel, J., Fischer, H., Kawamura, K. and Stocker, T. F.: High-resolution carbon dioxide concentration record 650,000–800,000 years before present, Nature, 453(7193), 379–382, doi:10.1038/nature06949, 2008.

Maeno, N. and Ebinuma, T.: Pressure sintering of ice and its implication to the densification of snow at polar glaciers and ice sheets, J. Phys. Chem., 87(21), 4103–4110, 1983.

Marcott, S. A., Bauska, T. K., Buizert, C., Steig, E. J., Rosen, J. L., Cuffey, K. M., Fudge, T. J., Severinghaus, J. P., Ahn, J., Kalk, M. L., McConnell, J. R., Sowers, T., Taylor, K. C., White, J. W. C. and

Clim. Past Discuss., doi:10.5194/cp-2016-91, 2016
Manuscript under review for journal Clim. Past
Published: 12 October 2016
© Author(s) 2016. CC-BY 3.0 License.

Brook, E. J.: Centennial-scale changes in the global carbon cycle during the last deglaciation, Nature, 514(7524), 616–619, doi:10.1038/nature13799, 2014.

Martinerie, P., Raynaud, D., Etheridge, D. M., Barnola, J.-M. and Mazaudier, D.: Physical and climatic parameters which influence the air content in polar ice, Earth Planet. Sci. Lett., 112(1–4), 1–13, 1992.

Martinerie, P., Lipenkov, V. Y., Raynaud, D., Chappellaz, J., Barkov, N. I. and Lorius, C.: Air content paleo record in the Vostok ice core (Antarctica): A mixed record of climatic and glaciological parameters, J. Geophys. Res. Atmospheres, 99(D5), 10565–10576, 1994.

Mellor, M.: Properties of snow, CRREL Monograph, Section III-A1., 1964.

Miller, D. A., Adams, E. E. and Brown, R. L.: A microstructural approach to predict dry snow metamorphism in generalized thermal conditions, Cold Reg. Sci. Technol., 37(3), 213–226, doi:10.1016/j.coldregions.2003.07.001, 2003.

Overly, T. B., Hawley, R. L., Helm, V., Morris, E. M. and Chaudhary, R. N.: Greenland annual accumulation along the EGIG line, 1959–2004, from ASIRAS airborne radar and detailed neutron-probe density measurements, Cryosphere Discuss., 9(6), 6791–6828, doi:10.5194/tcd-9-6791-2015, 2015.

Parrenin, F., Dreyfus, G., Durand, G., Fujita, S., Gagliardini, O., Gillet, F., Jouzel, J., Kawamura, K., Lhomme, N., Masson-Delmotte, V., Rizt, C., Schwander, J., Shoji, H., Uemura, R., Watanabe, O., and Yoshida, N.: 1-D-ice flow modelling at EPICA Dome C and Dome Fuji, East Antarctica, Clim. Past, 3(2), 243–259, 2007.

Parrenin, F., Petit, J.-R., Masson-Delmotte, V., Wolff, E., Basile-Doelsch, I., Jouzel, J., Lipenkov, V., Rasmussen, S. O., Schwander, J., Severi, M., Udisti, R., Veres, D. and Vinther, B. M.: Volcanic synchronisation between the EPICA Dome C and Vostok ice cores (Antarctica) 0-145 kyr BP, Clim. Past, 8(3), 1031–1045, doi:10.5194/cp-8-1031-2012, 2012.

Parrenin, F., Masson-Delmotte, V., Köhler, P., Raynaud, D., Paillard, D., Schwander, J., Barbante, C., Landais, A., Wegner, A., Jouzel, J.: Synchronous change of atmospheric CO2 and Antarctic temperature during the last deglacial warming, Science, vol. 339, 1060-1063, 2013.

Pimienta, P.: Etude du comportement mécanique des glaces polycristallines aux faibles contraintes: applications aux glaces des calottes polaires, PhD Thesis, Université Scientifique Technologique et Médicale de Grenoble., 166 pp, 1987.

Pimienta, P. and Duval, P.: Rate controlling processes in the creep of the polar glacier ice, J. Phys. Colloq., 48(C1), C1-243-C1-248, doi:10.1051/jphyscol:1987134, 1987.

Proksch, M., Rutter, N., Fierz, C. and Schneebeli, M.: Intercomparison of snow density measurements: bias, precision, and vertical resolution, The Cryosphere, 10(1), 371–384, doi:10.5194/tc-10-371-2016, 2016.

Ramseier, R. O.: Self-diffusion in ice monocrystals, CRREL Research Report no 232, 1967.

Rasmussen, S. O., Andersen, K. K., Svensson, A. M., Steffensen, J. P., Vinther, B. M., Clausen, H. B., Siggaard-Andersen, M.-L., Johnsen, S. J., Larsen, L. B., Dahl-Jensen, D., Bigler, M., Röthlisberger, R.,

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Fischer, H., Goto-Azuma, K., Hansson, M. E. and Ruth, U.: A new Greenland ice core chronology for the last glacial termination, J. Geophys. Res., 111(D6), doi:10.1029/2005JD006079, 2006.

Rhodes, R. H., Brook, E. J., Chiang, J. C., Blunier, T., Maselli, O. J., McConnell, J. R., Romanini, D. and Severinghaus, J. P.: Enhanced tropical methane production in response to iceberg discharge in the North Atlantic, Science, 348(6238), 1016–1019, 2015.

Salamatin, A. N., Lipenkov, V. Y., Barnola, J. M., Hori, A., Duval, P. and Hondoh, T.: Snow/firn densification in polar ice sheets, Phys. Ice Core Rec. - II, 68(Supplement), 195–222, 2009.

Schwander, J.: The transformation of snow to ice and the occlusion of gases, Environ. Rec. Glaciers Ice Sheets, 53–67, 1989.

Schwander, J., Sowers, T., Barnola, J.-M., Blunier, T., Fuchs, A. and Malaizé, B.: Age scale of the air in the summit ice: Implication for glacial-interglacial temperature change, J. Geophys. Res. Atmospheres, 102(D16), 19483–19493, 1997.

Severinghaus, J. P., Sowers, T., Brook, E. J., Alley, R. B. and Bender, M. L.: Timing of abrupt climate change at the end of the Younger Dryas interval from thermally fractionated gases in polar ice, Nature, 391(6663), 141–146, 1998.

Sowers, T., Bender, M. and Raynaud, D.: Elemental and isotopic composition of occluded O2 and N2 in polar ice, J. Geophys. Res. Atmospheres, 94(D4), 5137–5150, 1989.

Sowers, T., Bender, M. and Korotkevich, Y.: δ15N of N2 in Air Trapped in Polar ice, J. Geophys. Res., 97(D14), 15–683, 1992.

Veres, D., Bazin, L., Landais, A., Toyé Mahamadou Kele, H., Lemieux-Dudon, B., Parrenin, F., Martinerie, P., Blayo, E., Blunier, T., Capron, E., Chappellaz, J., Rasmussen, S. O., Seeri, M., Svensson, A., Vinther, B., and Wolff, E. W.: The Antarctic ice core chronology (AICC2012): an optimized multi-parameter and multi-site dating approach for the last 120 thousand years, Clim. Past, 9(4), 1733–1748, 2013.

WAIS Divide Project Members: Onset of deglacial warming in West Antarctica driven by local orbital forcing, Nature, 500(7463), 440–444, doi:10.1038/nature12376, 2013.

WAIS Divide Project Members: Precise interpolar phasing of abrupt climate change during the last ice age, Nature, 520(7549), 661–665, 2015.

Wilkinson, D. S. and Ashby, M. F.: Pressure sintering by power law creep, Acta Metall., 23(11), 1277–1285, 1975.

Witrant, E., Martinerie, P., Hogan, C., Laube, J. C., Kawamura, K., Capron, E., Montzka, S. A., Dlugokencky, E. J., Etheridge, D., Blunier, T. and Sturges, W. T.: A new multi-gas constrained model of trace gas non-homogeneous transport in firn: evaluation and behaviour at eleven polar sites, Atmospheric Chem. Phys., 12(23), 11465–11483, doi:10.5194/acp-12-11465-2012, 2012.

Zwally, H. J. and Li, J.: Seasonal and interannual variations of firn densification and ice-sheet surface elevation at the Greenland summit, J. Glaciol., 48(161), 199–207, 2002.