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

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The transformation of snow into ice is a complex phenomenon which is 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. Here we present modifications of the LGGE firn densification model, which significantly reduce the model-data mismatch for the gas trapping depth evolution over the last deglaciation at coldest sites of East Antarctica (Vostok, Dome C), while preserving the good agreement between measured and modelled modern firn density profiles. In particular, we introduce a dependency of the creep factor on temperature and impurities in the firn densification rate calculation. The temperature influence intends to reflect the dominance 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. We find that a very low sensitivity of the densification rate to temperature has to be used in coldest conditions. The inclusion of impurities effects improves the agreement between modelled and measured $\delta^{15}N$ at cold East Antarctic sites during the last deglaciation, but deteriorates the agreement between modelled and measured $\delta^{15}N$ evolution in Greenland and Antarctic sites with high accumulation unless threshold effects are taken into account. We thus do not provide a definite solution to the firnification at very cold Antarctic sites but propose potential pathways for future studies.

35

1. Introduction

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

39   They are particularly useful to reconstruct the past variations of polar temperature and greenhouse

40   gases. The longest record covers 8 last glacial – interglacial cycles (EPICA community members,

41   2004; Jouzel et al., 2007; Loulergue et al., 2008; Lüthi et al., 2008) and very high resolution climate

42   records can be retrieved from ice cores drilled in high accumulation regions (Marcott et al., 2014;

43   Rhodes et al., 2015; WAIS Divide Project Members, 2013, 2015).

44

45   Polar ice is a porous medium, and contains bubbles filled with ancient atmospheric air, allowing the

46   reconstruction of the atmospheric composition in the past. The air is trapped at about 50-120 m

47   under the ice sheet surface. Above that depth, the interstitial air in firn pores remains in contact

48   with the atmosphere. Consequently, the air is always younger than the surrounding ice and this age

49   difference, Δage, can reach several millennia at the low temperature and accumulation rate sites of

50   East Antarctica.

51

52   A precise determination of Δage is essential to quantify the link between temperature changes

53   recorded in the water isotopic measurements on the ice phase and greenhouse gas concentrations

54   recorded in the gas phase. Still, quantifying the temporal relationship between changes in

55   greenhouse gas concentrations in air bubbles and changes in polar temperature recorded in the

56   isotopic composition of the ice is not straightforward. One way to address this question goes

57   through the development of firn densification models that depict the progressive densification of

58   snow to ice, and the associated decrease of porosity. Below a certain threshold density, the pores

59   seal off and the air is trapped. The firn densification models thus calculate the Lock-in Depth

60   (hereafter LID) according to surface climatic conditions. A higher temperature accelerates the firn

61   metamorphism and leads to a shallower LID. On the other hand, a higher snow accumulation at the

62   surface will have the effect of increasing the firn sinking speed and hence deepening the LID.

63   On glacial – interglacial timescales, increasing temperature is associated with increasing snow

64   accumulation. Indeed, the thermodynamic effect dominates when dealing with long term averages

65   (several thousands of years), even if accumulation and temperature are not always correlated on

66   millennial and centennial timescale in polar regions, especially in coastal areas (e.g. Fudge et al.,

67   2016; Altnau et al., 2014). As a consequence, we observe for all available ice cores covering the last

68 deglaciation joint increases in both accumulation and temperature. In the firn densification model,
69 both effects partially compensate each other, with the temperature effect being dominant in the
70 current densification models for the LID simulation over glacial – interglacial transitions in deep
71 drilling sites of the East Antarctic plateau, hence leading to the modelled LID decrease.

72 A first class of densification models is based on an empirical approach to link accumulation rate and
73 temperature at different polar sites to densification rates (allowing the match between the
74 modelled and the measured density profiles) (e.g. Herron and Langway, 1980). The Herron and
75 Langway (1980) model assumes that the porosity (air space in the firn) variations directly relate to
76 the weight of the overlying snow, hence the accumulation rate. A temperature dependence
77 following an Arrhenius law is also implemented to account for a more rapid compaction at higher
78 temperature. Finally, the exact model sensitivity to temperature and accumulation rate is adjusted
79 empirically in order to simulate observed density profiles. Measured density profiles exhibit
80 different densification rates above and below 550 kg/m^3 so that different empirical laws are used
81 for densities above and below this threshold. Indeed, 550 kg/m^3 corresponds to the observed
82 maximum packing density of snow (e. g. Anderson and Benson, 1963), hence to a change in the
83 driving mechanism of firnification.

84

85 Despite its simple empirical description, and although more sophisticated empirical models have
86 been developed (Arthern et al., 2010; Helsen et al., 2008; e.g. Li and Zwally, 2004; Ligtenberg et al.,
87 2015), the Herron and Langway (1980) firn model often provides good quality results and is still used
88 in a number of ice core studies (e.g. Buizert et al., 2015; Overly et al., 2015, Lundin et al., 2017).
89 However, its validity is questionable when used outside of its range of calibration, such as glacial
90 periods at cold sites of the East Antarctic plateau for which no present-day analogue exists. As a
91 consequence firn models including a more physical description of densification have been
92 developed (e.g. Arnaud et al., 2000; Salamatin et al., 2009). The model developed over the past 30
93 years at LGGE (Arnaud et al., 2000; Barnola et al., 1991; Goujon et al., 2003; Pimienta, 1987) aims
94 at using a physical approach which remains sufficiently simple to be used on very long time scales
95 (covering the ice core record length). More complex models, explicitly representing the material
96 micro-structure have been developed but require a lot more computing time (Hagenmuller et al.,
97 2015; Miller et al., 2003). Still, the simplified physical mechanisms in our model include parameters
98 adjusted through comparison of modelled and measured present-day firn density profiles which
99 may induce biased results outside the range of calibration.

100

101   In parallel to firn densification modelling, past firn LID can also be determined using the $\delta^{15}N$

102   measurements in the air trapped in ice cores. Indeed, in the absence of transient thermal gradients,

103   the $\delta^{15}N$ trapped at the bottom of the firn is mainly related to the diffusive column height (DCH).

104   This is due to gravitational settling in the firn following the steady state barometric equation (Craig

105   et al., 1988; Schwander, 1989; Sowers et al., 1989):

106

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

108

109   Where Δm is the mass difference (kg/mol) between ^{15}N and ^{14}N, g is the gravitational acceleration

110   (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

111   diffusive column height noted (DCH). In the absence of convection at the top of the firn, the firn LID

112   is equal to the DCH.

113

114   In Greenland ice cores, where strong and abrupt surface temperature changes occurred during the

115   last glacial period and deglaciation, $\delta^{15}N$ is also affected by strong thermal fractionation. An abrupt

116   warming (on the order of 10°C in less than 50 years) indeed induces a transient temperature

117   gradient in the firn of a few degrees (Severinghaus et al., 1998; Guillevic et al., 2013; Kindler et al.,

118   2014). $\delta^{15}N$ is thus modified as $\delta^{15}N_{therm} = \Omega*\Delta T$, where Ω is the thermal fractionation coefficient

119   (Grachev and Severinghaus, 2003) and this thermal signal is superimposed on the gravitational one

120   (the $\delta^{15}N_{therm}$ observed is in most cases lower than 0.15‰).

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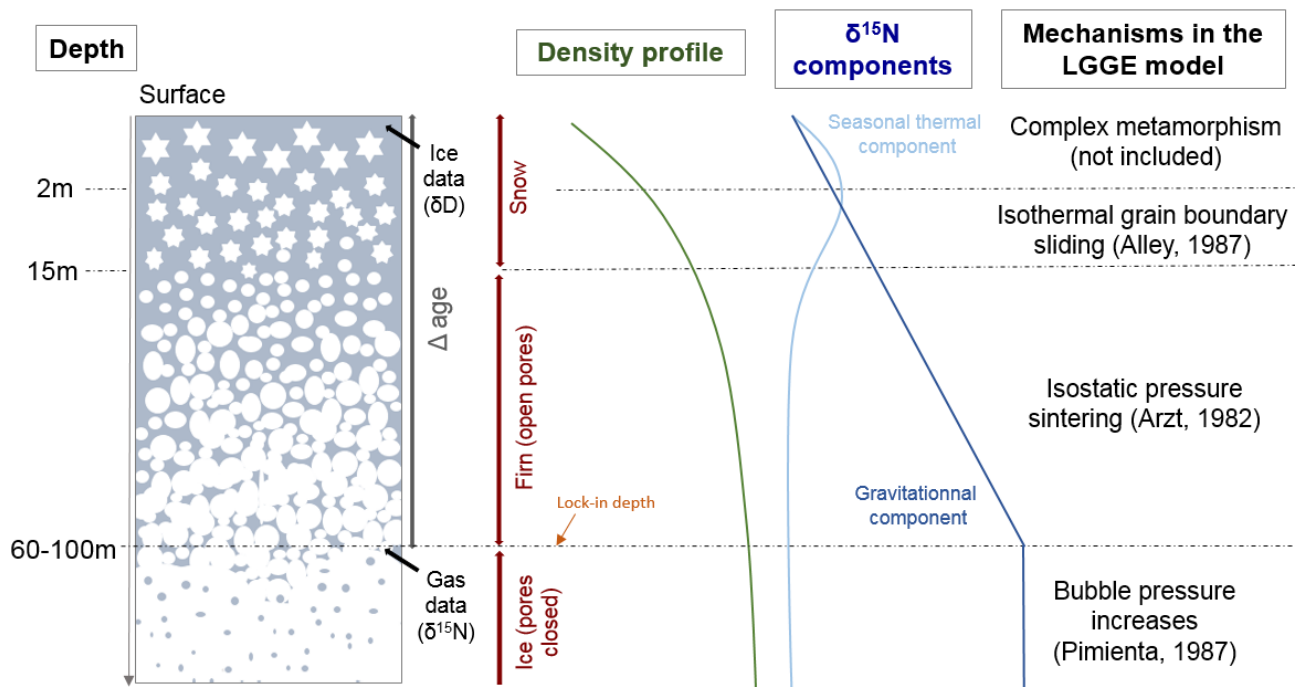
While models can reproduce the observed $\delta^{15}N$ at Greenland sites over the last climatic cycle, a strong mismatch is observed for cold Antarctic sites, especially on the East-Antarctic plateau (Dreyfus et al., 2010). In particular, both the empirical and physical models predict a decrease of 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. The differences in modelled and measured $\delta^{15}N$ for glacial periods in cold sites of the East-Antarctic plateau have important consequences for the Δage estimate and hence the ice core chronology: using the firn densification models, the modelled Δage for glacial period at Vostok and Dome C is too large by several centuries (Loulergue et al., 2007; Parrenin et al., 2012).

Several hypotheses have already been invoked to explain the $\delta^{15}N$ model-data mismatch in Antarctica as detailed in Landais et al. (2006), Dreyfus et al. (2010) and Capron et al. (2013). First, the firnification models have been developed and tuned for reproducing present-day density profiles and it is questionable to apply them to glacial climate conditions in Antarctica for which no present-day analogues are available. Second, increasing impurity concentration has been suggested to fasten firn densification during glacial period (Freitag et al., 2013; Hörhold et al., 2012). Third, a

~20 m deep convective zone has been evidenced in the megadunes region in Antarctica (Severinghaus et al., 2006) hence suggesting that deep convective zones can develop in glacial periods in Antarctica and explain the mismatch between firn densification model and δ^{15}N data (Caillon et al., 2003). This hypothesis can explain the mismatch between modelled and measured δ^{15}N at EDML during glacial period by invoking a 10 m convective zone (Landais et al., 2006). However, it has been ruled out for explaining the strong mismatch between model and δ^{15}N data at EDC for the last glacial period (Parrenin et al., 2012). Fourth, firn densification is very sensitive to changes in temperature and accumulation rate so that uncertainties in the surface climate parameters can lead to biased value of the modelled LID and hence δ^{15}N. Fifth, a significant thermal fractionation signal can affect the total δ^{15}N signal. However, this hypothesis has been ruled out by Dreyfus et al. (2010) based on δ^{15}N and δ^{40}Ar data on the last deglaciation at EDC.

In this study, we test whether 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 particular, it has been suggested by Capron et al. (2013) that the firn densification rate is underestimated at very low temperature. We also examine the possible influence of impurity concentration in the LGGE model following the approach by (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 output to present-day observed firn density profiles and δ^{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 (Supplementary Text S1). 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.

177 Using the resulting temperature profile in the firn, the mechanical module evaluates the
178 densification rates resulting from three successive mechanisms detailed below. Finally, a gas-age
179 module keeps track of snow layers sinking in a Lagrangian mode and uses a gas trapping criterion in
180 order to evaluate the gas trapping depth and the ice age – gas age difference (Δage).
181 The model does not take into account the complex mechanisms associated with snow
182 metamorphisms under the influence of strong temperature gradients, wind and sublimation/re-
183 condensation (Colbeck, 1983; Kojima, 1967; Mellor, 1964). This kind of metamorphism affects the
184 1-3 meters at the top of the firn and has a minor role on the modelled LID.
185 Below this depth, the densification of snow into ice has been divided into three stages (e.g. Maeno
186 and Ebinuma, 1983 and references therein; Figure 1). The first stage, named "snow densification"
187 as in Goujon et al. (2003), corresponds to a rearrangement and packing of snow grains until
188 approaching the maximum compaction at a density of about 550 kg/m^3 (or 0.6 on a unitless scale
189 relative to the density of pure ice) defined as the critical density. The second stage represents the
190 "firn densification" by sintering associated with visco-plastic deformation. Finally, when the bubbles
191 are closed (at a relative density of about 0.9), the ice densification is driven by the difference in
192 pressure between air trapped in bubbles and the solid ice matrix subject to the weight of the
193 overlying firn structure. In reality, the adjacent densification mechanisms likely coexist at
194 intermediate densities. Below we further describe the mechanical structure of the model with a
195 focus on recent modifications and proposed parameterizations. We refer to Arnaud et al. (2000)
196 and Goujon et al. (2003) for more details.
197
198 The model uses macroscopic (simplified) mechanical laws, which link the densification speed
199 (dD$_{rel}$/dt, in terms of relative density ($D_{rel} = \frac{\rho}{\rho_{ice}}$)) to its main driving force: the overburden
200 pressure of overlying snow. It is important to note that in our model, the accumulation rate
201 influences firn densification only through the overburden pressure:
202

203 $$P(h) = g \int_o^h \rho dz \qquad\qquad\qquad (2)$$

204

205 where g is the gravity constant and ρ is the density in kg/m^3. This differs from the Herron and
206 Langway (1980) model where the effect of accumulation rate is adjusted and expressed with a
207 different power law for snow and firn densification rates. In porous materials, the overburden
208 pressure P is transmitted through contact areas between grains rather than the entire surface of
209 the material. This is expressed by replacing P with an effective pressure P$_{eff}$ in mechanical stress-

7

210   strain laws. The relationship between P and P_{eff} depends on the material geometry (e.g. Equation

211   A4 in Goujon et al., 2003). A higher temperature (T) facilitates the deformation of materials, and

212   this effect is commonly represented by an Arrhenius law: $e^{\left(\frac{-Q}{RT}\right)}$ where R is the gas constant and Q

213   an activation energy. The value of the activation energy depends on the underlying physical

214   mechanism of ice and snow deformation but Arrhenius expressions cannot represent deformation

215   effects linked to ice melting. The relationships between densification speed and overburden

216   pressure take the following general form:

217

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

219

220   where A_0 = 7.89x 10^{-15} $Pa^{-3}.s^{-1}$ (Goujon et al., 2003, Eq. A5) and n is the stress exponent. In the rest

221   of the manuscript, we will refer to $A = A_0 \times e^{\left(-\frac{Q}{RT}\right)}$ as the creep parameter.

222

223   2.1 Densification of snow

224

225   During the first stage, the dominant snow densification mechanism is assumed to be isothermal

226   boundary sliding and the model of Alley (1987) is used (Figure 1). The geometrical approximation

227   used to build the model is to represent snow as equal size spheres with a number of contacts

228   between neighbours increasing with density. In the LGGE model, the Alley mechanism is

229   implemented as Equation A1 in Goujon et al. (2003):

230

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

232

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

234

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

236

237   where λ is the bond thickness, v the bond viscosity, R the grain radius and r the bond radius. P is

238   expressed as a function of accumulation and gravity (Equation 2).

239   The important simplification in the LGGE model is the replacement of geometry dependent

240   parameters, not available for past conditions, with a variable γ, adjusted in order to obtain a

241   continuous densification rate at the boundary between the first and the second stage of

242 densification.

243 A first modification in this module consists of extending the Alley (1987) scheme to the upper two

244 meters of the firn rather than using a constant density value. Indeed, since the model is not able to

245 represent the metamorphism of the first two meters, we impose a constant pressure of 0.1 Bar (see

246 Equation 6), which is an approximation of the pressure at 2-3 m depth. It results in a nearly constant

247 densification rate in the top 2-3 m rather than a constant density in the top 2 meters.

248 The second modification concerns the transition between the snow and firn densification stages at

249 the relative density of 0.6. In Equation (4), the term $\left(1 - \frac{5}{3} \times D_{rel}\right)$ implies that the densification

250 speed drops to zero at $D_{rel} = \frac{3}{5}$ (i.e. 0.6 the maximal compaction density). The second stage of

251 densification (firn densification) is driven by an important overburden pressure on the contact area

252 hence associated with a high densification speed. The transition between the sharp decrease of the

253 densification speed for D_{rel} values close to 0.6 in the snow densification stage and the high

254 densification speed at the beginning of the firn densification (i.e. in the same range of value for D_{rel})

255 causes some model instabilities especially at sites with high temperature and accumulation rate. In

256 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

257 initial formulation of Alley (1987). This term relies on a correlation between the coordination

258 number (N) and relative density: $D_{rel} = 10 N$. We slightly modified this relationship and impose $D_{rel} =$

259 *10 N - 0.5* which better matches the data on Figure 1 of Alley (1987). This results in replacing the

260 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

261 which the densification rate becomes zero from 0.6 to 0.65 and suppresses the model instability.

262

263 We also examine the effect of temperature on the first-stage densification mechanism and on the

264 critical density. Alley (1987) calculated a viscosity (ν) related activation energy of 41 kJ/mol,

265 consistent with recommended values for grain-boundary diffusion (42 kJ/mol) or measured from

266 grain growth rate (Alley, 1987 and references therein). In Goujon et al. (2003), no explicit

267 temperature effect is used but the parameter γ varies by several orders of magnitude from site to

268 site. The parameter γ is calculated to maintain a continuous densification rate between the first and

269 second stages at a chosen critical density. We translate the variations from site to site of $\gamma = (2 \lambda R)$

270 $/ (15 \nu r^2)$, where λ is the bond thickness, *R* the grain radius, ν the bond viscosity and *r* the bond

271 radius (as in Equation 5), into $\gamma = \gamma'$ exp(-Q/RT) , and calculate the activation energy Q using a

272 classical logarithmic plot as a function of 1000/T (see e.g. Herron and Langway, 1980). We obtain a

273 value of 48 kJ/mol. Using the revised temperature dependency for the firn densification mechanism

274 (see next section), a slightly higher value of Q =49.5 kJ/mol is calculated (Supplementary Figure S1).

275 This is fairly similar to the values in Alley (1987) but much higher than the value in the upper firn of

276 the Herron and Langway (1980) model: 10.16 kJ/mol. Incorporating this explicit temperature

277 dependency term, we obtain our new final expression for the upper firn densification rate:

278

279 $$\frac{dD_{rel}}{dt} = \gamma' \left(\frac{\max(P, 0.1\ bar)}{D_{rel}^2} \right) \left(1 + \frac{0.5}{6} - \frac{5}{3} \times D_{rel} \right) \times e^{\left(-\frac{Q}{RT} \right)} \tag{6}$$

280

281 where $\gamma' \times e^{\left(-\frac{Q}{RT} \right)}$ is equivalent to γ in Equation (4). However γ varies by two orders of magnitude

282 as a function of temperature whereas γ' remains in the range from 0.5×10^9 to 2×10^9 bar^{-1}.

283 Finally, the temperature dependency of the critical density, which defines the boundary between

284 the first and second stage densification mechanisms, is also re-evaluated. According to Benson

285 (1960) and Arnaud (1997; 2000), this critical density increases with temperature. However the slope

286 change in density profiles associated with the critical density may be difficult to locate and the

287 Benson (1960) and Arnaud (1997) parameterizations are based on only few observation sites. We

288 evaluate the critical density values which allow the best match of density data by our model results

289 at 22 sites and do not find any correlation between critical density and temperature or accumulation

290 rate (Supplementary Figure S2). We thus remove this dependency with temperature included in the

291 old version of the LGGE model and use a mean relative critical density of 0.56 at the boundary

292 between the first and second stage of densification in the new version of the model. The effect of

293 surface density was also tested and does not have a strong impact on the model results

294 (Supplementary Figure S3).

295

296 ## 2.2 Densification of firn

297

298 At this stage, the observation of density profiles with depth suggests that the densification rate is

299 controlled by a classical power law creep as used for ice deformation (Arzt et al., 1983; Maeno and

300 Ebinuma, 1983; Wilkinson and Ashby, 1975). Arzt (1982) proposed a pressure sintering mechanism

301 for firn densification following a power law creep and taking into account the progressive increase

302 of the coordination number. He solved the geometrical problem of compressing a random dense

303 packing of monosized spheres with associated deformation of each sphere into irregular polyhedra.

304 Equation (23) of Arzt (1982) is directly used in the firn densification model.

305

306 ### 2.2.1 Revised temperature sensitivity of the firn densification rate

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307

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 activation energy of 60 to 75 kJ/mol is associated with this mechanism (Arthern et al., 2010; Barnes et al., 1971; 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 (Ashby, 1974; Blackford, 2007; Maeno and Ebinuma, 1983; Wilkinson and Ashby, 1975): lattice diffusion from dislocations, grain surfaces or grain boundaries; vapor transport; 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 could be favoured (up to 177 kJ/mol between -1 and -5°C [Jacka and Li, 1994]) in order to best fit density profiles with firn densification models (Arthern et al., 2010; Barnes et al., 1971; Jacka and Li, 1994, Morgan, 1991). 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), by analogy with ceramic sintering, lattice diffusion from the surface of the grains and/or boundary diffusion from grain boundaries should be favoured (Ashby, 1974). The activation energy for surface diffusion is estimated to be in the range 14-38 kJ/mol (Jung et al., 2004; Nie et al., 2009).

Following these arguments and despite the lack of experimental constraints to test this assumption, we propose a new heuristic parameterization of the activation energy in the LGGE firn densification model which increases the firn densification rate at low temperatures. We have thus enabled introduction of three adjusted activation energies as proposed in Table 1 and Figure 2. We have replaced the creep parameter in Equation (3) by:

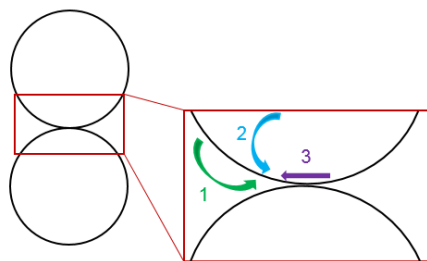$$A = A_0 \times \left(a_1 \times e^{\frac{-Q_1}{RT}} + a_2 \times e^{\frac{-Q_2}{RT}} + a_3 \times e^{\frac{-Q_3}{RT}} \right) \tag{7}$$

11

340

341   We have chosen a minimal number of mechanisms (3) for simplicity in the following but the

342   conclusions of our work would not be affected by a choice of more mechanisms.

343

- (1) mechanism 1: close to melting temperature - mass transfer by diffusion (potential mechanism for high temperature)

- (2) mechanism 2: low temperature - lattice diffusion (classical mechanism)

- (3) mechanism 3: very low temperature - boundary diffusion from grain boundary (potential mechanism for low temperature)

344
345

346 *Figure 2: Different sintering mechanisms of snow for different temperatures proposed by analogy with the*

347 *hot ceramic sintering (inspired by Figure 1 in Ashby, 1974). Note that more sintering mechanisms can be found*

348 *in the literature: in its initial figure, Ashby (1974) mentioned 6 different mechanisms but only 2 permit*

349 *densification (lattice diffusion and boundary diffusion from grain boundary). The attributions of 3 different*

350 *mechanisms for the firn densification model based on the powder aggregate study from Ashby (1974) is only*

351 *a working hypothesis here.*

352

353   When building the new parameterization of the activation energy (Equation 7), the determination

354   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

355   other. We first determine three temperature ranges corresponding to the dominant mechanisms,

356   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

357   finally adjusted to produce the expected evolution of the creep parameter with temperature, to

358   best reproduce $\delta^{15}N$ evolution over deglaciations (Section 3.2) and respect the firn density profiles

359   available (Section 3.1).

360   Hundreds of sensitivity tests have been performed imposing 3 activation energies at 3 different

361   typical temperatures, T_i. The initial values for Q_i are chosen as explained above (high value for Q_1

362   [Jacka and Li, 1994], classical value between 60 and 70 kJ/mol for Q_2 and low value for Q_3 to increase

363   the densification rate at low temperature). The initial values for a_i are derived through $a_i*exp(-$

364     $Q_i/RT_i)=a_0*exp(-60000/RT_i)$ and variations around the initial values of Q_i and a_i are randomly

365   generated. Only the values leading to realistic densification speed are kept and we found the

366   optimal tuning through reduction of the mismatch between model and data especially for the

367   deglacial amplitude of $\delta^{15}N$ in Dome C and Vostok. The constraint of keeping a correct agreement

368   of model results with present day density profiles and for the last deglaciation at warm sites strongly

369   reduces the possible choices of a_i and Q_i (Section 3). The best value obtained for Q_3 is lower than

370   published values for surface or boundary diffusion but is necessary to reproduce the deglaciation at

371   cold East Antarctic Sites. Sensitivity test C will illustrate the effect of using a higher value.

372

373   The resulting expression for the creep parameter A (Equation 7), does not strongly differ from using

374   simply $A = A_0 \times e^{\left(-\frac{60000}{RT}\right)}$, as used in the original model. To illustrate this point, we calculated an

375   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

376   54 and 61 kJ/mol (Supplementary Figure S4). Thus only moderate changes to the densification

377   equation are needed to improve the behaviour of the model at cold temperature. In addition, only

378   moderate changes in Q_{eq} are allowed to preserve the consistency between model results and

379   present-day density profiles.

380

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}

381

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

383

384   2.2.2 Sensitivity of the firn densification rate to impurities

385

386   Firn densification can be influenced by impurity content in snow. Alley (1987) already suggested

387   that grain growth is influenced by impurities dissolved in ice, and that impurities in the grain

388   boundaries affect the relative movement of snow grains. More recently, Hörhold et al. (2012)

389   observed a correlation between the small scale variability of density and calcium concentration in

390   Greenland and Antarctic firn cores. Based on this observation, Freitag et al. (2013) proposed that

391   the densification rate depends on the impurity content. They implemented an impurity

392   parameterization in two widely used densification models (Herron and Langway, 1980; Barnola et

393   al., 1991), and were able to reproduce the density variability in two firn cores from Greenland and

394   Antarctica.

395

396   We have implemented this parameterization in our model with the simple assumption that the

397   impurity effect is the same for all mechanisms. It allows us to keep the number of tunable

398   parameters to a minimum, even though this assumption is probably not correct for the vapor

399   diffusion process. Note however that this will not affect the applications discussed below since

400   vapor diffusion is only important for warm sites. Concretely, we start again from the evolution of

401   the creep parameter with respect to temperature given in Equation (7) and add a dependency to

402   calcium concentration such as:

403

404     $if\ [Ca^{2+}] > [Ca^{2+}]_{crit} : Q' = f_1 \times \left[1 - \beta \ln\left(\frac{[Ca^{2+}]}{[Ca^{2+}]_{crit}}\right)\right] \times Q$ (8)

405     $if\ [Ca^{2+}] < [Ca^{2+}]_{crit} : Q' = f_1 \times Q$ (9)

406

407   With, $[Ca^{2+}]_{crit}$ = 0.5 ng/g (the detection limit of continuous flow analysis). Q' represents the new

408   activation energy calculated as a function of the calcium concentration for each site. Our main

409   simulations are performed with the f_1 and β calculated by Freitag et al. (2013) for application within

410   the Herron and Langway model: f_1 = 1.025, β = 0.01. Using the values for application within the

411   Pimienta-Barnola model (f_1 = 1.015, β = 0.0105) leads to similar results (Section 3.2). For a first

412   evaluation of the impurity effect in our model, both the temperature and impurity effects are

413   combined through the application of Equations (8) and (9) to each of the three different activation

414   energies Q_1, Q_2 and Q_3. We use raw data of the calcium concentration for all the sites when available

415   even if question may arise on calcium concentration being the best diagnostic for dust content.

416   The values of a_i and Q_i were not readjusted after the implementation of impurity effects to avoid

417   adding tuning parameters. Still, because the large range of calcium concentrations encountered in

418   past climate conditions has a strong impact on model results, this may be a solution to reduce the

419   model-data mismatch. This is explored in Section 3 through a sensitivity test D. In the same section,

420   we will also propose a modification of the Freitag parameterization using thresholds to reduce the

421   model-data mismatch.

422

423   2.3 Densification of ice

424

425   As in Goujon et al. (2003), the final densification stage begins at the close-off density derived from

426   air content measurements in mature ice. Further porosity reduction results in an air pressure

427   increase in the bubbles (Martinerie et al., 1992, Appendix 1). This density is calculated using the

428   temperature dependent close-off pore volume given by Martinerie et al. (1994). Further

429   densification of this bubbly ice is driven by the pressure difference between ice matrix and the air

430   in bubbles (Maeno and Ebinuma, 1983; Pimienta, 1987). The densification rate strongly decreases

431   with depth as these two opposite pressures tend to balance each other (Goujon et al., 2003). This

432   stage is not essential for this study since $\delta^{15}N$ entrapped in air bubbles does not evolve anymore.

433

434   2.4 Lock-in depth

435

436   In the previous version of the model, the LID was computed as a fixed closed to total porosity ratio.

437   The ratio value used has been adjusted for each drilling site, for example it is 21% for Vostok and

438   13% at Summit in Goujon et al. (2003), but it was time independent and thus insensitive to climate.

439   We revised the LID definition in order to relate its present day geographic variations to climatic

440   parameters.

441

442   Ideally, $\delta^{15}N$ profiles in the open porosity of the firn follow the barometric slope in the diffusive

443   zone, and show no variations in the lock-in zone. However $\delta^{15}N$ data can deviate from this

444   behaviour, especially at the very low accumulation rate sites such as Dome C, Vostok or Dome Fuji,

445   where no $\delta^{15}N$ plateau is observed in the lock-in zone (Bender et al., 1994; Kawamura et al., 2006;

446   Landais et al., 2006). Moreover, as we aim at comparing our model results with $\delta^{15}N$ data in deep

447   ice cores, the most consistent LID definition should refer to $\delta^{15}N$ data in mature ice but very few

448   measurements are available for recent ice. Systematic $\delta^{15}N$ measurements in the closed porosity of

449   the deep firn or recently formed mature ice would be very helpful to better constrain the LID in the

450   future. We take advantage of recent advances in gas transport modelling (Witrant et al., 2012) that

451   allowed correct simulation of the $\delta^{15}N$ behaviour in deep firn. Observations of modern firn air

452   profiles show that the thickness of the lock-in zone (the zone in the deep firn with constant $\delta^{15}N$)

453   increases when the snow accumulation rate increases (Witrant et al., 2012). We estimate $\delta^{15}N$ in

454   ice, i.e. after complete bubble closure, at 12 firn air pumping sites with the Witrant et al. (2012)

455   model. For each site, the lock-in density (ρ_{LI}) is then defined as the density at which the modelled

456    $\delta^{15}N$ value in the open porosity of the firn equals the modelled $\delta^{15}N$ in ice. The resulting lock-in

457   density is strongly related to the accumulation rate (Supplementary Figure S5). As a result, we

458   parameterized the lock-in density (ρ_{LI}) as a function of the accumulation rate, following:

459

460    $\rho_{LI} = 1.43 \times 10^{-2} \times \ln(1/Ac) + 0.783$ (10)

461

462   This parameterization leads to ρ_{LI} variations in the range 780-840 kg/m^3 (Supplementary Figure S5)

463   and a much better agreement between the modelled LID and $\delta^{15}N$ measured in firn samples at

464   available sites than when using a fixed closed / total porosity ratio. However, when used for

465   simulating the LID during glacial periods with extremely low accumulation rate, it can predict a lock-

466   in density that is higher than the close-off density, which is unrealistic. We thus also added a

467   threshold in our new definition of the lock-in density: when ρ_{LI} exceeds the close-off density (ρ_{CO},

468   Section 2.3), we impose ρ_{LI} to be equal to ρ_{CO}.

469

470   ## 3. Results

471
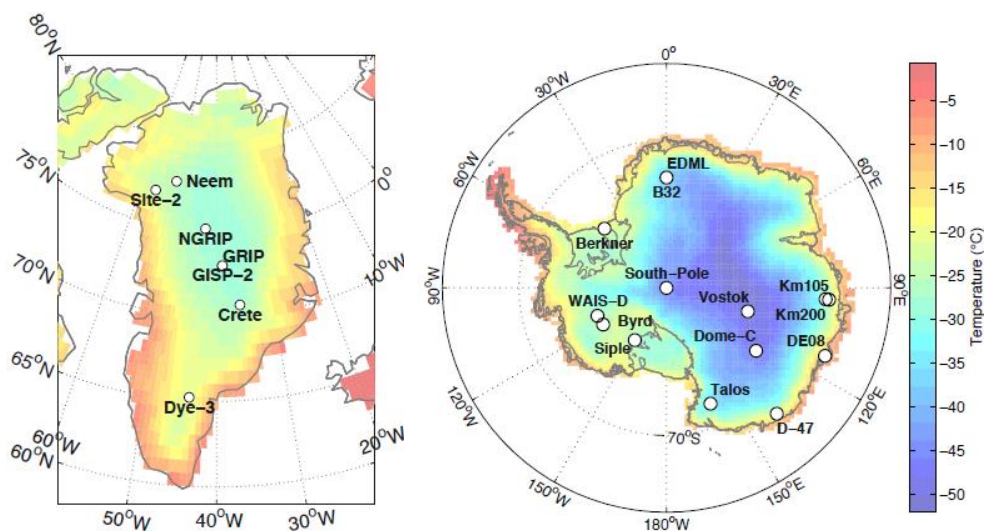
472
473

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

476

477   ### 3.1   Firn density profiles

478   We assessed the behaviour of the model by comparing measured and modelled firn density profiles

479   from 22 sites from Greenland and Antarctica (Figure 3). Figure 4 shows this comparison at Byrd,

480   NEEM, Dome C and Vostok, and other sites are displayed in the supplement (Supplementary Figure

481   S6). A polynomial fit was adjusted to the density data in order to facilitate the comparison with

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

483   measurement uncertainties.

484

485   A comparison of snow density measurement methodologies concluded that uncertainties are about

486   10 % (Proksch et al., 2016). Moreover, although firn density profiles are often used, the

487   measurement technique is not always well documented. Efforts were made in this study to mention

488   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 S6) 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:

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

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. $\sigma_{fit-data}$ generally lies below 10.0 kg/m^3 (Figure 5).

In order to visualize the model data comparison with the different versions of the model on the 22 selected sites, we calculate the following deviation in parallel to the $\sigma_{fit-data}$ above (Equation 11):

17

519 $$\sigma_{model-fit} = \sqrt{\left[\sum_{i=1}^{Nmax} \frac{\left(\rho_{model}^{i} - \rho_{fit}^{i}\right)^{2}}{N_{max}}\right]}$$ (12)

520

521 Note that we compare here the model to the fit of the data and not directly to data because of the

522 strong site to site differences in the data (e.g. data resolution, sample size). Figure 5 and

523 Supplementary Table S1 display the $\sigma_{model-fit}$ for the 22 different sites before and after modifications

524 detailed in Section 2.

525

526 3.1.1. Data – model comparisons using the old model

527

528 Comparing our model results to density data is not trivial due to the diversity in measurement

529 techniques and samplings discussed above, as well as the natural variability in density that we do

530 not capture with a simplified model aiming at simulating very long time scales. A rough indication is

531 given by comparing $\sigma_{model-fit}$ and $\sigma_{fit-data}$. They are of the same order of magnitude although $\sigma_{fit-data}$ is

532 always lower than $\sigma_{model-fit}$ (Figure 5), confirming that the old model is likely not able to fully

533 represent the diversity of the density profiles at the 22 measurement sites.

534 The model-data agreement is variable among the different sites even for those with similar surface

535 climatic conditions. The temperatures and accumulation rates at Dome C and Vostok being similar,

536 model results at these sites are similar, but the density data have a clearly different shape. At

537 Vostok, a high densification rate is observed well above the critical density of about 550 kg/m^3. One

538 possible reason is the very different flow regimes of the two sites, one being at a Dome summit, and

539 the other on a flow line and subject to a horizontal tension (Lipenkov et al., 1989). This is not taken

540 into account in our simplified 1D model. Some density data at other sites also show no densification

541 rate change near the critical density, resulting in model-data mismatches (see Siple Dome, km 105,

542 km 200, Mizuho on Supplementary Figure S6).

543 The main disagreement between the old model and data is observed at the transition between the

544 first and the second densification stage with too high modeled densities and an associated slope

545 change in the density profile that is too strongly imprinted. This effect is due to a densification rate

546 that is too high in the first stage.

547

548 3.1.2. Data – model comparisons using the new model with only one activation energy

549

550 The modifications of the first densification stage described in Section 2.1 mainly reduce the slope

18

551 change at the transition between the Alley (1987) and Arzt (1982) mechanisms (not shown). It also

552 suppresses an instability of the previous model version which could fail to find a continuous

553 densification rate at the boundary between Alley (1987) and Arzt (1982) mechanisms.

554 However the new model still shows a tendency to overestimate the snow densification rate and

555 then underestimate the densification rate in the firn, as shown for NEEM and Vostok on Figure 4.

556 Still, looking at all different firn profiles, the general agreement between modeled and measured

557 firn density profiles is preserved. The agreement between measured and modeled firn density is

558 increased for some sites at (1) low accumulation rate and temperature in Antarctica (Dome A,

559 Vostok and Dome C but not South Pole) and at (2) relatively high temperature and accumulation

560 rate (Dye 3, Siple Dome, NEEM). In parallel, a larger disagreement between model and data is

561 observed for some other sites particularly in coastal Antarctica (DE08, Km 200, WAIS Divide). When

562 introducing these modifications for simulating δ^{15}N evolutions over the last deglaciation, no

563 significant changes are observed with respect to simulations run with the old LGGE model. This is

564 not unexpected since most of the modifications concern the first stage of densification (top 10-15

565 m of the firn). The other modification concerns the LID definition, it only has a small impact on the

566 model results for the glacial-interglacial transitions and slightly increases the model – data mismatch

567 over deglaciations (Supplementary Figure S7).

568

569 3.1.3. Data-model comparisons using the new model with three activation energy and

570 implementation of impurity effect

571

572 The introduction of three different activation energies for different temperature ranges leads to

573 changes of the modeled density profiles at high densities (above about 800 kg/m^3). A clear

574 improvement is obtained for example at South Pole (Supplementary Figure S6), although the overall

575 impact of using three activation energies remains small.

576 The incorporation of the impurity effect following the Freitag et al. (2013) parameterization in our

577 model slightly deteriorates the model-data agreement because no specific re-adjustment of model

578 parameters was performed. However the model prediction of the density profiles remains correct

579 although the impurity effect parameterization was developed for a different purpose, i.e.,

580 simulating density layering (Freitag et al., 2013). This encouraged us to test this simple

581 parameterization in glacial climate conditions.

582

583   Overall, $\sigma_{model-fit}$ is only improved by 3% when using the modified model (3 activation energies and

584   implementation of impurity effect) instead of the former Goujon et al. (2003) mechanical scheme.

585   We thus conclude that the two versions of the model perform equally well.
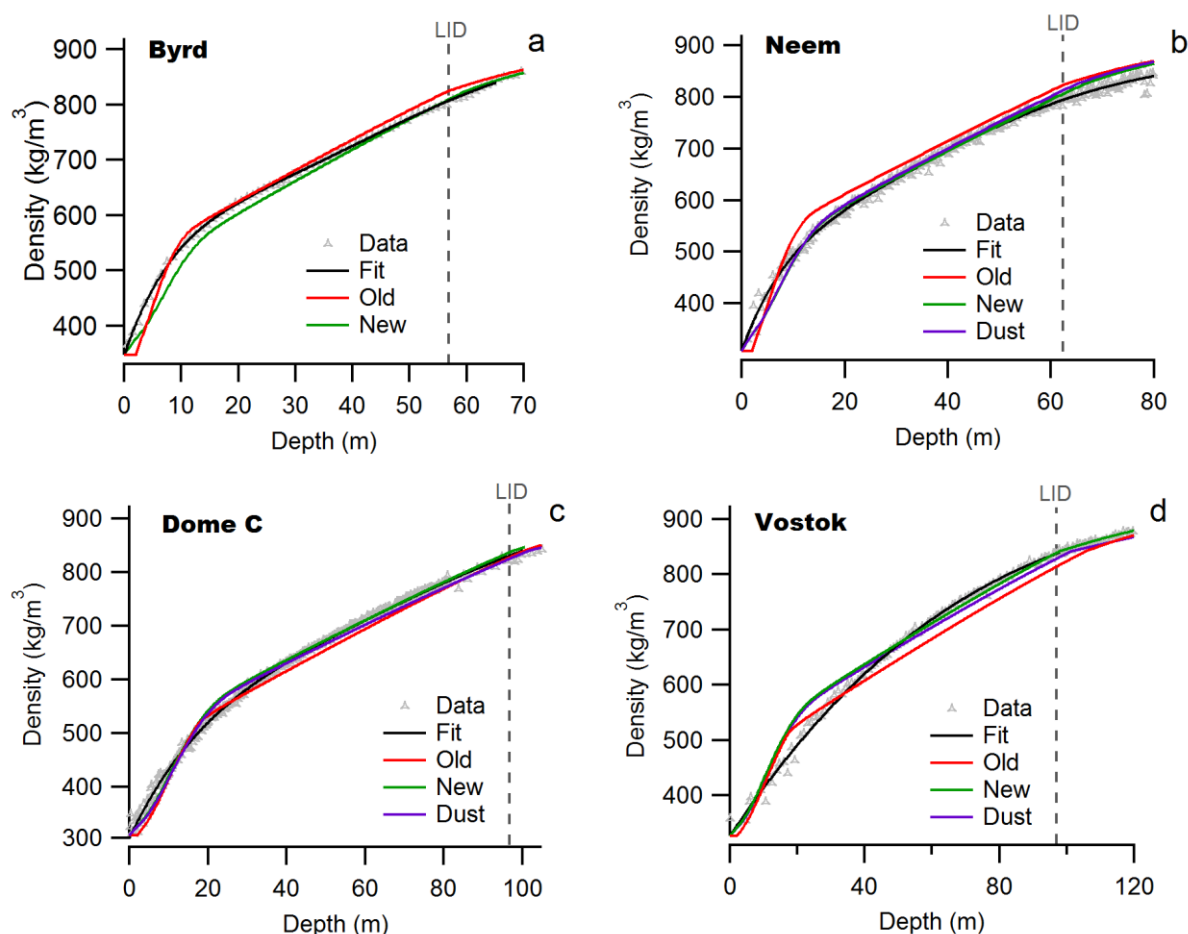
586
587
588   *Figure 4: Density profiles of Byrd (a), NEEM (b), Dome C (c) and Vostok (d). The grey triangles correspond to the data.*

589   *The black line corresponds to the polynomial fit, the red one to the old simulation, the green one to the new simulation*

590   *and the purple one to the new simulation with impurity effect.*

591

592   Finally, it should be noted that our main purpose is to improve the agreement between the

593   modelled LID and the evolution of $\delta^{15}N$ over deglaciations in Antarctica. Thus, in addition to the

594   above comparison of density profiles, we compared the depths at which the LID density, as defined

595   by Equation (10), is reached in the polynomial fit to the data and in the new model results. In the

596   old version of the model, the LID differences between the model and data range between -17.9 m

597   (at South Pole) and +8.6 m (at km 200) with a small mean value of -1.9 m and a standard deviation

598   of 6 m. In the new version, the LID differences between the model and data are comparable, ranging

599   between -14.1 m (at South Pole) and +12.8 m (at Talos Dome) with a small mean value of -0.7 m and

600   a standard deviation of 6 m. Similar results are obtained for Δage (see Supplementary Table S2): the

601 agreement with the data is similar for all model versions, and most cold sites are improved with the
602 new model. However the $\sigma_{model-fit}$ values remain high compared to the variability of the data ($\sigma_{fit-data,}$
603 black bars in Figure 5). We thus conclude from this section that the LGGE new firn densification
604 model preserves the good agreement between (1) modelled and measured firn density profiles and
605 (2) modelled and measured LID. We explore in the next section the performances of the new model
606 for coldest and driest conditions by looking at the modelled LID and hence $\delta^{15}N$ evolution over
607 glacial – interglacial transitions.

608
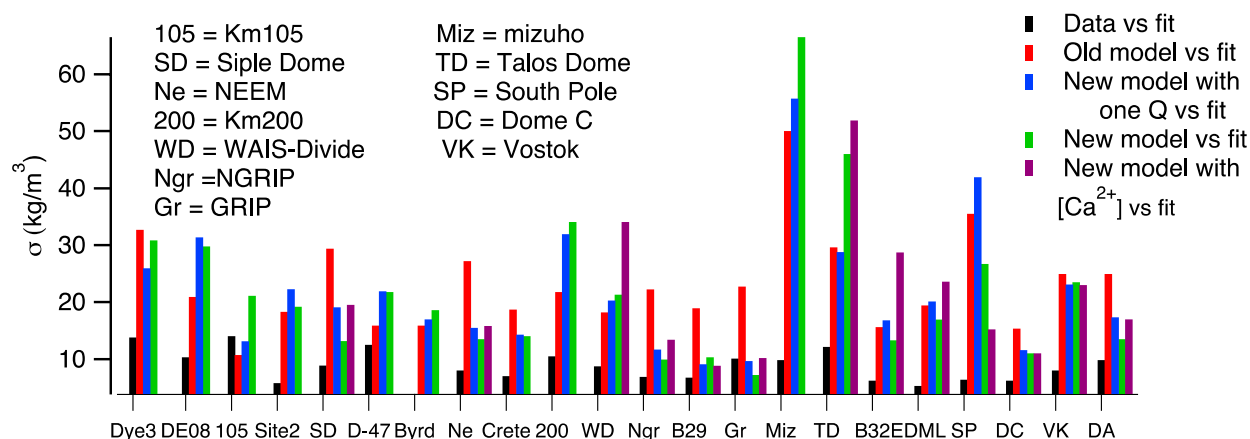
609

610 *Figure 5: Representation of the $\sigma_{fit-data}$ in black and the $\sigma_{model-fit}$ (in red for the old model, in blue for the model*
611 *with the new parameterization except the three activation energies, in green for the new model with three*
612 *activation energy and in purple for the new model with the impurity effect) at 22 Greenland and Antarctic*
613 *sites. The site characteristics are provided in Supplementary Table S1.*

614

615 ## 3.2 $\delta^{15}N$ glacial-interglacial profiles

616

617 In order to test the validity of the densification model in a transient mode, we model the time
618 evolution of $\delta^{15}N$ over the last deglaciation, and compare it to measurements at 4 Antarctic and
619 Greenland deep ice-core sites: Dome C (cold and low accumulation site in Antarctica with a strong
620 mismatch observed between data and the old model), EDML (intermediate temperature and
621 accumulation rate in Antarctica with a significant mismatch between data and the old model), WAIS-
622 Divide (high temperature and accumulation rate site in Antarctica with a good model-data
623 agreement) and NGRIP (Greenland site with a good agreement between model and data) (Figure 3).
624 The computation of $\delta^{15}N$ depends on the convective zone thickness, the LID and on the firn
625 temperature profile. The gravitational $\delta^{15}N$ signal is indeed calculated from the LID and mean firn

626 temperature according to the barometric equation (Equation 1). The thermal δ^{15}N depends on the

627 temperature gradient between the surface and the LID. A small thermal signal exists in Antarctica

628 because of geothermal heat flux (with an average change of about 0.02 ‰ during deglaciation) but

629 no millennial variations are expected because the temperature variations are slow (<2°C/1000

630 years) compared to abrupt climate changes observed in Greenland (e.g. NGRIP).

631 The model calculates for each ice core depth the firn diffusive column height and thermal

632 fractionation at the bottom of the firn. To take into account the smoothing due to gas diffusion in

633 the open pores and progressive bubble close-off (Schwander et al., 1993), we smooth the δ^{15}N

634 output with a log-normal distribution, of width Δage/5 and sigma=1 (Köhler et al., 2011; Orsi et al.,

635 2014). This formulation of the smoothing takes into account the variations of the gas-age

636 distribution with time. Note that it has been suggested that the width in Köhler et al. (2011) is too

637 wide (http://www.clim-past.net/7/473/2011/cp-7-473-2011-discussion.html). Still, using a smaller

638 width does not modify the modelled amplitude of the δ^{15}N signal over the deglaciation so that our

639 conclusions are not affected by such uncertainty.

640

641   3.2.1 Input scenarios

642

643 For the simulation of the δ^{15}N evolution over the last deglaciation, the firn densification model is

644 forced by a scenario of surface temperature and accumulation rate deduced from ice core data

645 (Supplementary Table S3). In Greenland (NGRIP, GISP2), the temperature is reconstructed using the

646 $\delta^{18}O_{ice}$ profiles together with indication from borehole temperature measurements (Dahl-Jensen,

647 1998) and δ^{15}N data for NGRIP (Kindler et al., 2014) for the quantitative amplitude of abrupt

648 temperature changes. Greenland accumulation rate is deduced from layer counting over the last

649 deglaciation (e.g. Rasmussen et al., 2006). The uncertainty in the temperature reconstructions can

650 be estimated to ± 3°C over the last deglaciation in Greenland (Buizert et al., 2014). As for the

651 Greenland accumulation rate, an uncertainty of 20% can be associated with the LGM value (Cuffey

652 and Clow, 1997; Guillevic et al., 2013; Kapsner et al., 1995). In Antarctica, both temperature and

653 accumulation rate are deduced from water isotopic records except for WAIS-Divide, where layer

654 counting back to the last glacial period is possible (Buizert et al., 2015). Temperature uncertainty for

655 the amplitude of the last deglaciation is estimated to -10% to +30% in Antarctica (Jouzel, 2003). The

656 reason for such asymmetry is mainly linked to outputs of atmospheric general circulation models

657 equipped with water isotopes. These models suggest that the present day spatial slope between

658 δ^{18}O and temperature most probably underestimates the amplitude of the temperature change

between glacial and interglacial period. We have used this estimate of asymmetric uncertainty on the amplitude of temperature change during deglaciation in our study. Recent studies have also suggested that the relationships between water isotopes and temperature and between water isotopes and accumulation rate can be applied with confidence in Antarctica for glacial temperature reconstruction (Cauquoin et al., 2015) while one should be cautious for interglacial temperature reconstruction with warmer conditions than today (Sime et al., 2009). Finally, a recent estimate of the deglacial temperature increase based on $\delta^{15}N$ measurements at WAIS (Cuffey et al., 2016) led to a 11.3°C temperature increase over the last deglaciation (1°C warming to be attributed to change in elevation). This is larger than the temperature increase reconstructed in East Antarctica from water isotopes by 2-4°C and again not in favour of a "warm" LGM.

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 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). Still, it should be noted that the uncertainty of 20% on LGM accumulation rate on central sites as given in the AICC2012 construction is probably overestimated. Indeed, deglaciation occurs around 500 m depth at Dome C, hence with small uncertainty on the thinning function and on the accumulation rate. 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)).

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).

23

3.2.2 Transient run with the old model

694

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 revised 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 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 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). In the absence of alternative explanations, we can thus question the existence and variations 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

725 thus explore further the influence of accumulation rate and temperature uncertainties on the δ^{15}N

726 modelling.

727

728 The uncertainties in the changes of temperature and accumulation rates over the deglaciation

729 significantly influences the simulated δ^{15}N, as already shown in previous studies and this sensitivity

730 of δ^{15}N has even been used to adjust temperature and/or accumulation rate scenarios (Buizert et

731 al., 2013; Guillevic et al., 2013; Kindler et al., 2014; Landais et al., 2006). We tested the influence of

732 the accumulation rate and temperature scenarios on the simulated δ^{15}N profiles for the last

733 deglaciation, but even with large uncertainties in the input scenarios, it is not possible to reproduce

734 the measured Antarctic δ^{15}N increase at Dome C and EDML with the old version of the LGGE model.

735

736 This result is illustrated on Figure 7 where we display a comparison between the amplitude of the

737 measured δ^{15}N change and the amplitude of the modelled δ^{15}N change with the Goujon version

738 over the last deglaciation. For this comparison, we calculated the Last Glacial Maximum (LGM) δ^{15}N

739 average over the period 18-23 ka and the Early Holocene (EH) δ^{15}N average over the period 6-10 ka

740 (or smaller, depending on available data, cf blue boxes on Figure 6). We estimated the uncertainty

741 in the measured δ^{15}N change by calculating first the standard deviation of the δ^{15}N data over each

742 of the two periods, LGM and EH as $\sigma_{15N\_data\_EH}$ and $\sigma_{15N\_data\_LGM}$ and then the resulting uncertainty

743 in the δ^{15}N change as: $\sigma_{15N\_EH-LGM} = \sqrt{\sigma^2_{15N\_data\_EH} + \sigma^2_{15N\_data\_LGM}}$

744

745 As for the modelled δ^{15}N change, associated error bars are deduced from the uncertainty in the

746 temperature and accumulation input scenarios (shown on Supplementary Figure S9 for the

747 improved model). The total error bar hence shows the difference between most extreme

748 accumulation rate or temperature input scenarios. In these sensitivity tests, we assumed that it is

749 not possible to have an underestimation of the temperature change while at the same time have an

750 overestimation of the accumulation rate (or the opposite) because changes in accumulation rate

751 and temperature are linked, at least qualitatively when comparing LGM and Holocene mean values.
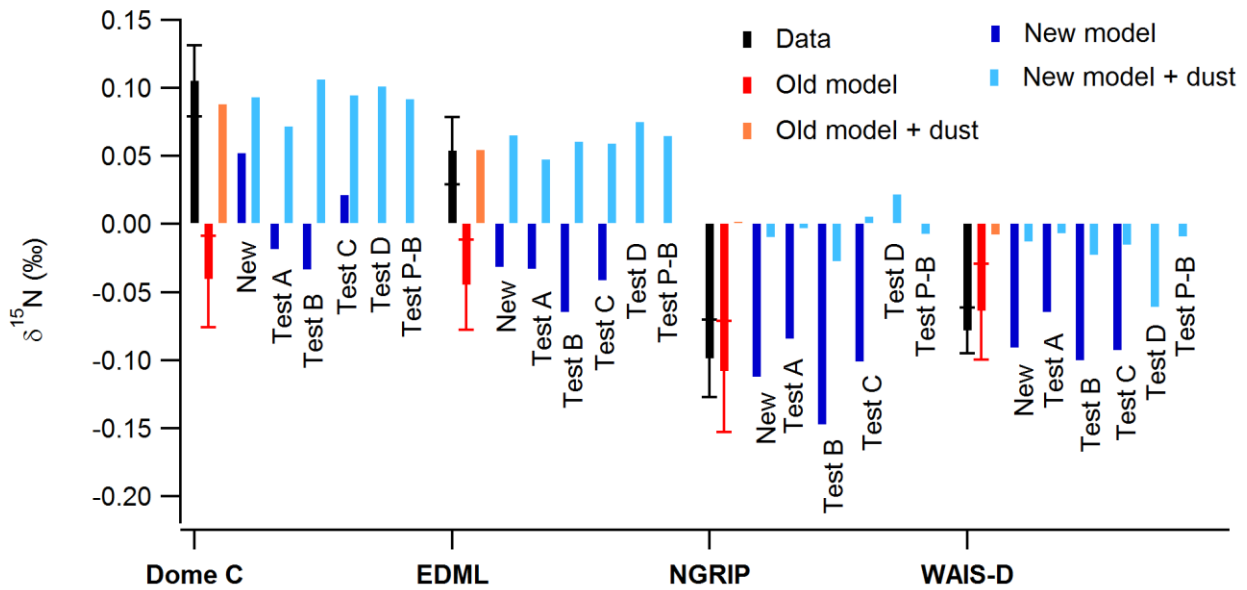
752

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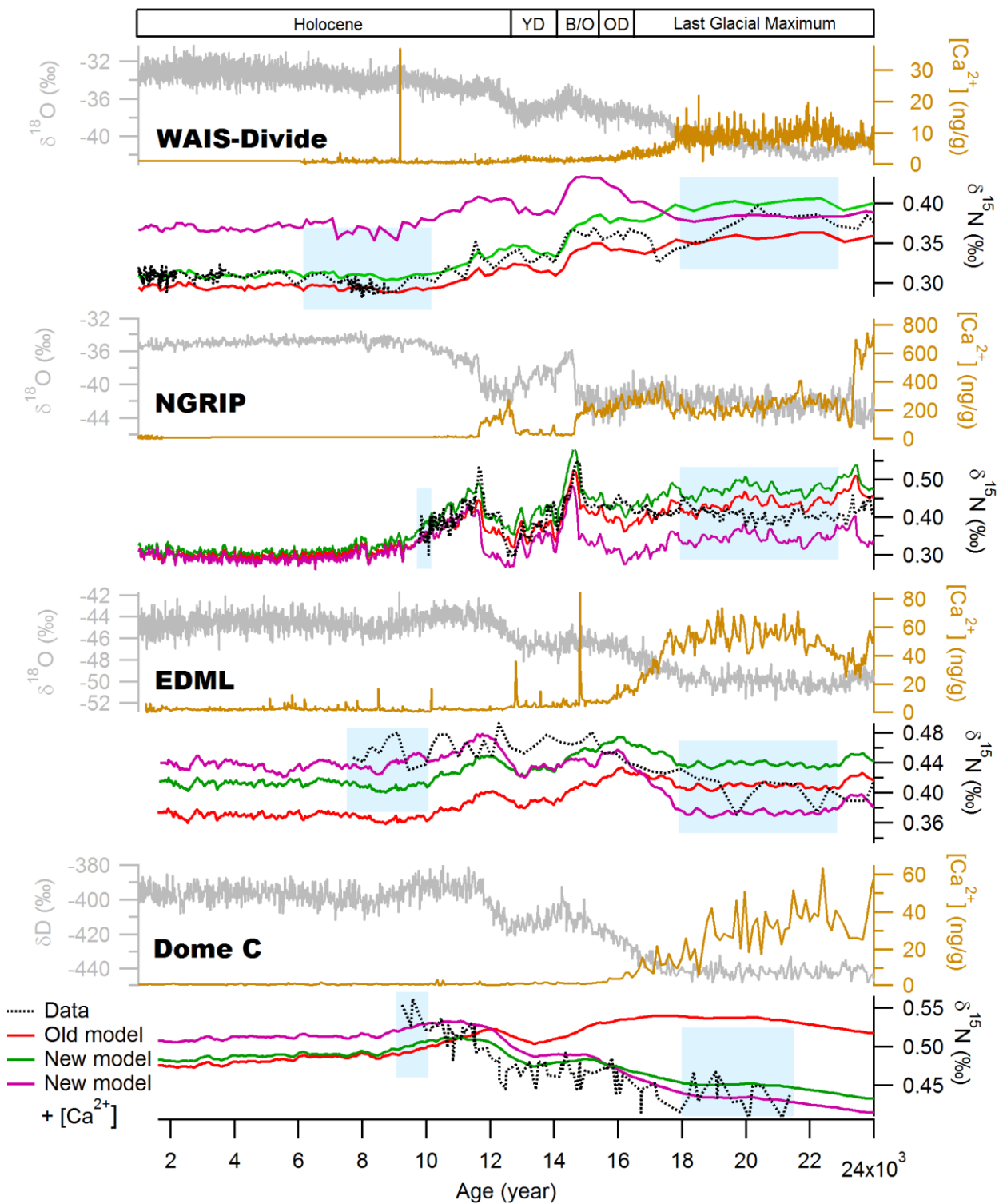
754 _Figure 6_: Comparison of the measured δ¹⁸O or δD (grey), the calcium concentration (gold), the measured δ¹⁵N (black)

755 and the modelled δ¹⁵N (old (red), new version (green) and new version with impurity (purple)) of the LGGE model for

756 WAIS-Divide, NGRIP, EDML and Dome C. Blue boxes for each sites indicate the periods over which the δ¹⁵N average for

757 the LGM and EH have been estimated for the calculation of the amplitude of the δ¹⁵N change over the deglaciation.

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3.2.3 Results with updated temperature parameterization

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773 By construction, the new LGGE firn model with the temperature dependency of the firn densification

774 module depicted on Section 2.2.1 is expected to improve the agreement between model and data

775 for cold sites of East Antarctica over the last deglaciation by increasing densification rates at low

776 temperature. This new parameterization modifies the densification rate through the creep

777 parameter given in Equation (7). Figure 8 shows the evolution of the creep parameter with

778 temperature for different choices of the three activation energies Q_1, Q_2 and Q_3. Compared to the

779 old model, the densification rate is higher at low temperature, below -55°C (i.e. for LGM at Dome C

780 and Vostok, Table 1). At higher temperature (between -55°C and -28°C corresponding to present-

781 day temperature in most polar sites), the creep parameter is slightly lower than in the old model.

782 The difference between the 2 curves is however not large so that densification rate is not strongly

27

783   modified over this range. This is in agreement with comparable firn density profiles obtained for the

784   different polar sites using the old or the improved LGGE model (Section 3.1, Figure 4).

785   In the improved model, the simulated profiles of δ^{15}N are comparable to δ^{15}N simulated with the

786   old model at the sites that were already showing a good agreement between the old model outputs

787   and data, for example NGRIP, GISP-2, Talos Dome and WAIS-Divide (Figure 6 and Supplementary

788   Figure S8). This is expected since the corresponding densification rate is only slightly reduced in the

789   temperature range of -55°C/-28°C which corresponds to the temperature range encompassed over

790   the last deglaciation at these sites. This results in a deeper LID and hence higher δ^{15}N level, which is

791   in general compatible with the data (except at Talos Dome). Some differences are also observed for

792   the timing of the δ^{15}N peaks for Bølling-Allerød and end of Younger Dryas at NGRIP when using the

793   different model versions reflecting variations in the simulated Δage (cf Supplementary Table S5);

794   the general agreement with the measured profile is preserved with even a slight improvement of

795   the modelled Δage with δ^{15}N constraints with the modified model. At the coldest sites (Dome C,

796   Vostok), the agreement between data and modelled profiles is largely improved with a modelled

797   LGM δ^{15}N smaller than the modelled EH δ^{15}N, but a perfect match cannot be found. At the

798   intermediate EDML site, it is not possible to reproduce the sign of the slope during the deglaciation.

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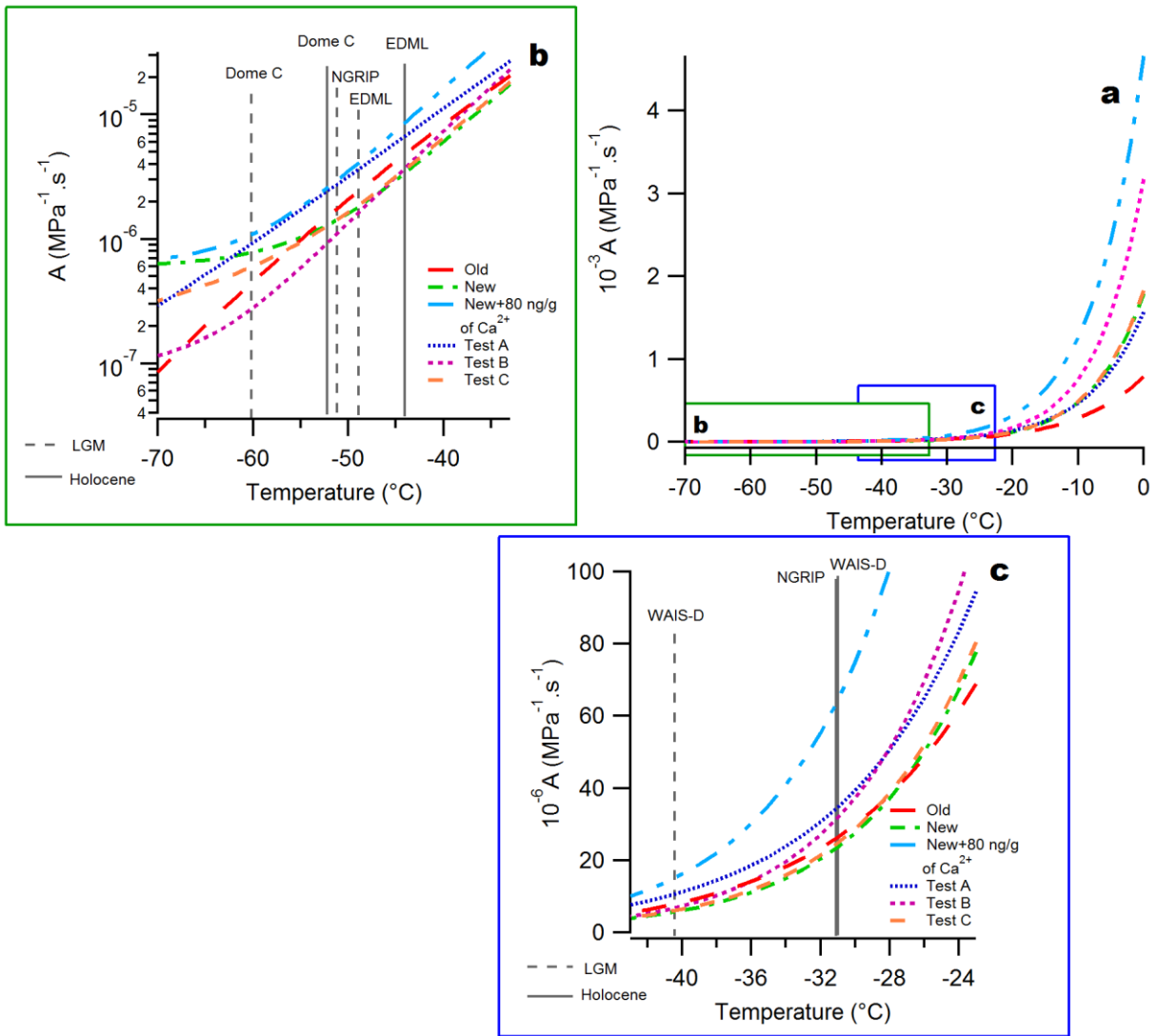
801

802 *Figure 8: Dependence of the creep parameter (Equation 7) as a function of temperature for 6 different*

803 *parameterizations. "Old" corresponds to the Goujon et al. (2003) version of the model; "New" corresponds to*

804 *the improved LGGE model with parameterization described in Table 1; "New + 80 ng/g of Ca^{2+}" corresponds*

805 *to the parameterization of Table 1 with the addition of the impurity effect following Equation (8) and a $[Ca^{2+}]$*

806 *value of 80 ng/g; Tests A, B and C are sensitivity tests run with the values presented on Table 3. Figure 8a*

807 *shows the creep parameter evolution for the whole temperature range, Figure 8b is a focus at very low*

808 *temperature and Figure 8c is a focus at intermediate temperature. The grey vertical lines indicates the*

809 *temperature for Early Holocene (EH, solid line) and LGM (dotted line) at the 4 study sites presented in Figures*

810 *6 and 7.*

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Test	Activation energy (J/mol)	Coefficient
Test A	$Q_1 = 90000$	$a_1 = 5.5*10^5$
	$Q_2 = 60000$	$a_2 = 1.0$
	$Q_3 = 30000$	$a_3 = 4.5*10^{-8}$
Test B	$Q_1 = 110000$	$a_1 = 5.5*10^9$
	$Q_2 = 75000$	$a_2 = 1950.0$

	$Q_3 = 1500$	$a_3 = 9.0*10^{-16}$
	$Q_1 = 110000$	$a_1 = 1.05*10^9$
Test C	$Q_2 = 75000$	$a_2 = 1400$
	$Q_3 = 15000$	$a_3 = 8.7*10^{-12}$
	$Q1 = 110000$	$a1 = 1.05*10^9$
Test D	$Q2 = 75000$	$a2 = 980$
	$Q3 = 1230$	$a3 = 3.6*10^{-15}$

Table 3: Values used for the different sensitivity tests for three activation energies. These values have been chosen to illustrate the effects of varying activation energy for the different temperature ranges on the densification rate for the different ice core deep drilling sites (cf figure 8) and support the tuning presented on Table 1.

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 in Figure 7 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 simulation of the $\delta^{15}N$ difference between EH and LGM at Vostok and Dome C. Indeed, the modelled EH-LGM difference now has the correct sign at very cold sites of East Antarctica (Figure 7) when compared with $\delta^{15}N$ measurements.

We present some sensitivity tests to illustrate the choice of our final parameterization (i.e. the new model) through influences on the creep parameters and LGM vs EH $\delta^{15}N$ changes. 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 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. Strong differences

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occur at high temperature (above -30°C) but it does not affect the modelled δ^{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 worse agreement between model and data for the Dome C deglaciation than when using the "new model". Test C has been designed so that the activation energy at low temperature corresponds to estimates of activation energy for ice surface diffusion (Jung et al., 2004; Nie et al., 2009), a mechanism that is expected to be important at low temperature (Ashby, 1974). Using such a parameterization leads to a fair agreement between the modelled and the measured δ^{15}N change over the last deglaciation for the different sites. At Dome C, the correct sign for the δ^{15}N evolution between LGM and the Holocene is predicted by the model. However, the modelled δ^{15}N increase is still too small compared to the data and the δ^{15}N calculated by the "new model". This is probably due to a too high creep parameter at low temperature.

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 δ^{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 δ^{15}N changes for all 4 sites. In the "new model" without impurity effect, it is not possible to reproduce the measured EDML δ^{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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874   during periods characterized by high impurity concentration in the ice (LGM). It thus leads to an
875   increase of the EH-LGM LID difference (Figure 7).

877   This effect clearly helps to bring in agreement modelled and measured $\delta^{15}N$ at Dome C, Vostok and
878   EDML (Figures 6, 7 and Supplementary Figure S8). The improvement through dust softening is
879   particularly important at EDML where the change of activation energy had only a modest effect. For
880   the 3 sites mentioned above, the model incorporating the parameterization of activation energy
881   depicted in Table 1 and the impurity effects is able to reproduce the $\delta^{15}N$ increase over the last
882   deglaciation. Note that short-lived peaks in impurities, likely triggered by volcanic events, have no
883   visible effect on bulk firn thickness (Figure 6). Contrary to the improved situation in cold Antarctic
884   sites, we observe that, at the warmer sites like NGRIP and WAIS-Divide, incorporating impurity
885   softening deteriorates the model data fit, which was already good in the older version of the model,
886   and also good with other firn densification models (Kindler et al, 2014; Buizert et al, 2015). It
887   produces almost no change in firn thickness between the LGM and the EH at NGRIP, which
888   contradicts $\delta^{15}N$ observations. The same mismatch is observed at WAIS-Divide using a different
889   model, as already noted by Buizert et al. (2015). We tested the sensitivity to the dust
890   parameterization by implementing the Freitag parameterization adapted to the Pimienta-Barnola
891   model instead of the parameters for the Herron and Langway model used with our improved model
892   (cf Section 2.2.2). The two different parameterizations of the impurity effect lead to very
893   comparable LGM to EH $\delta^{15}N$ changes over the last deglaciation on the 4 sites discussed here.
894   The model – data mismatch observed when incorporating the dust effect may be partially due to
895   the fact that we did not readjust a_i and Q_i after implementation of the impurity effect. To explore
896   this possibility, sensitivity test D has been designed with a re-parameterization of the a_i and Q_i values
897   after implementation of the impurity effect. To do so, we calculated the optimal creep parameter A
898   for each mean EH and LGM condition at each site, and adjusted sequentially a_3, a_2, a_1, Q_3, Q_2, and
899   Q_1 to minimize the model-data mismatch. Only a_3, a_2 and Q_3 needed adjustments, and their values
900   can be found in Table 3. We did not perform the adjustment on modern density profiles, because
901   these are only weakly sensitive to the dust parameterization, Ca^{2+} concentrations being low.
902   Impurity concentration is very high at NGRIP during the glacial period. As a consequence, even if our
903   new parameterization of a_i and Q_i (new model) properly reproduces the Greenland $\delta^{15}N$ level at the
904   LGM, this glacial modelled Greenland $\delta^{15}N$ level is too low when including the impurity effect. The
905   re-parameterization of a_i and Q_i, proposed as sensitivity test D, enables an improvement of the

906 agreement between model and data for glacial δ^{15}N at WAIS-Divide, maintain the results at Dome-

907 C and EDML, but can still not produce reasonable results at NGRIP (Figure 7).

908

909 The mismatch observed for the δ^{15}N simulations at WAIS-Divide and NGRIP when incorporating the

910 impurity effect suggests that the parameterization presented in Equations (8) and (9) is not

911 appropriate to be used on bulk [Ca^{2+}] concentration and/or for LGM simulation. Actually, the

912 proposed parameterization by Freitag et al. (2013) was tuned to density variability in present-day

913 firn, and may not be valid for LGM when [Ca^{2+}] concentrations were 10-100 times larger than

914 present-day. It is also possible that the dust effect saturates at high concentration, and is no longer

915 sensitive above a certain threshold. To further improve the model – data agreement with the dust

916 parameterization, a possibility is to add simple thresholds on a minimum and maximum effect of

917 calcium as proposed in supplementary material (Supplementary Text S2 and Figure S10).

918 Implementing threshold values on calcium reduces the largest inconsistencies between model

919 results and δ^{15}N data, in particular at NGRIP (through the threshold at high calcium concentration)

920 and at WAIS (through the threshold at low calcium concentration).

921

922 It is also possible that the impurity influence, like temperature, acts differently depending on the

923 dominant mechanism for firn deformation, and that the impurity effect is more important at colder

924 temperature. The mechanisms by which impurities influence firn deformation are still poorly

925 understood. Dust particles do not always influence densification in the same way: dissolved particles

926 soften firn and ice while the softening or hardening effect of non-dissolved impurities is less clear

927 (Fujita et al., 2016; Alley et al., 1987). More work is thus needed before the correct "impurity effect"

928 component and the mechanisms by which it acts on densification are identified (e.g. Fujita et al.,

929 2014, 2016). Here, we have shown that a simple parameterization as a function of [Ca^{2+}]

930 concentration does not provide uniformly good results, and seems only suitable for sites on the

931 Antarctic Plateau.

932

933 To sum up, the new parameterization of the creep parameter has been designed to preserve good

934 agreement between the old model outputs and data at sites that were already well simulated

935 (WAIS-Divide, NGRIP, Talos Dome). In addition, this parameterization improves the simulation of

936 the deglaciation at cold Antarctic Sites (Dome C, Vostok). However, the EH-LGM δ^{15}N change at

937 Dome C and EDML cannot be reproduced using only the temperature dependency of activation

938 energy. The inclusion of impurity effect following the Freitag parameterization improves the

939 situation for cold sites but leads to inconsistent δ^{15}N evolutions over the deglaciation at WAIS-Divide

940 and NGRIP unless threshold effects are implemented.

941

942 ## 4. Conclusion and perspectives

943

944 In this study, we have presented a revision of the LGGE firn densification model. We have

945 summarized the parameterization choices of this firn model that would explain a large part of the

946 disagreement between modelled and measured δ^{15}N evolution over the last deglaciation for

947 extremely cold sites of East Antarctica. Based on analogy with ceramic sintering at hot temperature

948 and recent observations of the impurity effect on firn density, we have improved the LGGE

949 densification model by incorporating new parameterizations for the evolution of the creep

950 parameter with temperature and impurity contents within the firn densification module. We follow

951 previous studies evidencing different dominant firn sintering mechanisms for different temperature

952 ranges that support a temperature dependency of the creep activation energy. We showed that

953 these new parameterizations improve the agreement between model and data at low temperature

954 (below -30°C), and retain the good agreement at warmer temperature. In particular, the improved

955 LGGE firn density model is now able to reproduce the δ^{15}N increase over deglaciations at cold sites

956 such as Dome C and Vostok.

957

958 The new parameterization implies a more rapid firn densification at lower temperature and high

959 impurity load than in classical firnification models. This result obtained with our associated

960 appropriate parameterization is in agreement with the study of Parrenin et al. (2012) showing that

961 the classical firn densification model overestimates LID during the last glacial period at EDC. With

962 our revised model, the simulated Δage is also significantly decreased for the glacial periods at low

963 accumulation and temperature sites of the East Antarctic plateau (Dome C, Vostok and Dome Fuji).

964 This has important consequences for building air vs ice timescales in Antarctica and hence for the

965 studies of the relationships between temporal evolutions of atmospheric composition vs. Antarctic

966 temperature. At EDC 21 ka (ice age), the modelled Δage decreases from 4840 years (old model) to

967 4270 years (new model) or 4200 years (new model including impurity effect). At Vostok 21 ka (ice

968 age), the modelled Δage decreases from 5630 years (old model) to 5030 years (new model) or 4900

969 years (new model including impurity effect). The latest results are in good agreement with the

970 recent determination of Δage within the AICC2012 timescale: 3920 years for EDC 21 ka (ice age) and

971 5100 years for Vostok 21 ka (ice age). This is not unexpected since the EDC LID in the construction

34

972 of the AICC2012 timescale is deduced from the EDC δ^{15}N scenario, a hypothesis supported by the

973 available gas and ice stratigraphic markers over the last deglaciation (Parrenin et al., 2012).

974

975 Our finding is, however, associated with several limitations so that this new model does not propose

976 a definite re-evaluation of the formulation of the activation energy but proposes some ways to be

977 further tested and explored to improve firn densification models especially for applications in

978 paleoclimate reconstructions. Our approach remains empirical and we could not identify separately

979 the different mechanisms involved. The problem of a δ^{15}N data-model mismatch in low temperature

980 and accumulation rate sites of East Antarctica is thus not definitively solved. Still, we showed that

981 revising the temperature and impurity dependence of firn densification rate can potentially strongly

982 reduce the δ^{15}N data-model mismatch and proposed preliminary parameterizations easy to

983 implement in any firn densification model.

984 Finally, the new parameterization proposed here calls for further studies. First, laboratory or field

985 studies of firn densification at very cold controlled conditions are needed to check the

986 predominance of one mechanism over another at low temperature such as the predominance of

987 the boundary diffusion over grain boundary mechanism around -60°C; this is a real challenge

988 because of the slow speed of deformation. Second, we have suggested that the current

989 parameterization of impurity on firn softening should be revised, especially for very high impurity

990 load (Greenland) using for example thresholds on impurity concentrations. Third, the separate

991 effects of impurities and temperature on firn densification and hence δ^{15}N evolution should be

992 tested on periods other than the last deglaciation. Sequences of events associated with non-

993 synchronous changes in surface temperature, accumulation rate and impurity content would be

994 particularly valuable for this objective. Finally, additional constraints on the firn modelling can also

995 be obtained through the use of cross-dating on new ice core with high resolution signals as already

996 used by Parrenin et al. (2012).

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