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Discussions

Interactive comment on “Numerical experiments on isotopic diffusion in polar snow and firn using a multi-layer energy balance model” *by* Alexandra Touzeau et al.

Anonymous Referee #3

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1 Overview

Firn isotope diffusion is a process that affects the δ^{18}O signal of polar snow from the time of deposition until pore close–off. Taking place in the vapor phase within the porous medium of the firn and driven by the apparent seasonal, annual and multiannual isotopic gradients it results in an attenuation of the δ^{18}O signal, often obliterating its annual component. Assuming a good estimate of the diffusive rates in firn is obtained, a “reverse calculation” of diffusion can be possible that allows the (almost) complete reconstruction of the initial signal. Additionally, knowledge of the diffusive rates offers valuable information on past firn temperatures and as a result can be used as a paleothermometry tool if ice core data of sufficient resolution and precision are available.

Previous studies have looked into the desciption and characterisation of these effects and part of these studies suggests that post depositional processes different to purely fickian diffusion of water isotopes can also be at play acting supplementary to the signal attenuation affects or even introducing biases (Town et al., 2008). These processes are mostly of advective nature caused by the bulk movement of air and vapor in the snow, driven by pressure and temperature variations.

In this work titled “Numerical Experiments on isotopic diffusion in polar snow and firn using a multi-layer balance model”, Touzeau et al attempt to build and test a water isotope module on top of the Crocus snowpack model. In particular, the authors focus on trying to simulate post-depositional effects that cause changes of the initial δ^{18}O signal in polar snow and firn. Processes related to snow/firn isotope diffusion as well as diffusive vapor transport due to temperature gradients in the firn are modelled assuming various scenarios. The study focuses on two different regimes that are representative of conditions typical for deep ice coring sites on Greenland and East Antarctica. Ice core data sets are also used in order to evaluate the performance of the model and the results are also compared to existing firn isotope diffusion modelling approaches.

This is a very welcome condtribution and it most certainly points to the correct direction with respect to future modelling efforts. The study also fits very well the description and scope of the GMD journal and the overall quality of the research conducted is of high level. Thus I would recommend it for publication in GMD after the following points are carefully considered by the authors.

2 General comments

1. Unfortunately the language of the manuscript requires a signifficant revision. In particular there are examples in the text where technical/physical terms are used

wrongly and many definitions appear to be loose. This is particularly problematic for a manuscript of this type, where modelling approaches and physical processes are described.

The most notable axample is the description of the transport mechanisms in snow in sections 2.1.1 and 2.1.2. Diffusion is a very well defined process and unfortuanately the term is used falsely several times in sections 2.1.1 and 2.1.2 (and elsewhere in the manuscript). After reading these two sections I feel confused about the meaning of many of the terms used here and as a result about the kind of methods followed and the assumptions made in this study.

What is an “oriented process” for example? In page7line73 the sentence “We focus on the impact of oriented vapor transport caused by vapor density gradients in the snow...” is very untechnical and unfortunately creates a lot of confusion about what the authors have done. If the term “vapor density” indeed refers to “vapor (molar?) concentration” as I assume then the process described here is a vapor diffusion process.

After having read the text several times and tried to infer what the authors try to describe in sections 2.1.1 and 2.1.2 I conclude that they split the processes under consideration in two kinds. The first, what they call “signal attenuation on a vertical profile”, is a the combination of two processes, (a) solid isotope diffusion and (b) firn isotope diffusion in the vapor phase. The first is extremely slow and can easily be neglected in this study. I find it important that the authors point out in the text that solid diffusion affects all isotopes equally. The second is a diffusive process taking place in the porous medium pf the firn driven by the isotopic gradients. Both processes introduced here follow the same physical principle ie transport of mass due to concentration gradients of a substance. The transport occur along (or down) the concentration gradients and not “against” as often described in the text.

The second category of processes outlined in section 2.1.2 and termed as “oriented processes”. My interpretation of the text is that this type processes are “bulk motion” processes either due to pressure or temperature gradients. The first case is a typical example of advective transport. The second is a bit more complicated however the term diffusion used by the authors is incomplete. Temperature gradients in the snow will eventually cause vapor concentration gradients. The latter, will drive a diffusion process for the vapor as a whole. However this cannot be seen as an isotope diffusion process due to the fact that the diffusive transport of vapor has nothing to do with isotopic gradients. Eventually of course the diffusive transport of water vapor will very likely bring vapor molecules in layers of the snow with different isotopic composition where subsequently an isotope diffusion process will occur localy.

This was only an example of how the loose use of technical terms and faulty language creates unnecessary confusion to the reader already from the introduction, leading possibly to confusion and misunderstandings of the methods and principles used in this study. I find it essential that the authors look into the manuscript carefully and revise the text accordingly. In the “Specific Comments” section I include more of these examples as they appear in the text.

2. There is an unclear situation regarding the vapor diffusivity parametrisation and value used in this study. It is not exactly clear if there is a temperature dependency of the effective diffusivity D_{eff} to temperature. Based on equation 5 in the manuscript and the comment on the value of D_v I conclude that the value of D_{eff} is taken constant and reflects a temperature of 263 K. If this is indeed the case I would be inclined to question the validity of many of the statements found in the manuscript that concern the comparison of this model with other models of diffusion or results from ice core data. The diffusivity coefficient is heavily dependant on temperature and thus a constant value is an oversimplification for such a study.

   I would strongly prefer a version of the manuscript where the diffusivity is allowed to depend on temperature. However, if the authors indeed choose to follow the approach of constant diffusivity they will need to stress out very clearly in the manuscript that the comparisons presented here are essentially between different things. This should be even more prominent for the case of the Dome C modelling experiments due to the very large difference between the site temperature and the temperature used for the diffusivity coefficient value (almost 40K).

3. Despite my belief that the work performed by the authors is of high quality I need to point out that several elements of the manuscript feel opaque not allowing the reader to judge for herself on the quality of the work and the significance of the results. I find this a fundamental weakness of the manuscript that needs to be addressed. In particular:
    - The authors claim that the model is evaluated for the top 10 m of snow. However only the top 50-60 cm are presented.
    - The authors do not provide any information about neither the ice core data used nor the method used to calculate peak-amplitudes. The latter is not a straight forward procedure and can have a significant influence on the result of such model-data comparisons for diffusion. Information about the depth interval the data originate from, the temperature, accumulation and pressure conditions of the sites as well as the resolution of the data are pieces of information a thorough reader needs to have access to. Present the ice core data.
    - The initial δ^{18}O profile as well as snapshots of some layers should be plotted. The difference plots with the plethora of colors do not add anything neither for the case of density nor for the case of δ^{18}O. The colormaps of these plots are unfortunately very ambiguous to read and despite having the max and min values it looks to me that some of these colormaps are non linear. In combination with the very small difference values for both the density and

the δ^{18}O these color plots leave me guessing. There is very little valuable information I can extract from them.
    - The study considers all three isotopologues of water (δ^{18}O, δ^{17}O and δD) however the authors choose to present only the results for δ^{18}O. Based on (Johnsen et al., 2000) the diffusive attenuation is expected to be stronger for δ^{18}O compared to δD. Can the model produce this differential signal? This is a very simple test.

4. The discussion about the comparison with GRIP data feels incomplete and not thorough. The actual data set is never shown in the manuscript while there is very little information about how diffusion is estimated for this data set. Measuring peak-to-peak amplitudes on ice core δ^{18}O data can be very misleading as the initial δ^{18}O value is unknown and most likely it has been variable through the time. One technically correct way to estimate diffusion on data is to look into the spectral domain and estimate diffusion length values. Either way the reader har practically no access to information about how diffusion is estimated from the GRIP data. Additionally, it should be noted that the GRIP data set, originating from a certain depth interval in the ice core (that is not given in the manuscript) it may have experienced a combination of temperature and acccumulation different from the modern one. Does the comparison presented here take this into account? In particular if the CROCUS model only uses a fixed diffusivity value for 263 K, there is no doubt that there will be a discrepancy with the data deduced diffusion. These are very important elements of such a study and are notaby absent in the manuscript.

5. Plots and captions need to be reworked. There are several stylistic inconsistencies that should not be allowed for a publication of this quality. A mixture of different font types, missing measurement units from axes, different approaches in presenting measurement units (using either parentheses or a / sign) and a ‰sign presented in two ways. I think that many of the captions are too long while

in the same time they miss one important piece of information that is the number of the experiment and maybe the ice core site under consideration. I do not think it is the job of a reviewer to go through every single detail and problem with the plots thus I will trust that the authors are certainly able to carefully go through the presented plots and make the necessary changes.

6. Regarding the references given, I think that for the introduction section there is probably an overwhelming number of works cited and a small clean-up is possible. More importantly though, some of the works cited are not peer reviewed belonging to the “Discussions” versions of some of the Copenicus publications journals. I believe that the authors should consider these cases and preferably either omit them or update their references list in case some of the papers in question have reached a post peer-review status.

3 Specific comments

Here some more specific comments for the authors.

P2L45

"and then only stacking...". As one looks in higher depths in a core this is less of an issue.

P3L57

Make sure the reader understands this is vapor-solid exchange in the porous medium of the firn.

P3L67

Diffusion length mentioned here but no definition given.

P3L74

"...and of diffusion against isotopic gradients" Is this vapor firn diffusion or solid?

P5L117

For an informative plot on the matter see Gkinis et al 2014. Higher accumulation rates also result in increased densification rates and therefore reduced diffusivities.

P5L120

Diffusion indeed takes place in the ice column but with rates orders of magnitude lower than that of firn. You want to be more specific about it in the text as you often mix the terms vapor and solid diffusion without being specific about the process taking place in the porous of the firn or in the solid ice.

P6L143

It would be helpful to add even one sentence where you explain why and how the spherical ice elements approach is too simplistic (is it?).

P7L161

"...the transfer of molecules from the grain boundary towards the center of the grain is very slow" Solid diffusion at the temperatures we are talking about is indeed slow. However this sentence gives a false impression that there is a 1-way motion from boundary to center. This is wrong for two reasons. Firstly, any diffusion process would not result in a 1-way motion of molecules. Secondly and more important, solid diffusion in ice seems to be a self-diffusion process following a vacancy mechanism. This means that there is no isotope effect and diffusion affects all isotopologues equally or in other words molecular transport does not take place along and due to the isotopic gradients in ice (therefore there is no index denoting isotopic species in Eq. 1 - ice diffusivity concerns water molecules in the solid phase regardless of their isotopic composition). As a result the model used here of an isotopically heterogenuous material with internal and external layers does not cause any isotope diffusion in the solid phase due to the radial gradients. In a perfectly homogeneous material you should be expecting the same magnitude of diffusive mixing in the solid phase as in the heterogenuous meterial assumed in the text. It would be good to correct these errors in section 2.2.2 and clarify the precence of the self-diffusion mechanism.

The calculations of characteristic times in this section look correct and are relevant though. Just make sure that you clearly explain that this characteristic time concerns not only movement of the different isotopologues along a specific path (surface to center of grain) but of ALL water molecules towards all directions in the grain and across the grains.

section 3.1.1

I was wondering if it would be possible to outline the components of the Crocus model in a summarising table and shorten this section significantly?

P10L221

There does not seem to be any dependence of the densification rate to temperature or accumulation rate. Neither is there a two or three stage densification process as done usually in some other densification models. Can you elaborate on this? Would this model be suitable for modelling the full firn profile from surface to firn–ice transition?

Eq.4

I think the right term for the quantity ρ_v should be *mass concentration* instead of *vapor density* (this term is wrongly used in more places in the manuscript). Density refers to the ratio of mass to volume of the same substance whereas what you use here is the mass of vapor devided by the volume of air in the open porosity of the layer under consideration. Accordingly I think you should change the symbol from ρ_v to C_v or similar. I may be missing something but if I use Fick's first law and a forward difference differenciation scheme I do not get the factor of 2 as in Eq. 4. Can you elaborate please?

P11L260

D_v is a function of temperature and pressure. How significant is the fact that you are using a fixed value?

Eq.5

The fact that the diffusivity used here is independent of temperature and site pressure seems problematic to me. Can you comment on this and add a line in the manuscript about the effect of this approach?

Eq. 7

Again strictly speaking the quantity you need here is a concentration and not a density. Change the symbols as well.

P14L312

Consider using the term *rare isotope* instead of *heavy isotope*. Also using an index i is more appropriate than a * sign as later on in Eq. 8 and 9 you use “17”, “18” and “D” in the position of the * sign.

Eq. 8 and 9

The term C^{i}_{vap} needs to be clarified both here and in Table 1. What I understand is that C^{i}_{vap} refers to isotope concentration as

$$C^{16}_{\mathsf{vap}} = \frac{[\mathsf{H}_2^{16}\mathsf{O}]}{[\mathsf{H}_2^{18}\mathsf{O}] + [\mathsf{H}_2^{17}\mathsf{O}] + [\mathsf{H}_2^{16}\mathsf{O}]} = \frac{{}^{16}R}{{}^{18}R + {}^{17}R + {}^{16}R} = \frac{1}{{}^{18}R + {}^{17}R + 1} \qquad (1)$$

(again (Mook , 2000) is a good source for definitions). However later in Eq. 11 you seem to be using the same quantity for something slightly different, this time the masses ratio and not the abundancies ratio. Can you comment on that and make sure the definitions are clear to the reader? If needed add a definition equation in Table 1.

P14L319

I would be very interested to know why you have used the fractionation factors from (Ellehoj et al., 2013)

P14l329

This note concerns the use of the term *kinetic fractionation* throughout the whole manuscript. Kinetic effects refer to anything that is non-equilibrium. And indeed fractionation due to the different diffusivity coefficients for the different isotopologues is a type of kinetic fractionation. Though it is an overstatement to claim that you have included all possible kinetic fractionation processes by only using the ratio of the diffusivities. Fractionation effects related to different binding energies of the molecules for example can also be affected by a non-equilibrium/kinetic regime and this is something that is not addressed by the D^{*}/D term. I would suggest that you go through the manuscript and clarify this (term kinetic is used in pages 1, 13, 14, 16, 30, 42 and 43). I would also refer the authors to the sections 3.1 to 3.5 in vol. 1 of (Mook , 2000). Even though some of this definitions sound trivial I think the manuscript can benefit greatly by getting these small details right, thus avoiding misconceptions.

Eq. 12

See previous comment on Eq. 4

P15l353

“Here the condensation of excess vapor occurs without additional fractionation”. Is this not unphysical. Can you comment?

P18l407

Rephrase the sentence. The term “oriented processes” (also used in 2.1.2) is not a technical term. From what I understand your use of the term “oriented processes” refers to advection–based processes that bias the isotopic signal. Diffusion is not such a process, it attenuates the isotopic signal and is driven by isotopic composition gradients as apposed to for example ventilation that is driven by a bulk motion of air in the open porosity. Additionally diffusion takes place for much longer than 12 m (depending on close–off depth) whereas the extend to which ventilation is apparent in polar firn can be debaded.

P18l414

“Thus the diffusion process can only be studied in the first 2 m of the model snowpack” Can you elaborate on this? Is it a computation time issue that does not allow for thinner layers below the top 2 m. How do the calculations look like below this depth?

P19l432

Stick to one name for GRIP/Summit throughout the manuscript.

P19l445

Citing a published work (Bréant et al., 2017) dealing with the density studies at DomeC and GRIP is of course acceptable though the density profile here is of great importance for the diffusion calculations, therefore giving some more information and possibly figures would be appreciated. Additionally you give the density as a function of n and t where t (the model time) is an independent variable to z. Can you explain this a little bit better? How do Eq. 16 and 17 give you an evolution of the column density and the densification rates? Please also update the reference to the one past the review process, published in the Climate of the Past.

P19l450

Earlier in the manuscript you mentioned that all diffusivity values are for a temperature of 263K. Does the isothermal profile at 241 K affect this and if yes how?

P20l457

In Table 2 you refer to a different work for the value of accumulation at GRIP. Be consistent and use only one reference.

P20l457

You can be a bit more specific and call it “peak to peak amplitude”.

P20l461

Please refer to general comment nr. 1 with respect to the difference between “isotope firn diffusion” due to isotopic gradients in the snow/firn and signal attenuation/alteration because of air or vapor “bulk motion” driven by pressure or temperature gradients in the snow.

P20l471

What does the term “densities” refer to here? Vapor densities (use term water vapor concentration instead) or firn densities. If it refers to firn densities can you be more specific about how your densification rates depend on temperature?

Section 3.3.3

In my view this section is unnecessary and its sole sentence can be included in the previous section.

P21l486

Is this peak to peak amplitude?? Also writing that maxima and minima are reduced sounds inaccurate. Attenuation would result in reduced maxima and increased minima, or in the difference between the two being lower. Lack of visual examples makes this type of language errors quite critical as they can be very confusing for the reader.

P21l490

The description of the model in the previous sections suggests that the diffusivity coefficient is independent of temperature. It is not clear though if there is some dependancy of the diffusivity to temperature for your model experiments. One possible cause of the increased depletion for the upper few cm could also be that the firn appears to be quite warmer, something that would result in enhanced diffusion rates for these few cm of the firn column thus attenuating this part more compared to the layers below. I also miss some info on the density profile here and specifically the surface density.

Section 4.1.2

This section lacks a proper description of the methods used in order to estimate the amplitude of the isotopic signal for the cores presented. In Johnsen et al. the amplitude of the annual signal is computed using a rather sophisticated modificaton of the Maximum Entropy Method where the annual signal spectral peak is integrated to give a value in permile. This of course is an estimate dependent on the initial isotopic signature (some years have a greater amplitude thatn others) and for this reason 5m intervals are considered in Johnsen et al. How is this analysis performed here? Can a 20cm interval produce satisfactory results when the layer thickness for these depths at NEEM is in the order of 50-60 cm? Also the term half–amplitude should be peak–amplitude or semi–amplitude.

P22l513

GRIP is also slightly colder.

P22l520

This is a very good point. Temperature has a strong impact on the diffusivity coefficient. It is certainly relevant to consider various other processes that can be the cause to these discrepancies though a very simple test you culd do here is to apply the Johnsen et al diffusivity parametrisation in Crocus and compare the results. I am puzzled by the values that are given here ofr the firn diffusivity. These are much closer to air diffu values. Firn diffusivity values for $\rho = 350\text{kgm}^{-3}$ around the temperature of 241 K are orders of magnitude lower. I attach a plot of the Johnsen et al diffusivity for a range of temperatures. What is the reason for such a large difference?

Fig. 1. Diffusivity in firn for O18 at $\rho = 350\text{kgm}^{-3}$

P23l530

It should be mentioned here that the van der Wel (Van der Wel et al., 2015) study is made by spraying a layer of isotopically spiked artificial snow on top of the natureal Summit snow. Such experiments are extremely challening and the approach of using artificial snow can pottentially introduce artifacts with respect to the diffusion processes.

P23l548

Perhaps you can slightly rephrase as "..are required to observe significant change in densities due to vapor transport at the seasonal cycle".

P24-25

The numbers of the experiments should be stated for clarity in the subsection titles or very soon after in the main body of each subsection.

P25l585

It is a little bit unclear here why and how the precipitation intermittency results in a biasing of the isotopic signal (from -53.2 ‰ to -49.8 ‰). I can see how the winter precipitation events are biased towards warmer temperatures and more enriched δ^{18}O values but cannot understand how this creates an additinaly bias in the isotopic composition of the snow.

P25l590

"As expected the maxima and the minima of δ^{18}O are further reduced as a result..." A more precise and careful writing would be very much appreciated. What does this sentence mean? Is this a decrease of the whole δ^{18}O signal, a decrease in the peak to peak amplitude of the signal or a decrease in only the minimum and the maximum of the sinal? Additionaly (see also general comments) you can technically not have isotopic diffusion because of temperature gradients. The latter can indeed create water vapor concentration gradients that will result in diffusive transport of all water vapor molecules. This is though not the same process as isotope diffusion.

P26l600

It is very difficult for the reader to follow the discussion of this paragraph when no access is given to the δ^{18}O profiles pre and after diffusion. The approach of using contour plots or tracking single layers does not give a good picture of the initial conditions and the evolution of the simulation experiments. Even when those plots are presented they only cover the top 40-50 cm of the studied snow-firn column. As a result, referring to gradients of for example 24 ‰/m feels as an irrelevant piece of information.

P26l605

Indeed lower temperatures will slow down diffusive fluxes. This though can only be modelled if the diffusivity coefficient is temperature dependent something that is not the case for this study. Can you comment on this?

P26l607

Which other parameters are loosely estimated? When the term “large uncertainty” is used it is only logical for the reader to ask how large is the uncertainty.

P28l644

Replace badly with poorly.

P28l645

Being able to implement more processes in a model sounds in principle as a step forward. However I think that a discussion on improving on the knowledge, assumptions and parameters used in the more dominating processes of diffusion is missing here. Integration of more processes that are poorly implemented can be misleading and give the false impression of an improved approach for the description of the problem. With this in mind I think that a comment on proposed improvements, measurements and proper tests with real data would be most welcome in this manuscript especially if it focuses on the more dominating processes of the problem.

P28l660

The top 10 m of snow may have been modelled in this study but results only the top 0.5 m are presented here. Thus I think this sentence should be rephrased in order to reflect the actual results presented in the study.

P29l675

Refer to my general comments on the GRIP case.

4 Comments on figures

Figures of experiments results

The experiment number should be included in the captions and titles of all relevant figures.

Color maps of figures

The color maps of the density and δ^{18}O change plots can become more readable if there is also some informationabout where the zero value is. I assume it is the white but cannot tell with certainty.

Density and O18 change plots

I find these plots confusing and not intuitive. The meaning of the term “density change” and “δ^{18}O change” appears only in the caption of fig. 7 and 8. It is very hard for the reader to understand what this change refers to. My impression until I reached figure 7 and 8 was that these were rates ie change per time. Please clarify in the main text and on the legends of the figures.

Figure 11

It is odd that while the slope for the 2000 winter layer is oposite to the other summer layers and you choose to comment on this, the scale of the axis for these data is inverted thus visually “masking” the event. I would really not mind of the lines end up crossing each other if all axis are plotted in the same way.

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