Response to RC1 [egusphere-2024-1012]

Black: Reviewer comments. Blue: Authors' response.

RC1: Anonymous Referee #1

This manuscript is a pure modelling study (following a recent study of the same type by the same author) of the diffusion through vein and grain boundary in addition to slow diffusion in ice. Initially, larger than expected diffusion (excess diffusion) has been observed in several cases; those cited in this study are GRIP Holocene, WAIS deglaciation and EPICA Dome over Marine Isotopic Stage 9. Studies of grain boundaries and vein contributions to the diffusion were already performed, e.g., in the book chapter of Johnsen et al. (2000) cited in the present study. The present study wants to go one step further compared to Johnsen et al. (2000) and following his recent paper to show the expected isotopic patterns to be observed at the grain scales for a range of parameters.

Thank you for your review. It is useful to read this summary, and your comments and suggestions in this report are valuable.

The main problem is that no observation is provided and even if laser ablation techniques are progressing, we are still far to the point where such observation can be done and it is also not clear that observations will actually be possible in a near future (see following comments). As it stands now, this study is focused on the resolution of the differential equations for diffusion through ice, grain boundary and vein in cylindrical coordinates. This is a serious calculation work giving the expected changes of patterns with changing parameters. I do not see how it can really be used by others as long as no observation is provided and there are no clear other scientific perspectives for this work. But the study is seriously conducted and well detailed.

I appreciate these comments, and thank the reviewer for positive appraisals on the mathematical calculations undertaken. I agree with the observations that the weak isotopic variations calculated cannot yet be resolved by analytical techniques, and laser ablation methods may have some way to go before being able to measure them.

I feel differently about this situation being a "main problem" with the study. I think that it is permissible for theoretical studies to produce results beyond the measurement capability of the time. In this case, analytical techniques are now actively being developed by researchers, who will benefit from knowing what they are up against – how strong or weak are the predicted/expected signals and what the signals look like, according to theories (which must be tested). As far as I know, prior to the submitted study, no information on this was available, at least not in sufficient detail. More generally, theoretical papers and theoretical results serve an important role in stimulating researchers to take up the challenge to push observational limits, through instrumentation design and innovation. Examples abound in the physical sciences where such interactions happen; observational advances do get made (often in a non-linear manner), and many observations made possible by new technical advances could have seemed far-fetched before those advances. Separately, there are countless publications across science that report theoretical analysis and that do not – in the same paper – measure or observational results pertaining to the phenomenon studied. Thus, I think that the "main problem" being alluded to here lies rather with today's state-of-play of this research area in glaciology and ice physics.

A key angle of the submitted work is that the short-circuiting mechanism of the Nye, Rempel and Wettlaufer, and Ng genre of theories has never been tested – unconfirmed by observations at the grain scale. These theories are at best "working hypotheses", obviously able to match the accelerated signal decay seen in the core sections that they were formulated to explain, but unproven. The theories may be far from reality. We won't know until independent observations are made. I haven't seen this realisation put across in the literature, and it is important that ice-core studies do not automatically invoke vein or grain-boundary short-circuiting as the explanation wherever an isotope record indicates excess diffusion, as if the explanation is firmly established. I think these points form a strong scientific perspective to be offered by a study, and cannot see what other clear perspectives are needed.

Having gathered these thoughts to answer the comments, I think that in a planned revision of the text, I will elaborate along these lines more in the Introduction (perhaps also in the Conclusions) in order to emphasise my study's rationale even more strongly.

I concentrate below on comments along the text.

- Introduction : the introduction is well written and summarizes previous findings on diffusion. It is interesting that the author mention the 3 cases where excess diffusion has been identified but I am wondering if the origin of the excess diffusion is the same for all three cases. Indeed in the case of EPICA Dome C, the ice is very deep and old, with relatively large ice crystals and the origin of the excess diffusion may be different than for WAIS and GRIP Holocene. It would be nice to have a discussion on these differences and perhaps discuss the possible mechanisms in each cases.

Thanks for this suggestion. Yes, to help the reader, I can add a passage in the Introduction to sketch the general state regarding the published/existing explanations for those observations, differences, and potential factors, notably, (i) that Pol et al. (2010) invoked fast diffusion in the vein system as a possibility when discussing long diffusion lengths deep in the EDC core; that (ii) Ng (2023) was able to recreate the vertical pattern of diffusion lengths in those core sections of the GRIP Holocene and EDC MIS 19 showing excess diffusion, by using the model with vein-water flow, and finding vein-water flow to be necessary; and that (iii) Jones et al. (2017) explored multiple hypotheses for the WAIS core section showing unusual isotopic diffusion rates, finding that no single hypothesis could straightforwardly explain the observations. Descriptions along these lines will enrich the contextualisation of the study, so I am happy to add them. (I won't be able to discuss those differences and factors on a firm or detailed basis, as we don't know whether or not the theory of vein/grain-boundary short-circuiting is correct, or even roughly correct.)

- 2.1- the system is clearly described

- 2.2- Figure 2 is complicated to understand and it was only much later during the reading of the manuscript that I could really understand what « high », « medium-high », …, « low » mean. It should be explained in this section as well as in the caption of figure 2.

Thank you for pointing this out. Yes, my descriptive scale for the chosen model values of Db should be better explained at the outset. I can do that, by extending the text on page 8 (around Lines 197-201) and the caption of Fig. 2 caption and coordinating them.

Also, in some places the description is not accurate, e.g. « departures from the formulas **by a few times** », « Pre-melting occurs **at high temperature** », « ice-core samples can be **very variable** in these », … and should be precised.

Yes. I plan to revise these passages for precision, to remove vagueness.

Line 160 : the author refers to the hypothesis of liquid diffusion at -32°C for Db and say that this estimate will be ruled out but they do not give the value for Db in this case and we can not really see it in Table 1.

Yes, I will state the value of Db used by Johnsen et al. (2000) on Line 160. (Most probably I won't show it in Table 1, for reasons explained below.)

In general, it would be nice to make a more clear link between the hypotheses listed in p. 7 and the values for Db explored in this manuscript and listed in Table 1. Perhaps the authors could take in Table 1 the values of Db from the litterature (or explain how the range of chosen values are linked to previous estimates) and refer to the different papers in Table 1 so that we can make the link between the present study and the previous studies.

Thank you for this suggestion. Extending Table 1 to clarify the links is tricky, as there are no laboratory measurements of Db below –18 °C (Lu et al. (2007, 2009) measured at –1 to –18 °C), and the single Db value simulated by Yagasaki et al.'s (2020) model is for –23.3 °C, while my model Db values lie at still lower temperatures: –32 and –52 °C. Given how scattered these values are on the diffusivity–temperature space, showing all of them (plus Johnsen et al.'s (2000) value) in one table to draw links between them may not work. Currently, I do this graphically with Figure 2. I think what your comments are telling me goes back to the point that Figure 2 should be better explained. Therefore, I plan to improve the text, to guide readers more clearly regarding what Figure 2 shows, how the different data on it should be read, and the interactions and linkages between them, including how extrapolation of the results of Lu et al. is used to choose model Db values, and my descriptive scale for those values. The current text covers these elements too quickly.

- The fractionation explanation is not very clear from l. 162. Which fractionation does the author refer to ? No data for fractionation is given nor its dependency to temperature.

I agree that the passage on l. 162-166 is brisk and might come across as unclear. I will revise it for clarity and detail and indicate fractionation values for oxygen and hydrogen where known (note that laboratory data are incomplete) and give references.

Essentially, if one assumes grain boundaries to be completely liquid, then fractionation will occur at the liquid-to-solid phase transition between them and the crystal lattice within grain interiors; there will be no fractionation where the grain boundaries meet veins, because both of these are liquid. In contrast, if one envisages grain boundaries to be solid-like (almost the same as crystal lattice), then no or negligible fractionation occurs between them and crystal lattice; but in this case, fractionation occurs where the (solid-like) grain boundaries meet (liquid) veins. The paragraph's last sentence on line 165-166 also suggests the possible hybrid scenario where grain boundaries behave as "disrupted lattice", with structural-molecular properties intermediate between solid and liquid. Then fractionation may be expected to occur at both locations. I hope that this description already improves upon l. 162-166. I plan to use what I have written here as the basis for revising the text.

- 2.3 – The formulation and resolution follow a classical mathematical approach. Still, because many parameters and variables are involved in this resolution, it would help to have somewhere a table gathering the different parameters and variables, explaining their meaning and giving their values. As it is now, it is difficult to read.

Yes, I can do this. Adding a table of mathematical symbols is straightforward.

It is also certainly possible to have the details on the resolution (e.g. the sections 2.4, 2.5 and 2.6) in an appendix and go directly to the results once the problem and the way to solve it has been defined.

Thanks for this suggestion. I have considered this, and prefer to keep these sections in the main text. Sections 2.4 and 2.5 are central to the description of the mathematical problem (for H) being solved, especially its formulation as eigenvalue problem; and H(r, theta) defines the isotopic fields shown and analysed in the Results sections. I doubt if these sections could be moved to the appendix. If I move them, I end up having to explain the same essential things at the beginning of the Results (section 3). For Section 2.6, I need to cater for readers interested in how the problem is actually solved, so I prefer keeping it in the text; doing this also maintains flow from 2.4 and 2.5. By analogy to experimental studies, I feel that moving sections 2.4, 2.5 and 2.6 to the appendix would be like moving their Experimental Methods section (detailing critical steps, choices and assemblage/units of the new technique that enabled the advance) to behind the text. I don't prefer such a move unless the material is really peripheral.

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-l. 369 : no reference nor explanation for the choice of the fractionation coefficients are given

Yes, I can give relevant references to published studies.

- l. 373 : I do not see why studying signal wavelength of 5 mm ? Such signal is not detectable in ice core, even in CFA because of mixing in the system – at best the resolution could be 1 cm which will not enable capturing such signal. Also the following discussion (section 3.1) and display of the results (figure 4 and all figures after figures 4) with a wavelength of 2 cm is not very realistic. Also because firn diffusion occurs with a diffusion length of several cm, it would be more realistic to discuss signals of wavelength 10 cm at least. This is a major limitation of this study and it is important to address it for more realism and potential use of this study for ice core people. Some figures are shown in the supplement (showing much less excess diffusion) but not really discussed in the main text.

Thank you. This is an important and valuable comment. I agree – it is much more useful to illustrate the study by analysing results for 10 cm or similarly long signals. The original choice of 2 cm was suboptimal. It is easy for me to update the text and figures to showcase findings for a longer signal, e.g. 10 cm or 12 cm, because I have the relevant results at hand (no new computation is needed; I had computed results across the parameter space) and the code and workflow to make Figs. 4 to 11 for any parameter combination; also, the conclusions of the study are not hinged on the 2 cm signal wavelength.

In the update, Figures 4–11 and the interpretations and conclusions drawn from them will in fact change only slightly. This is because the pole and spoke patterns, their transitions and excursion widths, and the parametric controls on their transitions, are mostly unchanged. The reason is that the wavelength affects the variation amplitude (as you pointed out) but not the patterns; examples already showing this are Supplementary Figures S3 – S6 for an 8 cm long signal (cf. Figs. 10 and 11). At longer wavelength, the patterns will still have higher variation amplitudes – and become more detectable – if vein-water flow occurs. Therefore, the inferences regarding instrumental sensitivity (e.g. on page 26) will probably be adjusted but not change drastically. In the revision, in various places I will of course modify the text for emphasis, order, or numerical detail, to coordinate with the changes.

Some figures are shown in the supplement (showing much less excess diffusion) but not really discussed in the main text.

Thanks for pointing out this. With the proposed plan of updating the manuscript above, the figures for 8 cm wavelength (Figs. S3–S6) will probably be redundant and removed. Note that long signals experience higher (not less) excess diffusion, as mentioned in Section 3.2. Higher enhancement factors can also be seen by comparing Fig. S3–S6 (8 cm) to their counterparts in Figs. 10 and 11 (2 cm).

- l. 376 : intermed**i**ate

- l. 408 and after : some terms need to be better explained : « vertical stretches », « stretch transition », « transitions » (from what to what ?), « hole type», « spoke type»

- l. 447 : The sentence lacks a word.

I will attend to the corrections described in the above 3 comments.

- l. 464 : when should we have vein-water flow – please explain this case a little bit

Yes, I will add description, referring to Nye and Frank (1973), who estimated the potential range of vein-water fluxes associated with gravity-driven percolation through ice sheets.

Reference: Nye, J. F. and Frank, F. C.: Hydrology of the intergranular veins in a temperate glacier, International Association of Scientific Hydrology Publication 95, Symposium at Cambridge 1969 – Hydrology of Glaciers, 157–161, 1973.

- when discussing enhancement factors in this study (e.g. figure 6), it should be compared to what has been measured (if possible on signals with similar wavelength in the data and modeling approach).

I am not sure that this study is the right place for such comparison. On the observational side of the subject, quantification of the diffusive smoothing rate on ice-core isotopic signals is done via the "diffusion length" estimated from the (Fourier) power spectral density of signals. An entirely different study is necessary for comparing theoretical-predicted enhancement factors and enhancement factors estimated from observations. Such study would need to simulate the diffusion-length profiles down core. Actually, this is the subject of the second half of the paper by Ng (2023); see their Section 4 and their Figs. 8–11. In the current manuscript, I might briefly outline this matter and refer readers to that paper.

- When showing isotopic patterns in the figure, the unit should be provided

Yes, I will clarify in the text in Section 3.1 and several captions (notably Figs. 4 and 5) that the unit shown in the figures is dimensionless, and elaborate on the reason. As explained in Section 3.1, the magnitude of the isotopic variations across a given isotopic pattern is scaled to the amplitude of the vertical bulk signal inducing it. Thus, its absolute magnitude (in per mil) can be known only if the absolute amplitude of the vertical bulk signal is known; i.e. the former changes proportionally to the latter. Real bulk signals can have a variety of absolute amplitudes --- there isn't a fixed value. The normalisation on H (prior to plotting) ensures that the figures show a unit (dimensionless) amplitude for the bulk signal, so that scaling can be used.

- l. 634 : I do not really see how a signal of 2 cm wavelength can be well determined by CFA, see comment above.

Please see my reply above to your comments regarding l.373. I will update the text to illustrate the analysis with a longer-wavelength signal.

- l. 670 and below: the author correctly notes that it is really difficult to find ice to test this effect since the isotopic signal usually measured has a wavelength much higher than 2 cm and for short wavelength, the amplitude of the signal is accordingly small.

Thank you for this observation.

- l. 729 : a sensitivity of 0.1 per mill is required but for which isotopic delta ? d18O or dD ?

Thanks for pointing this out. I will clarify this in the Conclusion passage, probably also on page 26, by saying more about the separate cases of d18O or dD, in view of their different ranges of variation observed on CFA records.