Response to RC2 [egusphere-2024-1012]

Black: Reviewer comments. Blue: Authors' response.

RC2: Anonymous Referee #1

General Comments

This paper deals with the modeling of the diffusion of stable water isotopes occurring in polycrystalline ice. The overall motivation of this work is to explore mechanisms that could explain the "excess diffusion" of stable water isotopes observed in some ice-cores. Understanding and quantifying diffusion of stable isotopes in ice cores is important as they are used as proxies for the reconstruction of past temperatures and post-deposition effects need to be quantified for a fine interpretation of these paleo-records.

Specifically, the paper models the combined impact of liquid water veins and crystals grain boundaries in the diffusion of water isotopes and to quantify the enhancement of the smoothing of isotopic signals (compared to a scenario considering diffusion through the ice phase only).

To my view, the paper offers three main points:
- The equations to model an idealized polycrystalline ice, including a water vein and grain boundaries, and a numerical methodology to solve them.
- To demonstrate the formation of specific spatial patterns, around the water vein and crystal boundaries, which constitute a robust signature of the proposed mechanisms to explain excess diffusion.
- To quantify the role of water veins and grain boundaries to the enhancement factor of diffusive-smoothing.

The paper is well constructed, follows a sound methodology, and offers valuable results for the interpretation of ice cores. I therefore think it is suited for the The Cryosphere and suggests minor corrections.

Thank you for your review and these appraisals, and for providing a very detailed set of comments and suggestions to help me improve the manuscript.

My main remarks are:

1 – I think the paper would benefit from a more systematic use of citations to published literature. It would help the reader not familiar with the overall scientific context and with the techniques used in the paper. Some examples are given in the specific comments below, but for instance one example that comes to my mind is L249 that refers to "past theories" without mentioning them (I guess the author meant Rempel and Wettlaufer et al., 2003).

Yes, the submitted text did skip some references and use umbrella terms for them in places to save space. I can revise the text to be specific in those instances. (I have noted the items in your "Specific Remarks" below about references.)

2 – The author assumes equilibrium fractionation at the interfaces between the grains boundaries, the vein, and the ice (L230). From what I understand, this assumption simplifies the system of equations (as Nv and Nb are now direct functions of Ns at these interfaces). Is it a common assumption for the diffusion of isotopes in polycrystalline ice? Also, since there is transport in the problem, I think that non-equilibrium fractionation could be possible. If so, what could be the impact on the diffusion of water isotopes? Can we justify that it is small?

Equilibrium fractionation was assumed in Johnsen et al.'s (2000) study, and assumed in the equations of Rempel and Wettlaufer (2003), which form the backbone of this part of my model – the formulation on L230 is closely analogous to their formulation. No fractionation was considered in Nye's 1998 model.

The possibility of non-equilibrium fractionation is interesting generally. However, I don't think that I will be elaborating the text to explore it. There are two reasons:

(1) I don't think that current knowledge allows us to address the process properly as a detail in this study. Experimental data are lacking on non-equilibrium fractionation at the ice–water interface. I looked and struggled to find any relevant literature. Borrowing concepts or results from other fields, e.g., from isotopic studies on igneous and metamorphic rocks or from other phase boundaries (ice–vapour or water–vapour) involve bold and uncertain extrapolations to the ice–water system, and stacking of more theories on top. Those theories will have still more assumptions behind them.

(2) More importantly, I don't think that the consideration of non-equilibrium fractionation aids this study. The purpose of the study is to bring together existing theoretical elements into a single representative model, and calculate results from it to inform observational testing of those existing theories. The "elements" referred to here include the veins considered by Nye (1998) [who didn't model grain boundaries], the grain boundaries explored by Johnsen et al. (2000) [who considered veins but didn't couple grain-boundary and vein diffusion], the extension to a finite liquid diffusivity by Rempel and Wettlaufer (2003) [whose model has veins but not grain boundaries], and the vein-water flow studied by Ng (2023) [whose model lacks grain boundaries]. Thus, the combined model is necessarily an extension of the individual models/theories. But the purpose of the study is *not* to build even more complexity into it to capture all conceivable aspects of the physical world, to form a 'kitchen sink' model and put it forward as a complete, robust description of excess-diffusion mechanism. Instead, the study emphasises testing the *existing* theoretical framework. Even if, under some conditions, non-equilibrium fractionation has a large effect in the system, the study's purpose is still to report predictions from the existing theories.

I will modify L230 to emphasise that equilibrium formulation is assumed in the model and in the theories informing its formulation, so it is clear to the reader.

3 – The paper mainly focus on the role of water vein and grain boundaries, and so little emphasis is put on grain size (which was studied before if I got it correctly). I understand this choice, but I'm still wondering to what extent the enhancement factor depends on the grain size. Section 3.2 refers to Rempel and Wettlaufer (2003) for this effect and mentions that the proposed model predict the same trends. Is it possible to mention them in the paper and to estimate what kind of impact can we expect the grain sizes variations observed in ice cores?

Thank you for this suggestion. Yes, I can summarise the trends from grain-size variations following L556-557, probably in a passage of several lines. In sketching the kind of impact, I will strive to give description that errs on the quantitative side, probably through giving examples of values. I think it is a difficult to go beyond that, given an already large number of parameters in the model (and here we're considering variation in one more parameter).

Still on grain size, the abstract and Section 4.1 mention that the patterns of δ correspond to 10 to 50% of the grain radius. Do they really scale with grain radius (i.e. does the 10-50% holds for very large or very small grain sizes or it is valid for millimeter grain sizes only)?

Good question. Yes, they scale with the grain radius, because the calculations are made on the scaled model using a radial variable that has been non-dimensionalised with the grain radius b (Sect. 2.4). This finding holds for very large or very small grain sizes, as long as the grain boundaries are much thinner than the vein radius, and the vein radius is much less than b; see Eq. (19) and the line after it. Strictly speaking, the pattern is scaled exactly to the grain size when the Péclet number representing the vein-water flow velocity doesn't change. But, as reported in the Results, the pattern changes only slightly with vein-water flow velocity (because noticeable changes occur only very close to the vein).

Specific remarks:

Thank you for the comments below. I will put them to use in the revision. Most of them are minor, some concerning clarity and precision (including addition of references), so I hope it is ok for me to omit a point-by-point answer in this initial reply, and write only to those items where I have more substantive things to say.

L19 I would rather write things in percents when possible, as I find them more natural to read ("10-50% of the grain size radius" rather than "0.1-0.5 of the grain size radius").

L29 Add references to the use of δ18O and δD in ice cores.

L32 Perhaps add general references to signal smoothing in ice cores.

L38 Add references to Beyond-EPICA Oldest Ice and the Little Dome C project.

L89 Add references to the use of laser-ablation in ice cores studies and its possibilities.

L139-141 References would be helpful here to justify that grain boundaries needs to be inferred from bulk measurements and that they size can greatly increase with impurities.

L189 Does "bulk" here refers to the combination of ice and grain boundaries? If so perhaps precise it so bulk is not confused with the ice only (my first thought when I read the paragraph).

Eqs 3 to 5 I would specify that the sources terms in Eq 4 and 5 also corresponds to BCs for Eqs 3 and 4.

L230 Is there a reference for α~1?

Yes, I can provide references.

Eqs 9 and 10 I would specify here that Eqs 9 and 10 are directly derived from Eqs 4 and 5, under the assumption of equilibrium fractionation at the vein/boundary/solid interfaces.

L250 Add references to the mentioned past theories.

L261 The form of the trial solution was explicitly chosen as a dampened traveling wave in Eq. 13 but this sentence could leave the feeling that the migration of the signal has been somewhat proven (rather than assumed). I would reformulate with something along the lines "As shown by the phase angle XX, the trial solution of Eq. 13 includes a potential vertical migration at the velocity XX."

Thanks for this suggestion. I will probably borrow or adapt this wording to improve the emphasis of the existing passage.

I also propose to replace "downward" by "vertical", as I assume it would depend on the sign of the water flow.

L282 Doesn't k_r require to be solved as well (along side the H pattern)?

Thank. In this section (Sect. 2.5), I will add a sentence to say that after finding the eigenvalue s^2, k_r is found via Eq. (26) and then used to calculate the enhancement factor f.

L299 It makes physical sense that the ξ_l is zero when there is no water flux (because then the isotopic signal is not traveling), but can it be justified a priori from the system of equation (perhaps already done in the literature)?

If I understand your idea correctly, this aspect has already been treated by Ng (2023), on page 3067 in that paper, 4 lines above their Eq. (10), by symmetry considerations. In the current study, I refrain from repeating this highly technical aspect, as it is far from the thread of Sect. 2.5 explaining the approach to solving the equations.

L300 Why only the slowest-decaying eigenmode?

I will add a sentence to clarify that the other eigenmodes decay faster, leaving the slowest mode to be the one observed. Therefore we are interested in calculating the slowest-decaying mode.

L301-305 Perhaps add references about the mathematical techniques discussed here and examples where they have been used.

L363 I do not really understand the normalization. It is normalized by the value of H at r=1,

θ=L/2, and z=0 (the last point missing in the text if I'm not wrong)?
The z-variations have been handled by the exponential in Eq. (21), i.e., in mathematical terms, they are treated as the sum of Fourier modes in *z* in a "separation of variables" approach to solving the scaled model in Eq. (18).

Therefore, as indicated on L284, H is a function of r and θ only, not a function of z. However, your comment is probably made with the amplitude of the vertical signal in mind. I can clarify (around L363) that H at r=1, θ=L/2 describes the maximum value of that amplitude, to help the reader.

L373 Why these particular choices for λ and w? I guess they correspond to typical values found in ice core, but extra context and justification would be a plus.
The λ-range is motivated partly by both the wavelengths explored in the earlier models of Nye (1998) and Rempel and Wettlaufer (2003), and partly by typical wavelengths seen on ice-core isotope records. The w-range is motivated by theoretical predictions of the water percolation through ice sheets – Reviewer 1 has asked me to add context about that. Yes, I will add suitable background for both choices in this section.

Section 3.1 This section presents and discusses a lot of results and is therefore a bit dense to read. Perhaps adding sub-sections could help follows the argument set up by the author. For instance something as
3.1.1 Impact of grain boundary and water flow on isotopic patterns
3.1.2 Impact of temperature
3.1.3 Impact of the bulk isotopic signal
Agree. Thanks for coming up with these headings – this is very helpful. I will consider how to sub-section the material and what headings best suit the different parts.

L402 I would say that "the solution *overall* shows what the axisymmetric theories predict", as the presence of small distortions near the grain boundaries discussed later are a notable difference with previous theories.

L449 I understand that the phase angle (defined in L261) is constant at the given position z, but is it really equals to zero? Or perhaps the phase angle here refers to the phase of H ($\tan^{-1}$(Im(H)/Re(H)).

L494-500 I would move this paragraph on the impact of the non-orthogonality between thin sections and triple junctions later in the text (L510). Here, I found that it cuts the reasoning on the impact of D_b and c on the spatial patterns.

L499 "Only some triple junctions may show the archetypal patterns" Is it because the tilt make them unrecognizable or because the pattern itself will deviate from the model (model assumptions being not met in real ice)?

L539 I would precise that the fact the patterns are unchanged does not presume that the enhancement factor is the same.

L544 I do not understand why the bulk δ signal has a scaled amplitudes <= 1 in the case of short-circuiting.
Yes, I will add a sentence to explain.

L608 Perhaps add references for the impurities.

L634 Add a reference to CFA technique.

Technical remarks:

As for the "Specific remarks" above, I will put your suggestions here to use, and hope that it is ok for me to omit a point-by-point response to them in this initial reply.

Title I would precise that the isotopes in questions are (stable) water isotopes.
Thanks for this suggestion. This is a good idea. I will consider whether to clarify this in the title or in the abstract (or in both places).

L1 I would also mention here that the article discusses stable water isotopes.
Yes, certainly.

L11 I would use "could explain" rather than "can explain".

L19 Perhaps rephrase to "[…] and variations in δ ranging from 1 to 10% of the amplitude of the bulk isotopic signal. This sets […]"

L20 Not sure the mention of the specific technique of laser-ablation mapping is necessary here.

L126-127 "Equation" and "Figures" should be written in full at the start of a sentence. Also both the abbreviations "Eqn." and "Eq." are used in the article. I think TC guidelines require the use of "Eq.".

L169 The authors sometimes uses here ≈ when the symbol ~ is used elsewhere to mean what I think is the same idea. Perhaps use the word "about".

Table 1 If possible perhaps also put the investigated grain boundary thicknesses.

L204 corroborates

L206 t is not defined at this point.

Eq. 6 I would give the definition of δ a bit above, when it first appears L228.

L324 I would rather define BC the first time Boundary Condition is used.

L327 and 660 I am not familiar with the use of "/" to mean respectively.

Figure 4 I It might be a problem from my printing set up, but I cannot easily read the scale and axis values. Perhaps try to increase the resolution of the Figures and to increase the font of the Figures' text. Also the use of dashed could help visualizing the black curve when it covered by the blue one.

L545 Remove the hyphen in amplitudes

L546 "Underestimation"?

L550 Perhaps replace "single-crystal diffusion" by "crystal (or solid) diffusion alone" or by "diffusion in single-crystal".

L640 Is the reference to Ng (2023)?