Line numbers in this document refer to the tracked changes version of our revised manuscript.

Reply to Reviewer 1, Alan Rempel.

We are grateful to Alan Rempel for his constructive and thoughtful review of our manuscript. We are confident that all concerns raised have been addressed in the revised manuscript. The Discussion section has improved thanks to his insights on the physical processes involved.

We do not reproduce the entire review here – sections of it are shown in italics. Our replies are given in regular font.

The discussion of previous theoretical results in the introduction is appropriately concise, but might be altered slightly to some benefit. On line 45, the 50 cm displacement noted in the abstract of the paper by Rempel et al. (2001) is quoted without sufficient context to enable the reader to understand the conditions that led to that particular figure, which applied to ice of Eemian age in the GRIP ice core. Since that theory would predict different displacements in the EPICA Dome C core at different depths, I'd suggest rewording to something like: \The implication was that a chemical signal of Eemian age in the GRIP ice core ...".

This suggestion has been adopted in revised manuscript (L60).

Regarding the following sentence, a half meter doesn't seem like much in a >2km deep core, so it isn't clear whether the consequences for cross-matching events between ice cores for stratigraphic purposes would in fact be \major", or typically quite minor { perhaps the adjective should be removed.

50 cm is indeed a small interval of depth but at the base of an ice core, where layers are thinned, it equates to a substantial amount of time. The word “major” has been removed as suggested.

On line 50, the claim is made that Ng's (2021) modified theory would prevent such compositional displacement, but destroy the chemical signals over time. This would be somewhat unsatisfying given that chemical signals clearly persist for long durations, but Ng does show that deep signals can remain intact if the effective dffusivity is reduced or if spatial variations in grain size are invoked. I'd suggest appending the sentence with something like: \... they will be destroyed over time if they are free to dffuse unimpeded through connected veins into adjacent low concentration regions."

This suggestion has been adopted in revised manuscript (L69-70).

The differences between the Rempel and Ng treatments are not central to this manuscript, but as the former model is disregarded following the opening sentences of this paragraph, for further context I think it worth clarifying my own understanding of the primary difference between these formulations…This has been a rather verbose digression. Perhaps rather than saying that the Gibbs{Thomson ffect was neglected, it would be more correct to say something along the lines of: \... challenged the impact of this phenomenon by noting that since soluble impurity content appears not to exert a dominant control on ice grain size (e.g. Durand et al., 2006) and by extension, vein density, the Gibbs-Thomson e ect should cause vein radii to adjust by producing solute concentration gradients that diminish bulk concentration anomalies."

We thank the Reviewer for taking the time to detail his insightful thoughts. We will considered them carefully and modified the manuscript in response (L63-66).

The approximately Gaussian form of observed volcanic sulfate anomalies is somewhat curious (line 74). One might have expected fallout and deposition to be concentrated at rst and subsequently diminish over time and so be \front-loaded" to some extent. Based on modern observations, could you comment on whether the Gaussian shape results from short-term post-depositional changes (e.g. due to Gibbs{Thomson dffusion), or whether this is instead the characteristic pattern of volcanic fallout from stratospheric levels?

The reviewer is of course correct that the accumulation of sulfur in the stratosphere and its subsequent deposition to the ice sheet will be asymmetric, with a relatively sharp onset and a decaying tail. This asymmetry is indeed seen in recent eruptions, but observations of eruption signals at EDC shows that the signals tend towards symmetry within a time (of order 1 kyr) that is relatively short compared to the >400 kyr of this study. For this reason, we chose the mathematical simplicity of assuming a Gaussian shape from the start. Our sensitivity studies (Fig. 3) where we changed the width of the initial peak between 1 and 5 years show that the exact width or shape of the initial peak does not materially affect the derived effective diffusion coefficients.
The text at L110-125 has been modified to make the difference in form (skewed versus Gaussian) between volcanic signals in the stratosphere versus an ice core clearer.

In Figure 1, comparisons of the displayed scale bars showing 5 yr of ice accumulation with the observed sulfate peaks provide vivid illustrations of post-depositional ffects. However, the 5 yr span collapses onto a vertical line in the final 3 examples. I appreciate that the text gives further context, with the quoted 30 yr span for the 364 ka peak. However, I'd suggest modifying the figure caption or annotating each panel with the number of years that the 1m depth range represents.

Figure 1 has been replaced following this suggestion.

I found the theoretical development in sections 3.2 and 3.3 somewhat confusing. The standard convention in the modeling literature with which I am most familiar is to treat equations as portions of sentences, with appropriate punctuation (e.g. see Ng's 2021 paper). Instead, here you refer to the equations by number, and subsequently separate them out from the text. To me, this seems disjointed.

We agree with the Reviewer's opinion and have modified sections 3.2 and 3.3 accordingly.

In equations (6) and (7) you note that the effective dffusivity is expected to be a function of time. However, my understanding is that your model calculations in fact treat the dffusivity as constant through time is this correct?

Yes, the Reviewer is correct. Effective diffusivity is treated as constant for each volcanic peak – it does not evolve with time. Equations 6 and 7 have been modified, following also the advice of Reviewer 2.

It wasn't immediately obvious to me how equation (12) came about and why there is no explicit dependence on time. Indeed, a is really a rate, so I believe at/H is needed in the argument of the exponential to ensure dimensional correctness, and integration of (9) would produces this result following correction of a sign error.

Yes, the equation should have at/H in the exponential. This has been corrected.

On line 248 temperature and chemistry are mentioned as controlling variables. Perhaps grain size, or more generally, microstructure, should be mentioned as well.

This suggestion has been adopted in revised manuscript (L810).

On line 295 the very low eutectic temperature of sulfuric acid is used to justify the expectation that sulfate ions can be dissolved in liquid at EDC temperatures. However, in the paragraph beginning on line 155 you mention the Traversi et al. (2009) finding that appears to suggest that sulfate reacts with dust to presumably form a solid precipitate. Would it possibly be worth saying more here about the potential effects of chemical reactions between different impurity species?

Yes, this is a good point. Mention of this possibility is now included (L876-879).

The brief discussion in 5.3 begins by noting that the simplest version of Ng's (2021) model predicts much faster diffusion than is observed in the Holocene ice, which itself is faster than that observed in deeper regions. That the inferred diffusivity does not appear to depend on signal size would also seem to differ from Ng's (2021) model predictions. The proffered suggestion that Gibbs{Thomson diffusion efficiently reduces vein concentration gradients would appear to e ectively transform Ng's model to the Rempel et al. (2001) model, albeit only if vein density can evolve to enable signal translation. As the Barnes et al (2003) treatment relies upon ffects of grain-size evolution, it perhaps might contain some of the essential elements that these other two models lack. I'm not sure I follow the reasoning behind the nal sentence of this section. You've shown that the e ective di usion rate in the Holocene and early Pleistocene is both much slower than Ng's Gibbs{Thomson mechanism would predict and not systematically dependent on anomaly magnitude, so what makes you conclude that Ng's model correctly describes the controlling mechanism? I thought that I understood the Barnes-type model to depend on grain growth, but in the nal clause you say that the rate of grain growth isn't important. Please clarify.

We thank the Reviewer for these insights thoughts and queries. Section 5.3 has been modified to make it clear that Ng's "Gibbs-Thomson" diffusion doesn't fit perfectly with our observations (it is too fast and we don't observe a rate dependence on signal size). At this stage we are not able to conclude on which mechanism(s) are operating but we do demonstrate that there must be a marked reduction in diffusion rate relatively early on.

There's a typo in the title of the penultimate reference.

Thanks.

Reply to Reviewer 2, Jeffrey L. Kavanaugh

We are grateful to Jeffrey L. Kavanaugh for his detailed and thoughtful review of our manuscript. We are confident that all concerns raised have been addressed in a revised manuscript. In particular, the description of our modelling approach is improved thanks to his queries and suggestions.

We do not reproduce the entire review here – sections of it are shown in italics. We note that some equations are not well-reproduced here. Our replies are given in regular font. Reviewer 2 also uploaded an annotated version of the manuscript, containing editorial suggestions that we are grateful for and have adopted with few exceptions.

1. Gaussian form

…Their use here is more than justified
– but they remain just an approximation of the measured peak forms. (I'll also note that the description of stratospheric concentrations of sulphates following a major eruption (Lines 75–77) is decidedly non-Gaussian, being strongly asymmetric around the peak, and therefore it's reasonable for the reader to question whether sulphate concentrations in snow and ice are similarly asymmetric. Some additional discussion would help clarify this.

A similar point was made by Reviewer 1 and our reply is repeated below. We note that the manuscript text states peaks are Gaussian in form "very shortly after deposition". We do not argue that the direct deposition of sulfate from the atmosphere is perfectly symmetric.

The reviewer is of course correct that the accumulation of sulfur in the stratosphere and its subsequent deposition to the ice sheet will be asymmetric, with a relatively sharp onset and a decaying tail. This asymmetry is indeed seen in recent eruptions, but observations of eruption signals at EDC shows that the signals tend towards symmetry within a time (of order 1 kyr) that is relatively short compared to the 400 kyr of this study. For this reason, we chose the mathematical simplicity of assuming an Gaussian shape from the start. Our sensitivity studies (Fig. 3) where we changed the width of the initial peak between 1 and 5 years show that the exact width or shape of the initial peak does not materially effect the derived effective diffusion coefficients.

…it's unclear to me why FWHM is used to describe peak widths observed in the EPICA Dome C core throughout Section 2 (which describes the data), but FWTM is used throughout Section 3 (which describes the model). This isn't a major issue, to be sure (as the two are always related as FWTM/FWHM = 1.83), but it seems an unnecessary switch to make given that one value should be as easy to determine as the other from the data (but again, the data are presented in terms of FWHM, not FWTM). If FWTM is preferred, please include a brief explanation as to why.

We agree, the use of FWHM and FWTM is confusing and not necessary. Section 2 has been modified to use the term peak width, which is close to FWTM that is used later in the analysis. Where peak width values are quoted for volcanic events in EDC (e.g., L131) these values can be found in the Supplementary Table. FWTM is preferred (relative to FWHM)) for the model because it is closer to the 'width' metric of volcanic events in ice core sulfate identified by previous studies, e.g., Sigl et al., 2013, and therefore useful for comparison.

Given that the objective here is to set up the numerical model, I recommend rearranging Section 3.2 somewhat, moving from expressing quantities in the time domain (FWTM/FWHM expressed in terms of years) to the spatial domain (FWTM/FWHM expressed in terms of distance) as quickly as possible, which could be accomplished by stating immediately stating that if the peak width is 3 years; moving Eq. 5 up to where it would become eq. 2; and then discussing relevant areas and fluxes (currently Eq. 2-4). (In my reading of this subsection, Eq. 2-4 needn't come before Eq. 5, but I might be missing something.)

Section 3.2 has been modified but after some thought we decided it was better not to rearrange the equation order exactly as suggested by the Reviewer. This is because the text describes the steps taken in the order that we carry them out. This may not be the most efficient way to describe our approach but we hope it is helpful for readers to understand what we have done.

2. Description of the forward model

Reviewer 2 suggested re-writing equations 6 and 7 to use partial differentials and we have followed this advice (L422 and L427).

Some clarification of the description of ice deformation at flow divides is also necessary. Lines 195-196 state "By assuming no lateral flow, the dynamics of the ice sheet consist only of one-dimension (vertical) flow, with ice layers thinning with increasing depth and pressure."
This misstates flow conditions in a couple of ways…

We thank Reviewer 2 for his suggestions on how to improve the section on ice deformation. We have now used more appropriate terminology and removed the inaccurate statements (e.g., L427-430).

It's important to also note that it is only because the same $\partial C/\partial x = 0$ and $\partial C/\partial y = 0$ conditions are met that diffusion (Eq. 6) can be treated as a 1-D problem here, rather than a 3-D one.

This is now noted explicitly (L423).

With respect to Eq. 6, the effective diffusion rate D'((is expressed as a function of time (i.e., D'(((t). However, given the description of the model in the text, it seems that the diQusion rate D'((is held constant for each model run (with the best-fit diffusion rate for each sulfate peak determined independently from a set of 50 runs with log-spaced D'((values). Is this correct?

Yes, correct. The time dependence of Deff has been removed from Eq. 6 and 7. Text has been altered to include statement that Deff is time-invariant in our model (L425).

If so, this would mean that the sulfate diffusion rate is determined by the time at which the snow fell, rather than by the length of time the snow is resident within the ice sheet – which *has implications for the interpretations regarding Gibbs-Thompson diffusion vs. slower processes discussed in Section 5.3.*

The ‘time at which the snow fell’ and the ‘length of time the snow is resident in the ice sheet’ are in effect the same value because the units of ice age (‘time at which the snow fell’) is thousands of years before present, if we understand the Reviewer correctly here.

We agree that using a constant effective diffusion coefficient negates the possibility of testing how a time-evolving diffusion coefficient (perhaps due to changes diffusion processes) impacts the outcome. In a future treatment we could attempt to derive the time varying diffusion coefficient under certain assumptions by starting diffusion from various depths or by adopting a finite difference calculation method, but that is beyond the scope of this paper. We have added a sentence to the summary to highlight this (L1141).

Related to the discussion of the material derivative, it is not specified in the text whether the model is constructed in a Eulerian (i.e., fixed) coordinate system or a Lagrangian coordinate system (in which the coordinates track the deforming material). The framing of the equations suggests that a Eulerian coordinate system is used; this should be stated. (This is a relevant question because the sulfate peaks are advected downward through time.)

A Eulerian coordinate system is used to generate a frame of reference relative to the centre of each peak.

There are a few other concerns I have regarding the equations and phrasing in Section 3.3:
• The depth variable z is defined (on Line 202) as the “height above the bed,” but is subsequently referred to as “depth” (e.g. Line 205, which describes Eq. 9, and Line 207, which sets up Eq. 10). This is unnecessarily confusing to the reader, as thinking of z as a depth-below-surface reverses the sign convention. It would be much clearer to refer to z as “height above bed” throughout the text.

Good point – manuscript has been modified.

In Eq. 6-12, the spatial variable switches back and forth between x and z. I suspect that z refers to “depth within the ice sheet” and x to “distance along the ice core,” but didn’t see this clarified in the text.

Again, good point. Thanks. x is the distance along core relative to the centre of frame of reference (L420). Manuscript has been modified to clarify this.

Eq. 8 is dimensionally incorrect: the left-hand side has units of m/m yr) = yr, whereas the right-hand side is dimensionless (units: m/m); the equation is therefore a mathematical impossibility.*

We should have clarified that both the layer thickness lambda and the accumulation rate a are in m yr^-1. This is now done in the text.

Equation 12 has a similar issue with dimensionality: the argument of an exponent must be dimensionless, whereas −a/H has units of yr).*

Yes, the equation should indeed have at/H in the exponential – thanks for spotting this typo.

The equation defining the downward velocity field (Eq. 9) has issues with sign… Eq. 9 defines the ice velocity as being downward (i.e., negative). The negative sign ahead of the velocity term in Eq. 7 (as written in the manuscript) would therefore result in an upward (i.e. positive) velocity field. This is why the second term on the right-hand side of the material derivative equations must be positive in both 3-D and 1-D forms of the expressions for the material derivative.

The sign error has been corrected.

3. Significant figures

We thank the Reviewer for his advice on significant figures, which we will followed throughout the manuscript. The only exception is the "median effective diffusion rate of sulfate ions of 2.4 ± 1.7 × 10^{-7} $m^2 yr^{-1}$ in Holocene ice" which appears in the Abstract and main text. Rounding both these values to 2 ± 2 × 10^{-7} $m^2 yr^{-1}$ would give the impression that Deff could be zero, which we are reluctant to do.

4. Section 5.3 Implications

I'm not convinced this material needs to be presented separately from that presented in Section 5.1 ("Factors potentially influencing diQusion rate"), as the discussion as to whether and when the slower Barnes [2003]-type diQusion or the more rapid Gibbs-Thompson Ng [2023]-type diQusion might operate seems to fit well within that general topic.

We respectfully disagree with the Reviewer's opinion here. We have modified the sub-heading of Section 5.3 to make the distinction between Section 5.1 and Section 5.3 clearer.

I'm also not sure whether the study directly addresses whether Gibbs-Thompson diQusion might explain initial (high) sulfate diQusion rates, but not later (lower) rates of diQusion. This relates back to my earlier question regarding whether the eQective sulfate diQusion rate D'((is held constant for a given sulfate peak during the model runs. If D'((is held constant throughout each model run, the model does not directly answer the question: no "old" ice would have been modeled with high initial (Gibbs-Thompson) diffusion, followed by lower (Barnes-type) diffusion.

The Reviewer is correct in stating that the diffusion rate does not change as a function of time for each individual peak. Each peak is modelled with a constant effective diffusion rate (Deff). However, Deff does not represent the instantaneous diffusion rate in ice of that peak's age but a time-weighted rate of diffusion over the entire history of the peak. By analysing each individual volcanic peak and assigning the 'best-fit' Deff for each one, we are able to ascertain that effective diffusion rate (and therefore diffusion rate) decreases with time. We are not able to quantify the change in instantaneous diffusion rate with time with our approach.

In a future treatment we could attempt to derive the time varying diffusion coefficient under certain assumptions by starting diffusion from various depths or by adopting a finite difference calculation method, but that is beyond the scope of this paper. But the reviewer is correct, at present we have not modelled any ice as having a high initial rate followed by a lower rate at some depth, although this is what we suspect is happening.