

# Doomed descent? How fast sulphate signals diffuse in the EPICA Dome C ice column

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**Abstract.** The loss of climate information due to smoothing of ionic impurity signals in ice provides a strong motivation for understanding their diffusion rates at ice-core sites. By analysing sulphate signals in the EPICA Dome C (EDC) core, recent studies estimated the vertical profile of effective diffusivity  $D_{\text{eff}}$  at that site. However,  $D_{\text{eff}}$  crudely approximates the local diffusivity  $D$  in the ice, it being a nonuniform-weighted average of  $D$  over large intervals. We formulate the mathematical inversion for retrieving the  $D$  profile from observed signals, which reconciles the findings of the earlier studies as well as elucidating the averaging approximation. Inversion for EDC sulphate reveals a rapid decrease in  $D$  through the firn layer – from  $\approx 10^{-6} \text{ m}^2 \text{ yr}^{-1}$  at the surface to  $\approx 1.7 \times 10^{-8} \text{ m}^2 \text{ yr}^{-1}$  at the firn-ice transition ( $\approx 100 \text{ m}$  depth,  $\approx 2.5 \text{ ka}$ ), followed by a gradual decline to  $\approx 10^{-10} \text{ m}^2 \text{ yr}^{-1}$  through 100–2700 m (2.5–390 ka). This profile enables new interpretation of sulphate transport in the EDC column. We propose vapour diffusion of  $\text{H}_2\text{SO}_4$  through interconnecting air pores as the cause of the high firn diffusivity. By evaluating the mechanisms controlling  $D$  below the firn (diffusion through ice crystals, liquid veins and grain boundaries and diffusion arising from interfacial motion), we infer a dominant partitioning of signals immediately below the firn to a connected vein system, and progressive smoothing of vein signals by Gibbs–Thomson diffusion down to  $\approx 2000 \text{ m}$  depth, which leaves more and more of the remaining signals to grain boundaries. We conclude that those sulphate signals that survive the initial fast diffusion in the firn to “punch through” to its base might survive into deep ice, and that EDC sulphate preserves a strongly filtered history of volcanic and climatic forcing that underrepresents changes and events shorter than a few years. For the Beyond EPICA – Oldest Ice and Million Year Ice Core drilling sites on Little Dome C, calculations assuming a diffusivity profile like our EDC profile and not exceeding  $10^{-10} \text{ m}^2 \text{ yr}^{-1}$  in ice older than 450 ka constrain the sulphate diffusion length in ice 1–2 Ma old to 2 cm at most, and probably as low as  $\approx 1 \text{ cm}$ , for atmospheric-sourced signals that experienced only diffusion and mechanical shortening in the column.

## 1 Introduction

30 Ionic impurities in ice cores provide valuable records of climate and environmental change (e.g. Legrand and Mayewski, 1997). The realisation that impurity signals in ice may be altered – not necessarily carrying climatic information “written in stone” – motivates study of the post-depositional processes threatening their integrity. Diffusion attenuates and broadens signals as they descend the ice column, potentially causing severe signal loss at depth, where the diffusion rate may be enhanced by higher temperature. The vertical pattern of the diffusion rate is of interest to questions about the reliability of ice-  
35 core ion records, the amount of climatic information retrievable from their signals, and the methods of reconstructing past forcings at the ice-sheet surface – questions that matter the more as ice-coring campaigns seek older and older records, such as in the Beyond EPICA – Oldest Ice project (BE-OI, 2017) and Million Year Ice Core project (MYIC, 2020).

Recently, Fudge et al. (2024) and Rhodes et al. (2024) quantified diffusion on the high-resolution sulphate record of the EPICA (European Project for Ice Drilling in Antarctica) Dome C or “EDC” ice core (EPICA community members, 2004) from  
40 Antarctica. This record of sulphate concentration, measured by fast-ion chromatography (FIC) on bulk ice samples at  $\approx 4$  cm spacing down to 770 m depth and 1–2 cm spacing at greater depths (Traversi et al., 2002, 2009), is shown in Fig. 1a. By analysing how its signals vary along the core, together with a signal-evolution model that accounts for diffusion and vertical mechanical shortening of the ice, Fudge et al. (2024) and Rhodes et al. (2024) estimated the “effective diffusivity”  $D_{\text{eff}}$  of sulphate at EDC.

45 Sulphate is relevant in the diffusion context because volcanic events, which occur as sharp peaks on such records, provide data for synchronising ice-core timescales (e.g., Severi et al., 2012; Svensson et al., 2020) and inferring the history of volcanism – the record in Fig. 1a has been used to study eruption frequency back as far as 200 ka (Castellano et al., 2004; Lin et al., 2022; Wolff et al., 2023). Sulphate may also experience rapid transport in the liquid veins of polycrystalline ice, given the low eutectic temperature of sulphuric acid ( $-73^{\circ}\text{C}$ ) implies its likely dissolution in vein water located at grain triple junctions  
50 (Mulvaney et al., 1988; Wolff et al., 1988; Nye, 1989; Mader, 1992), and given theoretical modelling which shows that ionic signals residing in a network of connected veins diffuse rapidly due to the Gibbs–Thomson effect (Ng, 2021). However, when studying impurity transport in ice, it is difficult to know how the bulk concentration of an ion partitions into contributions from different impurity sites – the ice-crystal lattice, grain boundaries, veins, and micro-inclusions; the mechanisms of impurity transfer between these sites also remain elusive (Barnes et al., 2003; Ng, 2021; Stoll et al., 2021). Thus, our understanding of  
55 how signals on the bulk concentration evolve is incomplete. Because the model used by Fudge et al. (2024) and Rhodes et al. (2024) in their diffusivity inversions tracks sulphate bulk concentration without resolving the partitioning, their effective diffusivities ( $D_{\text{eff}}$ ) estimates for the EDC site reflect the overall outcome of different grain-scale transport processes. Yet, for this reason, their estimates provide global constraints on how these processes operate.

In this paper, we formulate a theory of diffusivity inversion that extends the methods of Fudge et al. (2024) and Rhodes  
60 et al. (2024), and which may be applied to other ions and to other ice cores besides EDC. Their studies referred to the “effective diffusivity” in part because of the caveat about impurity partitioning, but more specifically because their inversions assumed

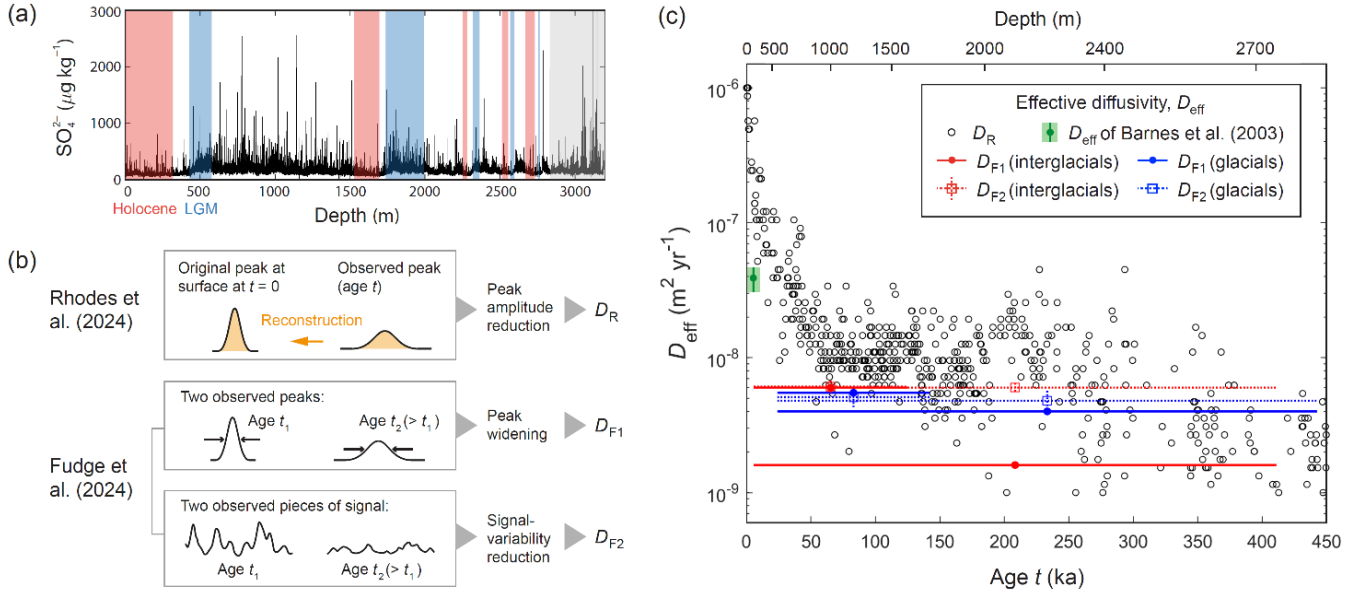


Figure 1. Approaches and results of the inversions for effective diffusivity  $D_{\text{eff}}$  by Fudge et al. (2024) and Rhodes et al. (2024), for sulphate at the EPICA Dome C ice-core site. (a) Depth profile of sulphate concentration from fast ion chromatography (Traversi et al., 2009), showing abundant peaks, many of them recording volcanic eruptions. Interglacial and glacial maximum periods are highlighted by red and blue shading, respectively; for their age and depth ranges, see Table A1 of Fudge et al. (2024). Grey shading marks the record > 2800 m, which is not studied herein. (b) Schematic of the approaches of Rhodes et al. (2024) and Fudge et al. (2024) for finding their  $D_{\text{eff}}$  estimates –  $D_R$ ,  $D_{F1}$ , and  $D_{F2}$ , which are based on peak-amplitude decay, peak widening and signal-variability reduction, respectively. (c) Plot of their  $D_R$ ,  $D_{F1}$ , and  $D_{F2}$  results versus age back to 450 ka. The depth scale is indicated on the top axis. Horizontal bar shows the age range of each  $D_{\text{eff}}$  estimate, and vertical bar its uncertainty. Green point plots the  $D_{\text{eff}}$  estimate of Barnes et al. (2003) for the Holocene part of the record.

constant diffusivity acting on each signal as it evolves. Accordingly, they recognised  $D_{\text{eff}}$  as some weighted average of the true diffusivity. The averaging process has not been made clear though. We show mathematically that their  $D_{\text{eff}}$  estimates, owing to the averaging approximation, deviate significantly from the true diffusivity  $D$  (unless noted otherwise, all diffusivities in this paper pertain to sulphate). We improve upon their results to obtain the vertical profile of  $D$  in the EDC ice column, deriving new information about ionic impurity transport there. Notably, we discover high  $D$  values localised to the firm layer, whose cause is discussed towards the end. We also briefly consider what the findings mean for signal survivability at the sites of the BE-OI and MYIC projects. For convenience, we abbreviate Fudge et al. (2024) and Rhodes et al. (2024) as “F2024” and “R2024”, respectively, given how often they are referenced below.

Figure 1 illustrates their diffusivity inversions. R2024’s approach utilised the decay of signal peak amplitude, whereas F2024 employed two approaches, one based on signal peak widening and the other on the decay of signal variability down

core (Fig. 1b). In R2024, 537 sulphate peaks were identified in the record down to  $\approx 2800$  m depth (0–450 ka). For each peak, the height of the corresponding original peak at deposition on the ice-sheet surface is reconstructed, by assuming that it held the same amount of sulphate as the observed peak (after removing local background concentration due to non-volcanic sources of sulphate such as marine biogenic emissions) and that it was Gaussian-shaped, with a duration of 3 years at “full width at tenth maximum” (FWTM), as is typically found for the width of volcanic sulphate peaks in Antarctica snow; see R2024 for detailed justification. Then, using their model, which we give in Eq. (1) below, R2024 numerically simulated the evolution of the reconstructed peak forward in time, tuning the diffusivity in multiple model runs to match the observed peak’s height at its recorded age, to find  $D_{\text{eff}}$  for the peak. We denote by  $D_R$  their amplitude-based  $D_{\text{eff}}$  estimate.

In contrast, F2024 studied only signals in interglacial and glacial maximum periods (red and blue shading in Fig. 1a) and made separate inversions for these period types, to cater for the possibility of interglacial ice and glacial ice having different diffusivities. This is motivated by the idea that the different ice-column conditions (e.g. strain rate, mean crystal size) in these periods might affect impurity transport differently. Their width-based inversion, which gauges each peak’s width by its “full width at half maximum” (FWHM), performs best-fit numerical simulations as R2024 did, but uses two peaks below the surface (Fig. 1b) rather than one peak and its reconstructed surface counterpart. Specifically, for interglacials and glacial maxima separately, they ran simulations to evolve a Gaussian signal with an initial width equal to the median width of observed peaks in the most recent period (either the Holocene or LGM) to match the median width of observed peaks in the earlier interglacials or glacial maxima, thus backing out  $D_{\text{eff}}$  for the intervening intervals. We denote by  $D_{F1}$  their width-based  $D_{\text{eff}}$  estimate.

The other approach of F2024 uses a method pioneered by Barnes et al. (2003) for quantifying signal variations in terms of “mean absolute gradient” (explained in Sect. 2.3) to estimate  $D_{\text{eff}}$  from the decrease of signal variability down core. Using the method, Barnes et al. (2003) had estimated  $D_{\text{eff}} = 3.9 \pm 0.8 \times 10^{-8} \text{ m}^2 \text{ yr}^{-1}$  for the Holocene part (top 350 m) of the sulphate record in Fig. 1a. F2024 essentially applied the method to older parts of the core, focussing on the sequence of interglacials and glacial maxima. We denote by  $D_{F2}$  their gradient-based  $D_{\text{eff}}$  estimate (Fig. 1b).

The effective diffusivities of R2024 and F2024 (Fig. 1c) show striking differences. Although  $D_R$ ,  $D_{F1}$  and  $D_{F2}$  in the deeper record  $\approx 200$  to 450 ka ( $\approx 2100$ –2800 m) have similar magnitudes,  $\sim 10^{-9}$ – $10^{-8} \text{ m}^2 \text{ yr}^{-1}$ ,  $D_R$  is much higher (up to  $10^{-6} \text{ m}^2 \text{ yr}^{-1}$ ) than  $D_{F1}$  and  $D_{F2}$  in ice  $\lesssim 50$  ka, where it decays with age and depth. As R2024 reported, their median  $D_R$  value for Holocene ice (0–10 ka),  $2.4 \times 10^{-7} \text{ m}^2 \text{ yr}^{-1}$ , is nearly ten times the  $D_{\text{eff}}$  estimate of Barnes et al. (2003) (green data point in Fig. 1c). Beyond its initial decay,  $D_R$  averages at  $\approx 10^{-8} \text{ m}^2 \text{ yr}^{-1}$  in 50–200 ka, still about twice that of  $D_{F1}$  and  $D_{F2}$ . On seeing that  $D_{F1}$  and  $D_{F2}$  ( $\approx 5 \times 10^{-9} \text{ m}^2 \text{ yr}^{-1}$ ) are not much higher than the self-diffusivity of ice ( $\approx 3 \times 10^{-10}$  to  $3 \times 10^{-9} \text{ m}^2 \text{ yr}^{-1}$  at  $-50$  to  $-35^\circ\text{C}$ ; Ramseier, 1967), F2024 inferred that the fast signal diffusion in liquid veins modelled by Ng (2021) occurs only to a limited extent for sulphate in the upper  $\approx 90\%$  of the ice column, and hence most sulphate there resides within ice crystals and at grain boundaries – not in the veins. On the other hand, R2024 interpreted the initial high (falling)  $D_R$  values for significant (diminishing) diffusion of sulphate in interconnected veins in the top quarter of the ice column.

115 Resolving these differences is imperative because the diffusivity profile is key to understanding how the crystal-scale diffusion mechanisms vary with depth and the factors involved, such as impurity partitioning. Besides adopting different inversion approaches, R2024 and F2024 processed the FIC data differently. R2024 only analysed sulphate peaks that are certainly volcanic by omitting others coincident with dust peaks, whereas F2024 applied the scaling procedure of Barnes et al. (2003) to the sulphate record to reduce the influence of background climate variations before extracting signals for analysis.

120 These methodological differences can only explain minor discrepancies, not the overall incompatibility, between  $D_R$  and  $D_{F1,2}$ . The results in Fig. 1c also raise intriguing questions, notably the cause of the near-surface decay in  $D_R$  in  $\approx 0$ –50 ka, which seems to continue through  $\approx 100$ –450 ka at lower rate, and why (as both their studies pointed out)  $D_{\text{eff}}$  does not increase with depth, against the expectation that molecular diffusivity increases with temperature. The ice temperature at the EDC site increases monotonically from  $\approx -53^\circ\text{C}$  at the surface to  $\approx -12^\circ\text{C}$  at 2800 m (Fig. S1 in the Supplement).

125 Herein, our theory not only allows estimating the true diffusivity  $D$ , which is a more fundamental quantity than  $D_{\text{eff}}$  for probing impurity transport mechanisms; it also shows how the  $D_R$ ,  $D_{F1}$  and  $D_{F2}$  estimates may be reconciled on account of their underlying averaging and two needed corrections in the  $D_{F2}$  inversion. A key insight is that the signal-evolution model of F2024 and R2024 can be solved analytically, so the inversions can be done without numerical simulation. While our inversion results draw interest to the firm diffusivity, their signal-evolution model ignores firm densification; we therefore also examine

130 its validity when used for inversions within the firm.

We focus on the EDC record in 0–2800 m (Fig. 1) by using the data collected by R2024 and F2024 without reprocessing the FIC sulphate concentrations. The record at depths  $> 2800$  m (which features in part of F2024’s study) is excluded for the reason given by R2024: there, some sulphate peaks may be non-volcanic and shaped by post-depositional processes other than diffusion and vertical mechanical shortening. This is shown by the presence of (i) anomalous peaks below 2800 m depth that

135 have been chemically modified, as evidenced by ion association (Traversi et al., 2009), and (ii) other anomalous peaks starting from  $\approx 2700$  m (perhaps as shallow as 2500 m) that exhibit side troughs, indicating sulphate being “sucked” from neighbouring background levels towards zones with high cation concentration to form the peaks (Wolff et al., 2023). These artefacts reflect added complexity in the evolution of signals in deep ice at EDC that makes their origin uncertain. Our theory and analyses strictly concern signals without such artefacts, which give the ideal input data for inversion. While R2024’s data mitigate the

140 issue by excluding potential artefact peaks during data collection, the deepest data of F2024 used by us may contain artefact signals, especially anomalous peaks of type (ii); but, for reasons explained later, this should not affect our conclusions.

## 2 Mathematical theory

### 2.1 Signal evolution

We begin with the advection–diffusion equation for signal evolution down the ice column, used by F2024 and R2024. In a

145 coordinate frame moving with the ice, where  $z$  denotes distance below a material horizon descending towards the bed, signals in the bulk impurity concentration  $C(z, t)$  (measured in  $\mu\text{g kg}^{-1}$ , or  $\mu\text{g L}^{-1}$  of meltwater) evolve according to

$$\frac{\partial C}{\partial t} = D(t) \frac{\partial^2 C}{\partial z^2} - \dot{\epsilon}_z(t) z \frac{\partial C}{\partial z}. \quad (1)$$

Here,  $t$  is the age of the horizon,  $D$  is the impurity diffusivity, and  $\dot{\epsilon}_z (< 0)$  is local vertical strain rate. Eq. (1) encapsulates the effects of mechanical shortening and diffusional spreading. Table A1 lists other mathematical symbols used in the paper.

150 Following F2024 and R2024, we use Eq. (1) to model sulphate signals, assuming an invariant strain-rate profile and constant surface accumulation rate at the core site – thus, a steady-state column with constant thickness and vertical velocity profile. In this system, signals travel through fields that are functions of depth in the column only, not time, so the age–depth scale allows translation between  $D(t)$  and its vertical profile. Material at age  $t$  has shortened from its original thickness at the surface by the thinning factor  $S$ , given by

$$155 \quad S(t) = \exp \int_0^t \dot{\epsilon}_z(\eta) \, d\eta, \quad (2)$$

where  $\eta$  denotes the variable of integration. Differentiating Eq. (2) gives  $dS/dt = \dot{\epsilon}_z S$ . The thinning function  $S$  decays with age  $t$  from its value at the surface,  $S_0 = S(t = 0) = 1$ .

The inversion methods of R2024 and F2024 (elaborated in Sects. 2.2 and 2.3) use Eq. (1) as the basis, but as noted earlier, assume a constant  $D$  for each signal as it evolves down column. The resulting effective diffusivities  $D_R$ ,  $D_{F1}$  and  $D_{F2}$  do not  
160 strictly represent the true (local) diffusivity  $D$ , instead averages measuring its cumulative effect over finite age and depth intervals; as we shall see, these intervals are large. By solving Eq. (1) analytically below, we develop exact inversions for  $D(t)$  that circumvent this assumption, at the same time deriving equations linking  $D(t)$  to  $D_R$ ,  $D_{F1}$  and  $D_{F2}$ . How Eq. (1) is affected by firn densification will be examined in Sect. 3.5, after we glimpse high firn diffusivity from our inversions.

## 2.2 Theory: peak-based inversions

### 165 2.2.1 The inversion possibility

A key property we exploit is that a Gaussian signal stays Gaussian under the combined mechanical shortening and diffusional spreading described by Eq. (1). F2024 and R2024 both initialised their simulations with Gaussian peaks, but did not harness this property. As alluded to by R2024, the sulphate flux from eruptions reaching the ice sheet often varies asymmetrically in time, but the deposited peaks rapidly relax to near-Gaussian. This motivates a Gaussian approximation to their shape.

170 To see the property, define the transformed depth

$$\zeta = \frac{z}{S(t)} \quad (3)$$

and define the variable

$$\tau(t) = \int_0^t \frac{D(\eta)}{S^2(\eta)} \, d\eta + \tau_0, \quad (4)$$

where  $\tau_0$  is the value of  $\tau$  at zero age. Here,  $\zeta$  is the destrained or unthinned thickness, and  $\tau$ , an indirect proxy of age or time, accounts for the histories of diffusion and layer thinning. On letting  $C(z, t) = f(\zeta, \tau)$ , these changes of variable convert Eq. (1) to the classical heat equation

$$\frac{\partial f}{\partial \tau} = \frac{\partial^2 f}{\partial \zeta^2}, \quad (5)$$

which has the well-known (Gaussian) similarity solution

$$f(\zeta, \tau) \propto \frac{1}{\sqrt{\tau}} e^{-\zeta^2/4\tau}. \quad (6)$$

In the  $\zeta$ -direction, this Gaussian's width expressed as a standard deviation is  $\sigma = (2\tau)^{1/2}$ . Eqs. (5) and (6) mean that in  $\tau$ - $\zeta$  space, signals experience uniform diffusion at unit rate, and a Gaussian peak decays in amplitude following the factor  $1/\sqrt{\tau}$  and widens following  $\sqrt{\tau}$ . Consequently, observations of peak widening or amplitude reduction down core, which provide data on  $\tau(t)$ , can be used to recover  $D(t)$  via Eq. (4). This idea forms the basis of the peak-based inversions.

For example, consider an amplitude-based inversion, where the “relative peak amplitude” (the ratio of a peak's observed amplitude to its original amplitude on deposition at the surface at  $t = 0$ ) has been compiled for different peaks along the core, as done by R2024. Suppose the relative amplitudes vary with age to trace out the function  $\alpha(t)$ . Then we have  $\alpha(t) = \sqrt{\tau_0/\tau}$  according to Eq. (6), and differentiating Eq. (4) with respect to  $t$  gives the inversion

$$D(t) = S^2(t) \frac{d\tau}{dt} = S^2 \frac{d}{dt} \left( \frac{\tau_0}{\alpha^2} \right) = -\frac{2\tau_0 S^2 \alpha'}{\alpha^3} \quad (7)$$

(the ' denotes derivative). This inversion requires the value  $\tau_0 = \tau(t = 0)$ . For each observed peak, R2024 reconstructed the amplitude of the original peak by assuming it to be Gaussian, with a 3-year duration at FWTM and carrying the same total impurity load as the observed peak. They ignored firm densification effects and used the ice density in the reconstruction. We therefore set  $\tau_0 = \sigma^2/2$ , with  $\sigma = 3 \text{ yr} \times a/4.2919$ , where  $\sigma$  (m) is the standard deviation mentioned above,  $a$  is the ice-equivalent accumulation rate (m/yr), and the factor 4.2919 converts the FWTM of the Gaussian to  $\sigma$ . Positive  $\tau_0$  ensures a finite amplitude for the initial peak in Eq. (6). The differentiation in Eq. (7) assumes  $\alpha$  to be smoothly varying; in practice, one fits a curve to the  $\alpha$ -data prior to inversion.

Similarly, in a width-based inversion, where data on “relative peak width” (the ratio of observed width to original width) trace out the function  $\beta(t)$ , such that  $\beta(t) = \sqrt{\tau(t)S^2(t)/\tau_0 S_0^2} = S(t)\sqrt{\tau(t)/\tau_0}$ , we derive

$$D(t) = S^2(t) \frac{d\tau}{dt} = S^2 \frac{d}{dt} \left( \frac{\tau_0 \beta^2}{S^2} \right) = 2\tau_0 \beta (\beta' - \beta \dot{\varepsilon}_z). \quad (8)$$

Applying this inversion necessitates an assumption for the original peak width (for compiling  $\beta$  and  $\tau_0$ ). However, for  
 200 comparing against the width-based inversion of F2024, Eq. (8) first needs to be adapted for use on two peaks below the surface,  
 rather than one at the surface and one below (Fig. 1b). We attain the relevant result via a different route below.

### 2.2.2 Full-fledged theory

Before applying the above theory to data, we expand the mathematical analysis to unravel how peak-based inversions work  
 and establish the relationship between  $D(t)$  and the effective diffusivities of F2024 and R2024.

205 The ratio  $D/S^2$  recurring in Eqs. (4), (7) and (8) relates a physical effect. As a signal shortens mechanically, its variations  
 steepen, so it diffuses faster than if shortening were absent. With  $S < 1$  below the surface,  $D/S^2$  represents the amplified  
 diffusivity. Another way of picturing this effect is to imagine the signal experiencing the diffusivity  $D$ , but over a longer time  
 – longer by  $1/S^2$  times. This motivates us to introduce another age variable,  $\psi$ , defined by  $d\psi = dt/S^2(t)$ . Specifically, we set  $\psi$   
 $= 0$  at  $t = 0$ , so that

$$210 \quad \psi(t) = \int_0^t S^{-2}(\eta) d\eta. \quad (9)$$

This function has unit slope at  $t = 0$  (since  $S(t = 0) = 1$ ) and curves upward (e.g. Fig. 3c). We call  $\psi$  the *dilated age* because it  
 accounts for thinning but excludes diffusion, unlike the proxy variable  $\tau$ , which accounts for both.

On moving from  $t$ - $z$  to  $\psi$ - $\zeta$  space (Fig. 2), the transformation  $z$  to  $\zeta$  geometrically destrains the signal to track material  
 horizons, whereas the transformation  $t$  to  $\psi$  stretches time to capture the mechanically-induced enhanced diffusion on the  
 215 signal. With coordinate stretching absorbing both effects, the transformed signal obeys  $\partial C / \partial \psi = D(\psi) \partial^2 C / \partial \zeta^2$  without a  
 shortening term (Fig. 2b). Crucially, under the move, Eq. (4) is converted to

$$\tau(\psi) = \int_0^\psi D(\psi) d\psi + \tau_0, \quad (10)$$

which shows that inversion for  $D$  fundamentally involves

$$D(\psi) = \frac{d\tau}{d\psi}. \quad (11)$$

220 In other words, as a Gaussian peak evolves in  $\psi$ - $\zeta$  space, its unthinned width squared and its inverse squared amplitude (recall

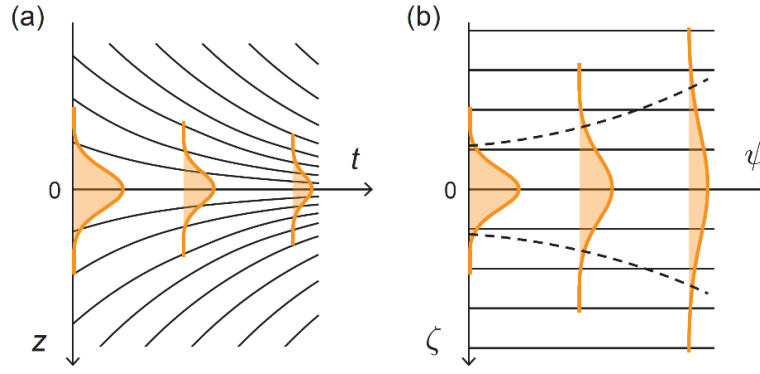


Figure 2. Evolution of a Gaussian signal in (a)  $t$ - $z$  space and (b)  $\psi$ - $\zeta$  space. Solid black curves signify material trajectories. Dashed curve in (b) marks the unthinned signal width, whose square increases at a rate with respect to  $\psi$  that reflects the instantaneous diffusivity.

that unthinned width  $\propto \sqrt{\tau}$  and amplitude  $\propto 1/\sqrt{\tau}$  ) increase at a rate with respect to  $\psi$  that equals the instantaneous or local  
 225 diffusivity. Equivalently, the local diffusivity is given by the rate of change of these peak-form parameters with respect to  
 dilated age  $\psi$  (Fig. 2b). Not surprisingly, the age-domain inversions in Eqs. (7) and (8) also involve rates of change.

Given these insights, we can calculate the effective diffusivities  $D_R$  and  $D_{F1}$  of R2024 and F2024 analytically, which  
 obviates need to integrate Eq. (1) numerically and perform multiple simulations to fit data. As noted before, their inversions  
 assumed constant  $D$  during each signal's descent. If Eq. (10) is used to reproduce their inversions, then we set  $D \equiv D_{\text{eff}}$   
 230 (constant) in its integral, which gives

$$\tau(\psi) = D_{\text{eff}} \psi + \tau_0, \quad (12)$$

or

$$D_{\text{eff}} = \frac{\tau - \tau_0}{\psi} = \frac{\tau_0}{\psi} \left( \frac{\tau}{\tau_0} - 1 \right), \quad (13)$$

which describes the inversion based on a subsurface peak and its reconstructed original (surface) peak. Where the inversion  
 235 uses a pair of subsurface points, say,  $\tau_1$  at dilated age  $\psi_1$  and  $\tau_2$  at dilated age  $\psi_2$ , differencing the application of Eq. (12) to  
 these data yields

$$D_{\text{eff}} = \frac{\tau_2 - \tau_1}{\psi_2 - \psi_1}. \quad (14)$$

From these results, it follows that the R2024 inversion is equivalent to

$$D_R(t) = \frac{\tau_0}{\psi(t)} \left( \frac{1}{\alpha^2(t)} - 1 \right), \quad (15)$$

240 with  $\psi$  given by Eq. (9) and the data for  $\alpha$  and  $\tau_0$  gathered as before (Sect. 2.2.1), whereas the width-based inversion of F2024 for two peaks of age  $t_1$  and  $t_2$  has the analytical counterpart

$$D_{F1} = \frac{\tau(t_2) - \tau(t_1)}{\psi(t_2) - \psi(t_1)}, \quad (16)$$

in which the  $\tau$  values derive from observed peak widths. F2024 measured the unthinned FWHM of each peak, so  $\tau = \sigma^{*2}/2$ , where  $\sigma^* = \text{FWHM}/2.3548$  is the destrained standard deviation of the Gaussian.

245 The effective diffusivity from Eq. (15) or (16) is valid for the specific interval bracketed by the paired data, as in R2024 and F2024’s simulation-based inversions. The interval in R2024’s inversion spans each peak’s entire history. In F2024’s inversion, which uses paired data between the Holocene and earlier interglacials or between the LGM and earlier glacial maxima, the intervals exceed  $\sim 100$  kyr. Thus,  $D_R$  of R2024 and  $D_{F1}$  of F2024 are effective diffusivity estimates for different periods – this is a key reason behind their discrepancy, which we will point out again when analysing results in Sect. 3.

250 Next we relate the effective diffusivities to the true diffusivity  $D(t)$ . Applying Eq. (10) to paired data  $(\psi_1, \tau_1)$  and  $(\psi_2, \tau_2)$ , eliminating  $\tau_0$ , and using Eq. (14), yields

$$D_{\text{eff}} = \frac{1}{\psi_2 - \psi_1} \int_{\psi_1}^{\psi_2} D(\psi) d\psi, \quad (17)$$

or

$$D_{\text{eff}}(\psi) = \frac{1}{\psi} \int_0^{\psi} D(\psi) d\psi \quad (18)$$

255 if the upper data point lies at the surface. These results show that  $D_{\text{eff}}$  is the interval average of  $D$ , not over  $t$  but over the dilated age  $\psi$ . Since  $\psi(t)$  curves upward (Fig. 3c),  $D_{\text{eff}}$  is biased towards  $D$  in the older part of the averaging interval; but it is influenced by  $D$  in the younger part. The larger is the interval, the more crudely  $D_{\text{eff}}$  approximates  $D$  at the lower (deeper) data point.

Equation (18) leads to further insights on the profile  $D_R(t)$  retrieved by the R2024 inversion. By evaluating its integral, working with time rather than  $\psi$  as the integration variable, we derive

$$260 \quad D_R(t) = \frac{1}{\psi(t)} \int_0^t D(\eta) \psi'(\eta) d\eta = D(t) - \frac{1}{\psi(t)} \int_0^t D'(\eta) \psi(\eta) d\eta. \quad (19)$$

According to this expression,  $D_R$  found from an observed peak not only reflects the local diffusivity  $D$  at its depth, but also inherits a signal from the variations in  $D$  throughout its earlier shallower history: we call this the “memory effect”. Notably,  $D_R(t)$  overestimates (underestimates)  $D(t)$  if  $D(t)$  is a decreasing (increasing) function.

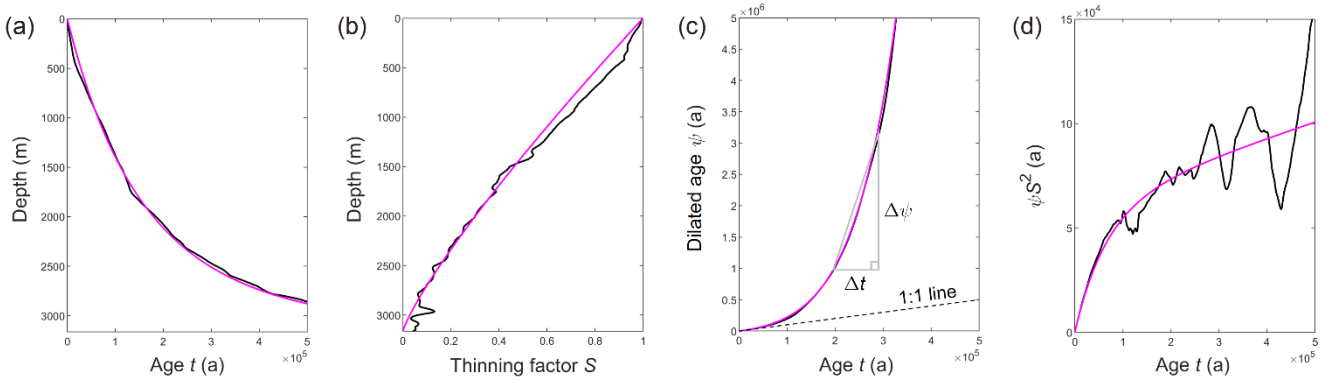


Figure 3. Functions used in our diffusivity inversions for the EPICA Dome C ice-core site: (a) the AICC2012 age–depth scale (Bazin et al., 2013; Veres et al., 2013) and the corresponding (b) depth profile of thinning factor  $S$ , (c) dilated age  $\psi$  versus age  $t$ , and (d)  $\psi S^2$  versus age.

Black curves derive directly from the AICC2012 scale. Magenta curves, used in our inversions, are smooth approximations based on an ice-flow model assuming the submergence velocity  $w_i = a_s(h/H)^{1.2}$ , where  $h$  is height above the bed,  $H = 3165$  m (mean ice thickness chosen by Rhodes et al., 2024), and surface accumulation rate  $a_s = 0.0195$  m yr $^{-1}$ . Grey triangle in (c) illustrates the misamplification factor (Sect. 2.3).

Differentiating the first equation in Eq. (19) gives the opposite conversion from  $D_R$  to  $D$ ,

$$D(t) = \frac{1}{\psi'} \frac{d}{dt} [\psi D_R(t)] = D_R + D_R' \psi S^2, \quad (20)$$

which shows that  $D$  is less (greater) than  $D_R$  wherever  $D_R$  decreases (increases) down core. R2024 recognised  $D_R$  as a “time-weighted diffusivity” and took care when interpreting their  $D_R(t)$  profile; but without the analytical result in Eq. (20), inferring  $D$  from  $D_R$  is challenging. The present analysis also reveals the weighting to be highly nonlinear. In Sect. 3, we use Eq. (20) to estimate  $D(t)$  from  $D_R(t)$  and Eq. (19) to predict  $D_R(t)$  from  $D(t)$ , discovering a marked difference between these curves.

### 2.3 Theory: gradient-based inversion

We turn to F2024’s inversion for the effective diffusivity  $D_{F2}$ , which calculates the “mean absolute gradient”  $\bar{m}$  of signals with the Barnes et al. (2003) method, which in turn is based on the diffusion-length theory of Johnsen (1977). We extend this framework to derive an exact inversion for  $D$  from  $\bar{m}$ , exposing the averaging approximation behind  $D_{F2}$ . We find that the Barnes et al. method – and thus the  $D_{F2}$  estimates – require two corrections.

In the Barnes et al. (2003) method, the concentration record  $C$  is first destrained and processed to suppress unwanted signals from background climate variations. Signal peaks on the processed record,  $C_p$ , are thought to reflect the sulphate input from volcanic events more reliably (with less bias) than  $C$ . To quantify the signal variability on  $C_p$ , they studied different 10-m long sections down core by calculating their signal mean absolute gradient,

$$\bar{m} = \frac{1}{n\Delta\zeta} \sum_{i=1}^n |C_{p,i+1} - C_{p,i}|, \quad (21)$$

where  $C_{p,i}$  denotes individual processed concentration measurements,  $\Delta\zeta$  is the destrained interval between measurements, and  $n$  is the number of intervals in each 10 m. Eq. (21) is the same as their Eq. (1), despite written with different symbols.

290 Their method quantifies the rate of diffusive smoothing by using the observed decrease in  $\bar{m}$  down core (Fig. 1b) and retrieves  $D_{\text{eff}}$  from the rate. Notably, they regard the principal signals on  $C_p$  as periodic, with a wavenumber  $k^*$  that does not vary with depth on the destrained record (we use  $*$  to signify destraining). Accordingly, the ratio of  $\bar{m}$  of a core section at depth to the mean absolute gradient  $\bar{m}_0$  of a reference section higher in the column measures the amplitude decay of the signals, and they equate this ratio to the signal attenuation predicted for Eq. (1) by Johnsen (1977) – thus,

$$295 \quad \frac{\bar{m}}{\bar{m}_0} = \exp(-k^{*2}\sigma^{*2}/2), \quad (22)$$

in which  $\sigma^*$  is the destrained value of the diffusion length  $\sigma$ ; that is,  $\sigma^* = \sigma/S(t)$ .

In Johnsen's theory, the diffusion length  $\sigma$  evolves according to the ordinary differential equation

$$\frac{d\sigma^2}{dt} = 2D(t) + 2\dot{\varepsilon}_z(t)\sigma^2, \quad (23)$$

and transforming this to the destrained coordinate system yields

$$300 \quad d\sigma^{*2}/dt = 2D(t)/S^2(t). \quad (24)$$

However, Barnes et al. (2003) took  $d\sigma^{*2}/dt = 2D$  without the final  $1/S^2$ , assuming Eq. (23) with  $\dot{\varepsilon}_z$  set to zero to be a valid diffusion-length equation for unthinned records. On taking a constant (effective) diffusivity, they then found  $\sigma^{*2} = 2D_{\text{eff}}t$ , which, together with Eq. (22), led them to the inversion formula

$$D_{\text{eff}} = -\frac{1}{k^{*2}t} \ln\left(\frac{\bar{m}}{\bar{m}_0}\right). \quad (25)$$

305 When rewritten for a pair of subsurface data points, this gives the F2024 inversion formula:

$$D_{\text{F2}} = -\frac{1}{k^{*2}(t_2 - t_1)} \ln\left(\frac{\bar{m}_2}{\bar{m}_1}\right). \quad (26)$$

These formulas are approximate because of the missing  $1/S^2$  in the underlying diffusion-length model: strictly, Eq. (24) should be used instead. In particular, for the EDC core site, the approximation is reasonable for signals in  $t \lesssim 10^4$  yr (because  $S \approx 1$  up to that age; Fig. 3a, b) but not beyond. It follows that the  $D_{\text{eff}}$  estimate of Barnes et al. (2003) for the Holocene ice (Fig. 1c) is approximately valid, but the  $D_{\text{F2}}$  estimates of F2024 for older sections of ice suffer large inaccuracies.

310

Having explained the Barnes et al. method, we modify it to derive an exact inversion for  $D$ . In the  $\psi$ - $\zeta$  coordinate system, Johnsen's diffusion-length equation (Eq. (23) or (24)) takes the form<sup>1</sup>

$$\frac{d\sigma^{*2}}{d\psi} = 2D(\psi), \quad (27)$$

and substituting for  $\sigma^{*2}$  from Eq. (22) gives

$$315 \quad D(\psi) = -\frac{1}{k^{*2}} \frac{d(\ln \bar{m})}{d\psi}. \quad (28)$$

This inversion formula involves a rate of change, as in the peak-based inversions, and shows that  $D$  can be estimated from the slope of the logarithmic plot of  $\bar{m}$  versus dilated age  $\psi$  (we will explore this with EDC data in Sect. 3.3).

One can again relate the effective diffusivity to  $D$ . Suppose  $D$  in Eq. (27) equals a constant,  $D_E$ ; this is the effective diffusivity that is found by the inversion without the approximation of Barnes et al. (2003) described above. Then  $\sigma^{*2} = 2D_E\psi$ .

320 Using this together with Eq. (22) for paired data leads to the inversion formula

$$D_E = -\frac{1}{k^{*2}(\psi_2 - \psi_1)} \ln\left(\frac{\bar{m}_2}{\bar{m}_1}\right) \quad \left( \equiv \frac{1}{\psi_2 - \psi_1} \int_{\psi_1}^{\psi_2} D(\psi) d\psi \right). \quad (29)$$

We see that  $D_E$  is the average of  $D$  over the dilated age  $\psi$ , as for  $D_R$  and  $D_{F1}$ . On comparing  $D_E$  against the effective diffusivities in Eqs. (25) and (26), we find

$$D_{F2} = \frac{\psi_2 - \psi_1}{t_2 - t_1} D_E, \quad (30)$$

325 which means that  $D_{F2}$  of F2024 (also  $D_{\text{eff}}$  of Barnes et al. 2003) is misamplified by  $(\psi_2 - \psi_1)/(t_2 - t_1)$  and strongly overestimates the effective diffusivity in deep intervals (see triangle in Fig. 3c). The issue stems from the missing  $1/S^2$ . The misamplification ratio allows the effective diffusivities of Barnes et al. (2003) and F2024 to be corrected to give the desired value,  $D_E$ .

The other correction in the mean absolute gradient approach concerns the signal wavenumber  $k^*$ . Barnes et al. (2003) and F2024 estimated it via  $k^* = 2\pi/\bar{w}$ , where the mean destrained wavelength  $\bar{w}$  of the signals is found by calculating

$$330 \quad \bar{w} = \frac{4}{\bar{m}L} \sum_{i=1}^n |C_{p,i} - \bar{C}_p| \Delta\zeta \quad (31)$$

---

<sup>1</sup> Eq. (27) can also be derived from the  $\tau$ - $\zeta$  formulation (Sect. 2.2.1). It is well known that given the Gaussian solution of Eq. (5), its general solution can be written as the convolution integral  $f(\zeta, \tau) = \frac{1}{\sigma^* \sqrt{2\pi}} \int_{-\infty}^{\infty} F(\eta) e^{-(\zeta-\eta)^2/2\sigma^{*2}} d\eta$ , where  $F$  is the initial condition (e.g. Johnsen, 1977). Substituting this into Eq. (5) yields  $d\sigma^{*2}/d\tau = 2$ , which, after a change of variable from  $\tau$  to  $\psi$ , gives Eq. (27).

for a long record (F2024 used the Holocene or LGM part of the EDC record for this);  $L$  is the length of the record and  $\bar{C}_p$  its mean impurity concentration. Barnes et al. (2003) idealised the signals as triangular-shaped when deriving Eq. (31), but our repeat derivation in Appendix B shows that its right-hand side should be doubled, or  $\pi/2$  times larger if one assumes sinusoidal signals. Consequently, their method overestimates  $k^*$  by  $\approx 1.6$ –2 times, and the  $D_{F2}$  estimates of F2024 and the  $D_{\text{eff}}$  estimate of Barnes et al. (2003) for Holocene ice ( $3.9 \pm 0.8 \times 10^{-8} \text{ m}^2 \text{ yr}^{-1}$ ) are too small by a factor of  $k^{*2} \approx 2.5$ –4 times. In our  $D_{F2}$  inversions below, we remedy both issues by correcting the results with this factor and the misamplification ratio.

### 3 Diffusivity inversions: results and analysis

We proceed to estimate the true diffusivity profile  $D(t)$  at the EDC site, using the theory of Sect. 2 and data from F2024 and R2024 as input. The work is done in stages. In Sects. 3.1, 3.2, and 3.3, we undertake inversions from peak amplitude, peak width, and signal gradient in turn, exploring avenues including the conversion of  $D_{\text{eff}}$  to  $D$  and direct inversion of data, as well as finding the effective diffusivities  $D_R$ ,  $D_{F1}$  and  $D_{F2}$  with analytical formulas. While these sections allow gleaning information about  $D(t)$ , we further constrain its form by forward modelling in Sect. 3.4. In Sect. 3.5, after inferring high sulphate diffusivity confined to the firn layer, we examine how firn densification impacts the diffusivity inversion.

F2024 and R2024 used the AICC2012 chronology of the EDC site (Fig. 3a; Bazin et al., 2013; Veres et al., 2013) throughout data compilation and analyses. To maximise compatibility of our results with theirs, we employ the same chronology, rather than the newer AICC2023 chronology (Bouchet et al., 2023). In particular, our inversions use what we call “AICC2012-based” functions – smoothed forms of the thinning factor  $S$  and dilated age  $\psi(t)$  (Fig. 3, magenta curves), which we derive from a power-law model of the ice submergence velocity in the EDC column fitted to the AICC2012 age–depth scale; see the caption of Figure 3 for the details. Although the smoothing injects minor differences between our  $D_{\text{eff}}$  estimates and those of R2024 and F2024, it is desirable because the thinning function provided with the AICC2012 dataset is non-monotonic (black curve, Fig. 3b), with small bumps that imply negative strain rate at various depths.

#### 3.1 Inversions from peak-amplitude decay

Figure 4a shows the relative amplitudes  $\alpha$  of the peaks studied by R2024, obtained from their Supplementary data by dividing observed peak heights by original peak heights. The values show considerable scatter but generally decay with age.

To compute the effective diffusivity  $D_R$  for each peak, we apply Eq. (15) to its  $\alpha$ -value, setting  $\tau_0$  as described in Sect. 2.2.1. When calculating the strain rate  $\dot{\epsilon}_z$  for simulating Eq. (1), R2024 adopted an ice submergence velocity profile derived not from the AICC2012 scale, instead from a Nye model with an ice thickness of 3165 m and a surface accumulation rate that puts the peak at its observed depth, so that its age and depth agree with the AICC2012 scale. Thus, their inversion of  $D_R$  envisages a slightly different steady-state ice column for each peak. Their use of the Nye model, which does not resolve the

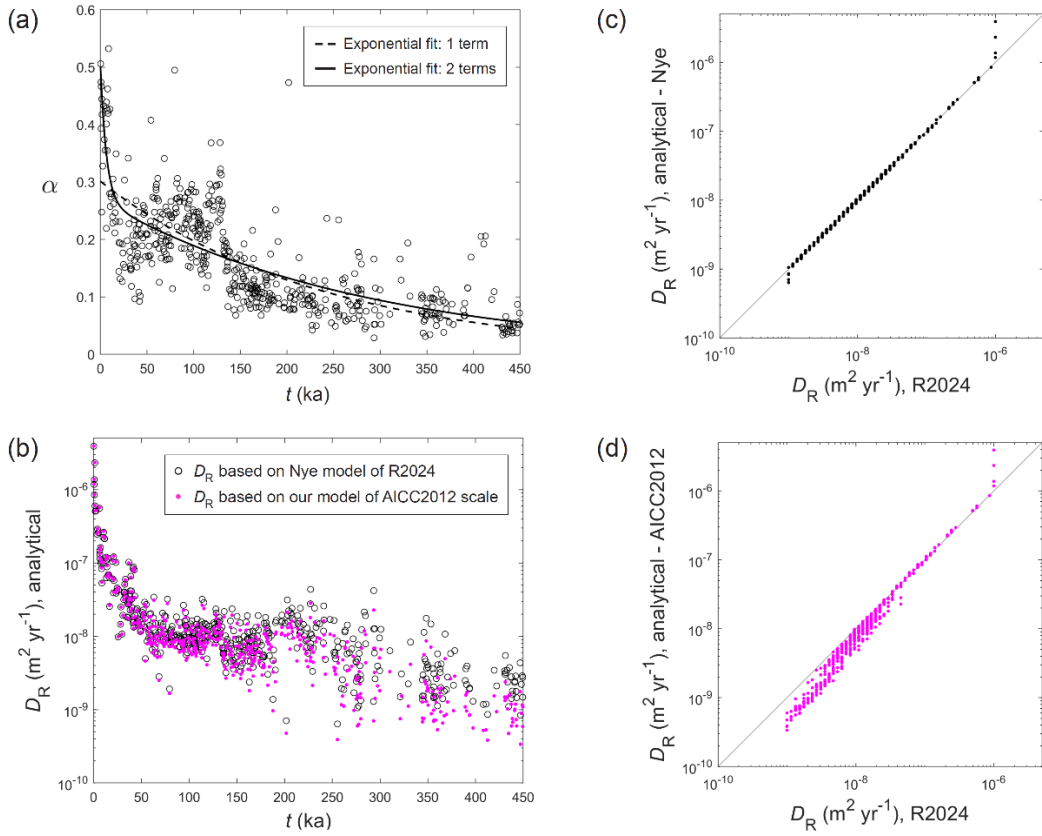


Figure 4. Analytical inversion for the effective diffusivity  $D_R$  from the peak-amplitude data of Rhodes et al. (2024). (a) Amplitude ratio  $\alpha$  versus age  $t$  for 537 peaks. Dashed curve plots best-fit exponential  $\alpha(t) = 0.301\exp(-4.22 \times 10^{-3}t)$ ; solid curve, best-fit exponential sum  $\alpha(t) = 0.232\exp(-0.157t) + 0.268\exp(-3.49 \times 10^{-3}t)$ . (b) Computed  $D_R$  values versus age. Black circles plot results of the inversion assuming the Nye model of Rhodes et al. (2024); magenta points plot results of the inversion assuming our AICC2012-based ice-flow functions in Fig. 3. Following Rhodes et al. (2024), each  $D_R$  value is plotted at the age of the observed peak, rather than as a bar spanning the period over which it applies. (c) Scatterplot of the black-circled  $D_R$  values in (b) against the  $D_R$  estimates of Rhodes et al. (2024), which they found by simulating Eq. (1) to match peak-amplitude decay. (d) Scatterplot of the magenta  $D_R$  values in (b) against the  $D_R$  estimates of Rhodes et al. (2024).

details of firm compaction near the top of the column, seems consistent with their choice of working with ice-equivalent depths when compiling original peak amplitudes (Sect. 2.2.1). We shall say more about the effect of the firm processes in Sect. 3.5.

To show that our analytic approach can reproduce the  $D_R$  estimates of R2024, in our first use of Eq. (15) we adopt their ice-flow approximation by using  $\psi(t)$  based on their peak-specific Nye model instead of our AICC2012-based model. The corresponding  $D_R$  results (Fig. 4b, circles) agree closely with their estimates (Fig. 1c), decaying from  $\sim 10^{-6}$  to  $\sim 10^{-9} \text{ m}^2 \text{yr}^{-1}$ ,

375 rapidly in  $\approx 0\text{--}50$  ka and slowly beyond. We find four values exceeding  $10^{-6} \text{ m}^2 \text{ yr}^{-1}$  near  $t = 0$  and four values below  $10^{-9} \text{ m}^2 \text{ yr}^{-1}$  not reported by R2024 (Figs. 4c and 4b). These and other minor discrepancies between our results arise because Eq. (15) is an exact formula for  $D_R$ , whereas their  $D_R$  estimates are constrained to 50 graded values (visible from the banding in Fig. 4c) on the log scale between  $10^{-9}$  and  $10^{-6} \text{ m}^2 \text{ yr}^{-1}$  (values outside these bounds are clipped to them).

Performing the same inversion with our AICC2012-based function  $\psi(t)$  (Fig. 3c) yields lower  $D_R$  estimates, especially  
 380 for deeper peaks (Fig. 4b & d, magenta points). This is because their Nye model tends to overestimate  $S$  (underestimate the amount of thinning) at depth; less of the thinning-induced enhancement in signal diffusion (Sect. 2.2.2) is captured, making their  $D_R$  estimates larger. The lowering helps explains some of the difference between  $D_R$  and F2024's  $D_{\text{eff}}$  estimates.

Next, we attempt to estimate the true diffusivity profile  $D(t)$  by two approaches. The first applies the time-domain inversion in Eq. (7) (same as Eq. (11) in the  $\psi\text{--}\zeta$  domain) to a smoothed version of  $\alpha$ , which we derive by fitting the  $\alpha$ -data with  
 385 the sum of two exponentials (solid curve, Fig. 4a). This function is preferred to a single exponential (dashed curve, Fig. 4a) because it captures the high  $\alpha$ -values near  $t = 0$  better. In Eq. (7) we use the AICC2012-based thinning function  $S$  (Fig. 3b).

The second approach converts  $D_R$  to  $D$  with Eq. (20), assuming the AICC2012-based function  $\psi^{S^2}$  (Fig. 3d). To derive a smooth input for Eq. (20), in which the derivative  $D_R'$  appears, we spline-fit our AICC2012-based  $D_R$  estimates from Fig. 4b on log-10 scale. These estimates show pronounced fluctuations and scatter on time scales shorter than  $\approx 20$  kyr that indicate  
 390 uncertainty and noise on the relative amplitudes  $\alpha$ , so we choose a level of spline smoothing to suppress these fluctuations; see Spline 2 in Fig. 5b, e, h. However, the exact time scales on which fluctuations in  $D_R$  reflect true changes in diffusivity is unknown, so we experiment also with less and more smoothing by using Spline 1 and Spline 3 (the left-hand and right-hand columns of panels in Fig. 5). Spline 3 strongly suppresses fluctuations in  $D_R$  shorter than about 50 kyr.

The curves of  $D(t)$  computed by this second approach (Fig. 5, solid black curves) indicate high, steeply-decaying  
 395 diffusivity in the first  $\approx 2$  to 8 ka – from  $\sim 10^{-6} \text{ m}^2 \text{ yr}^{-1}$  to well below  $10^{-7} \text{ m}^2 \text{ yr}^{-1}$ , followed by generally low diffusivity beyond ( $\sim 10^{-8} \text{ m}^2 \text{ yr}^{-1}$ ) and even negative diffusivity in some age ranges (see comments below). Although stronger spline smoothing lengthens the initial fast decay, all three curves portray  $D$  as greatly diminished from its surface value by several ka (Fig. 5d–5i). Because the firm-ice transition at EDC lies at  $\approx 100$  m depth (e.g. Landais et al., 2006; Calonne et al., 2022), where  $t \approx 2.5$  ka, much of the initial steep drop in  $D$  apparently occurs in the firm layer; we explore the cause of this later in Sect. 4.1. In  
 400 contrast,  $D(t)$  retrieved by the first approach (Fig. 5, dashed black curve in all panels) shows a much more subdued decay over the first 30 ka, starting from a lower surface diffusivity  $\approx 6 \times 10^{-8} \text{ m}^2 \text{ yr}^{-1}$ . We think that this is because the two-term exponential in Fig. 4a does not adequately capture the high negative slope of the  $\alpha$ -data near  $t = 0$ , which is necessary for Eq. (7) to reconstruct the details of  $D$  there.

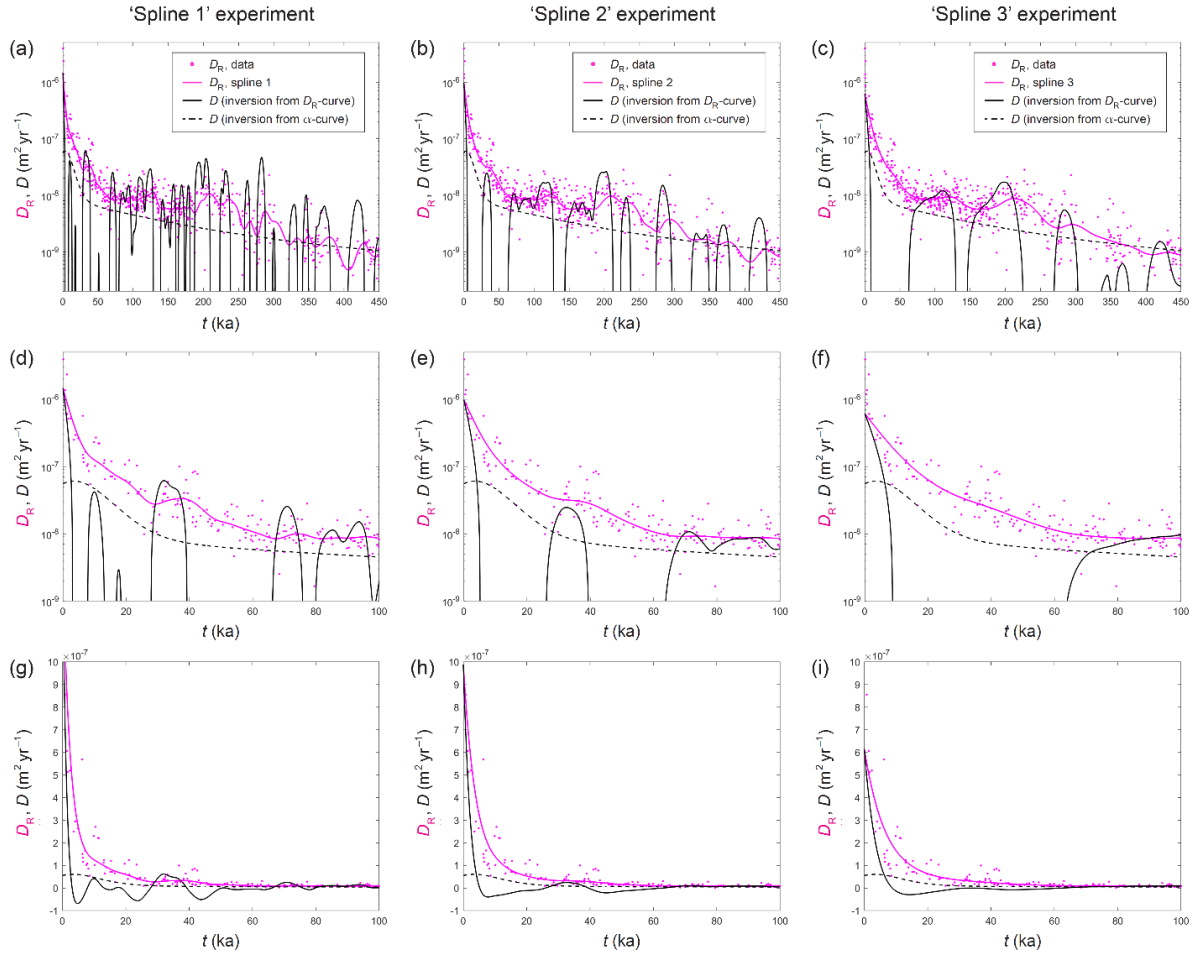


Figure 5. Analytical inversions for  $D(t)$  from  $D_R$ . The left, middle, and right columns of panels document three different experiments where the curves of  $D_R$  serving as input to the inversion (“Splines 1, 2 and 3”; magenta curves) have been derived by spline-fitting the  $D_R$  point data at different smoothness. The level of spline smoothing increases from left to right. In each panel, magenta circles plot the  $D_R$  data from Fig. 4b; black curve shows  $D(t)$  obtained by using Eq. (20) with the chosen spline for  $D_R$ ; dashed black curve shows  $D(t)$  obtained by using Eq. (7) with the two-term exponential curve of  $\alpha$  in Fig. 4a as input. Each row of panels displays results on the same axes: (a–c) over 450 ka; (d–f) over the last 100 ka in log scale; (g–i) over the last 100 ka in linear scale.

In the second approach, the curves of  $D(t)$  lie below the  $D_R$  estimates in many places. As expected from our theory in Sect. 2.2.2,  $D(t)$  lies above (below) the spline curve of  $D_R$  where this curve rises (drops). Where  $D_R$  increases with age, high  $D$  ( $> D_R$ ) is retrieved because peaks with much lower amplitude than overlying peaks in the column imply high diffusivity in the intervening depth interval. Where  $D_R$  decreases with age, low  $D$  ( $< D_R$ ) is retrieved because peaks with undiminished (or higher) amplitudes compared to overlying peaks can be explained only by low (or negative) diffusivity in the intervening interval. In this connection, a robust feature of all three curves of  $D(t)$  is that they and their initial steep drops lie well below

the curves of  $D_R$  in the first few tens of ka, where the  $D_R$  estimates decay much more gradually (Fig. 5d–5i). This feature, which remains if we use the  $D_R$  values of R2024 as input to the conversion, implies that  $D_R$  contains a long memory of the initial high diffusivities. We anticipated this memory effect in Sect. 2.2.2. Here, it operates because the effective diffusivity  $D_R$  “remembers” the initial rapid lowering of the peaks by fast diffusion during their first few thousand years of evolution, which cannot be undone however slow is diffusion afterwards. This finding is supported by the relative amplitudes in Fig. 4a, which evidence more than 40 % reduction in peak height ( $\alpha < 0.6$ ) on even the shallowest peaks.

The second inversion approach is not without limitations. First, the real original sulphate peaks at the surface might have durations (FWTMs) different from the 3 years assumed in the inversion and durations different from each other, as shown by the large scatter in the  $\alpha$  and  $D_R$  values. Second, the level of spline smoothing is uncertain. Indeed, it may not be possible to obtain the ideal input – one giving the true  $D(t)$  profile – by smoothing the  $D_R$  estimates at all age by an equal amount. Of the three inversion experiments, we regard the one with Spline 2 as giving more reliable insights about  $D(t)$ , because Spline 1 yields many short fluctuations on  $D(t)$  that are likely spurious (Fig. 5a), and Spline 3 strongly underrepresents the decrease of the  $D_R$  estimates near  $t = 0$  (Fig. 5f & 5i). Third, the inversion constrains  $D(t)$  poorly after its initial drop; there,  $D$  going negative and oscillating about zero is unphysical, although the experiments generally indicate  $D$  as very low. Occurring where the  $D_R$  curves drop rapidly with age, the stretches of negative  $D$  may arise from estimation noise/errors on the input  $D_R$  values, incorrect splining of those values, and a non-steady column whose strain-rate profile varied with time or where different ice layers inherited properties (e.g., grain size, dustiness) that led them to have different diffusivity histories. Our steady-state model does not account for such variations and might therefore yield negative  $D$  in an inversion.

In summary, estimating  $D$  from  $D_R$  has been possible due to the memory effect. Fast diffusion in the shallow subsurface reaching back a few ka (in the firm?) seems responsible for the elevated values of  $D_R$  for  $t \lesssim 50$  ka reported by R2024. Consequently, sulphate diffuses rapidly only near the top  $\approx 100$  m, not across the whole of the Holocene stretch of the EDC column. In Sect. 3.4, we will back out  $D(t)$  by going the other way – forward modelling from  $D$  to  $D_R$ , which reveals how the memory preconditions a long tail on  $D_R$  at EDC, whose continuation to several hundred ka is perceptible in Figs. 1c and 4b.

### 3.2 Inversions from peak widening

To calculate  $D_{F1}$  analytically, we use Eq. (16) with input data for  $\tau$  and  $\psi$  from paired depths (Sect. 2.2.2); for these, we use the  $\tau$  values of sulphate peaks derived from the destrained FWHMs measurements of F2024 (Fig. 6a) and the AICC2012-based function  $\psi(t)$ . As noted in Sect. 1, F2024 treated interglacials and glacial maxima separately and used the median FWHM of the peaks in each period as the input to their inversions. Here we explore a variation to their scheme, by calculating the  $D_{F1}$  values for all paired combinations of individual peaks from each two periods being studied, which allows us to find the median  $D_{F1}$  and the associated uncertainty (interquartile range in  $D_{F1}$ ) for each interval.

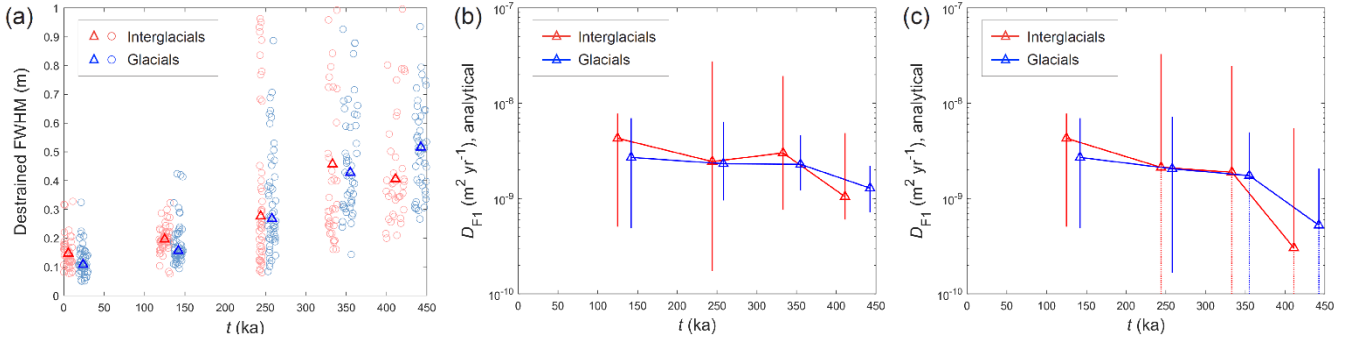


Figure 6. Analytical inversion of effective diffusivity  $D_{F1}$  from peak widths in interglacial and glacial maximum periods. (a) Destrained full width at half maximum (FWHM) of individual peaks, plotted against age (circles); data from Fudge et al. (2024). Triangle plots the median FWHM of each period. (b & c)  $D_{F1}$  computed from the data in (a) with Eq. (16). Triangles plot median values; and vertical bars, interquartile ranges (dotted if the lower quartile is negative and cannot be shown on logarithmic scale). The inversions in (b) study intervals between the Holocene and earlier interglacials (red) and between the LGM and earlier glacial maxima (blue). The inversions in (c) study intervals between successive interglacials or successive glacial maxima. Each triangle is plotted at the age of the older of each two periods.

In a first set of inversions, we follow F2024 by referencing each older interglacial or glacial maximum period to the most recent period, so every interval studied includes the Holocene or LGM part of the core. These inversions yield median  $D_{F1}$  values  $\approx 1.0\text{--}4.3 \times 10^{-9} \text{ m}^2 \text{ yr}^{-1}$  (Fig. 6b), agreeing overall with F2024’s results ( $1.6\text{--}6.0 \times 10^{-9} \text{ m}^2 \text{ yr}^{-1}$ ; their Table 1), although our glacial-maxima values ( $1.3\text{--}2.7 \times 10^{-9} \text{ m}^2 \text{ yr}^{-1}$ ) are lower than theirs ( $4.0\text{--}5.5 \times 10^{-9} \text{ m}^2 \text{ yr}^{-1}$ ). Our scheme variation and the smoothing behind  $\psi(t)$  explain the minor differences between our results and F2024’s results.

In a second set of inversions, we reference each period to the next younger period, to study how  $D_{F1}$  varies with depth. Interestingly, these inversions (Fig. 6c) yield median  $D_{F1}$  values that decrease more clearly with age – to less than  $10^{-9} \text{ m}^2 \text{ yr}^{-1}$  beyond 400 ka, although the uncertainties are large. The trend may indicate a real decline in the true diffusivity down core because these  $D_{F1}$  results pertain to successively deeper intervals (the shallowest results at 125 ka and 142 ka are necessarily unchanged from those in Fig. 6b). In contrast,  $D_{F1}$  in the first set of inversions always includes a memory of the high diffusivities of the shallowest results; recall that the effective diffusivities are interval averages of  $D$  (Sect. 2.2.2). Thus, the use of Holocene/LGM as the reference period explains why  $D_{F1}$  in Fig. 6b and the  $D_{F1}$  results of F2024 are roughly level, at most hinting at a decline.

### 3.3 Inversions from mean absolute gradient, $\bar{m}$

To find  $D_{F2}$  and  $D_E$  analytically, we use Eqs. (26) and (29), with the data from F2024 for  $\bar{m}$  in different ice sections in interglacials and glacial maxima (Fig. 7a) and the signal wavenumbers  $k^*$  measured by them for these periods,  $33.3 \text{ m}^{-1}$  and  $32.7 \text{ m}^{-1}$ , respectively. As with  $D_{F1}$ , we calculate  $D_{F2}$  and  $D_E$  for all paired combinations of input data from each two periods,

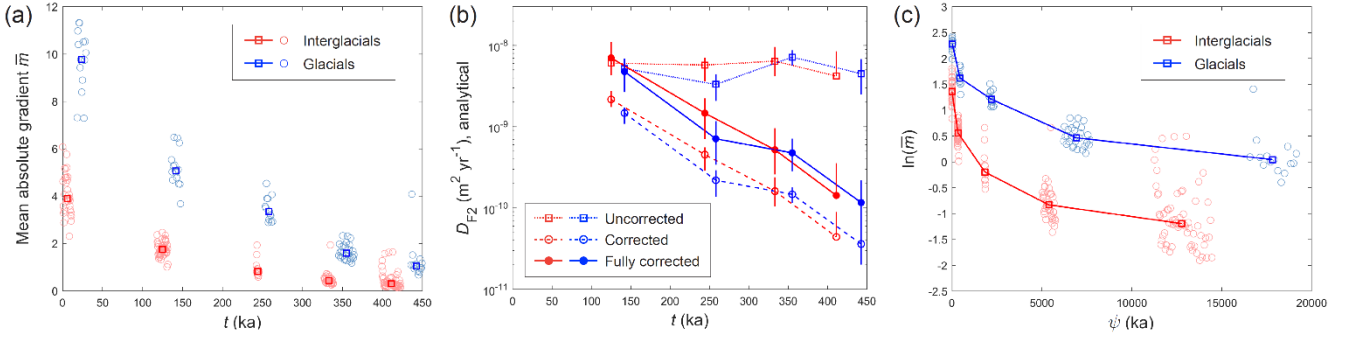


Figure 7. Inversion of effective diffusivity  $D_{F2}$  from mean absolute gradient  $\bar{m}$  of signals in interglacial and glacial maximum periods. (a)  $\bar{m}$  of multiple ice stretches in each period, plotted against age; data from Fudge et al. (2024). Square plots the median  $\bar{m}$  of each period. (b)  $D_{F2}$  values computed from the mean absolute gradient data with Eq. (26) (“uncorrected”), with Eq. (29) (“corrected”, i.e.,  $D_E$  values), and with Eq. (29) and a further multiplication by 2.5–4 times (“fully-corrected”; the multiplicative range extends the uncertainty around each value). All of these inversions study the intervals between successive interglacials (red) and between successive glacial maxima (blue), as in Fig. 6c. Symbols plot median values, and vertical bars plot interquartile ranges; the lower quartile is missing if it is negative and cannot be shown on log scale. (c)  $\ln(\bar{m})$  against the AICC2012-based dilated age  $\psi$  for the periods studied. The squares plot median values.

to gauge the uncertainty around each median. Given a key interest is how these effective diffusivities vary with depth, and both are interval averages (Sect. 2.3), we reference each period to the next younger period in these inversions.

Recall that  $D_{F2}$  is the uncorrected effective diffusivity, equivalent to F2024’s estimate, and  $D_E$  corrects  $D_{F2}$  for misamplification by the factor  $(\psi_2 - \psi_1)/(t_2 - t_1)$ , which is larger the older is the interval (Sect. 2.3). Indeed, the inversion results in Fig. 7b show that whereas the median  $D_{F2}$  values ( $\approx 3.3\text{--}7.2 \times 10^{-9} \text{ m}^2 \text{yr}^{-1}$ ; squares) are broadly level and consistent with the  $D_{F2}$  estimates of F2024 ( $4.8\text{--}6.1 \times 10^{-9} \text{ m}^2 \text{yr}^{-1}$ ; see their Table 1), the median  $D_E$  values (open circles) decrease with age and are much lower than  $D_{F2}$ . The difference attests a strong overestimation in  $D_{F2}$ , even for the shallowest results at 125 and 142 ka.

We further correct  $D_E$  for the issue with  $k^*$  in the Barnes et al. (2003) method by multiplying them by 2.5–4 (Sect. 2.3). This yields the “fully-corrected”  $D_{F2}$  estimates in Fig. 7b (filled circles). This correction returns the shallowest results roughly to the uncorrected  $D_{F2}$  medians. But the strong decreasing trend remains: the deepest fully-corrected estimates at  $\approx 400$  ka are nearly 2 orders of magnitude less than the shallowest values. The uncertainties in Fig. 7b are relatively small, so the trend cements the finding from  $D_{F1}$  (Sect. 3.2) that the true diffusivity decreases with age.

This decrease in  $D$  is confirmed separately by the exact inversion  $D = -(1/k^{*2})d(\ln \bar{m})/d\psi$  in Eq. (28). Figure 7c plots  $\ln(\bar{m})$  against dilated age  $\psi$ , showing a reduction of the slope of the plot trajectories – and thus  $D$  – with age. For both

interglacials and glacial maxima, the slopes of the segments linking the plot points essentially give the fully-corrected  $D_{F2}$  estimates of Fig. 7b. Since a smooth curve through the points won't deviate much from the segments,  $D(t)$  is well approximated by these estimates (more precisely,  $D$  will be somewhat less than these estimates, as the local slope of the curve through each point would be shallower than the segment leading left from it). Consequently, the fully-corrected  $D_{F2}$  results in Fig. 7b approximately describe how the true diffusivity varies from  $\approx 100$  to 400 ka. These results, except perhaps the shallowest interglacial result, should be free from bias by the high, steeply decreasing  $D$  in the shallow subsurface inferred in Sect. 3.1.

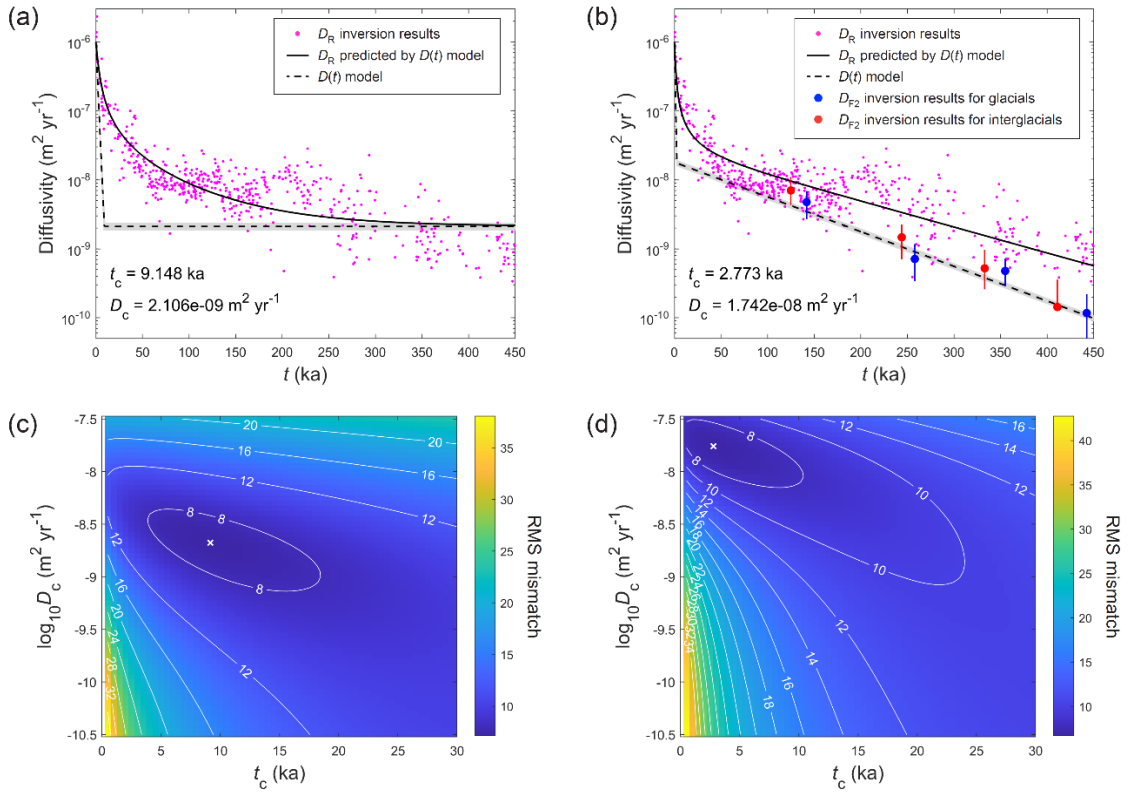
The deepest values of  $\bar{m}$  that we use from F2024 (between 400 and 450 ka, Fig. 6a) might include signal variability from the anomalous trough-sided peaks at depths  $\gtrsim 2700$  m (Sect. 1). If so, our deepest two fully-corrected  $D_{F2}$  values in Fig. 7b would be underestimated, but this does not affect the decreasing trend in 100–360 ka. Also, any underestimation is probably limited because F2024 found an unusual increase in  $\bar{m}$  only in ice older than 550 ka (their Fig. 6). Our  $D_{F1}$  results (Sect. 3.2) may be also corrupted by the anomalous peaks, but, as noted next, will not be used in our final inversion.

### 3.4 Forward modelling to estimate $D(t)$

So far, we learned that the true diffusivity  $D$  drops steeply in the first few ka from  $\approx 10^{-6} \text{ m}^2 \text{ yr}^{-1}$  by at least an order of magnitude (Fig. 5h; Sect. 3.1) and decays further from  $\approx 100$ –450 ka, roughly following the fully-corrected median  $D_{F2}$  estimates (Fig. 7b; Sect. 3.3). What profile of  $D(t)$  with these characteristics best explains the effective diffusivity estimates  $D_R$  and  $D_{F2}$  (after full correction)? Can it explain these simultaneously, and thus reconcile R2024's and F2024's findings?

To study this, we use Eq. (19) to predict the  $D_R(t)$  profile from  $D(t)$ , posing the following form for  $D(t)$  on the semi-logarithmic plot. Starting from  $10^{-6} \text{ m}^2 \text{ yr}^{-1}$  at  $t = 0$ , it decreases linearly to a corner value  $D_c$ , at age  $t_c$ , followed by either a flat floor ( $D = D_c$ ) or an inclined floor for  $t > t_c$ . The inclined floor is assumed to have a slope equal to the mean slope of the fully-corrected median  $D_{F2}$  estimates (Fig. 7b), but its level is fixed by the corner location, not by the estimates. For either floor type, we find the combination of  $D_c$  and  $t_c$  that best-fits the  $D_R(t)$  profile to our AICC2012-based  $D_R$  estimates (Fig. 4b, magenta points). The  $D_{F1}$  results (Fig. 6c) are excluded from the exercise, given their large uncertainties.

Figure 8 shows the best-fit profiles and maps of misfit over the  $t_c$ – $D_c$  parameter space from the forward modelling. In the flat-floor experiment (Fig. 8a, c), the predicted  $D_R(t)$  profile fits the  $D_R$  estimates moderately well, and  $D$  decreases from its surface value to the corner diffusivity  $D_c \approx 2.1 \times 10^{-9} \text{ m}^2 \text{ yr}^{-1}$  in 9.1 ka. In the inclined-floor experiment (Fig. 8b, d),  $D_R(t)$  fits the  $D_R$  estimates better, capturing their gentle decay trend at large  $t$ . Here,  $D(t)$  has a shorter initial drop (2.8 ka),  $D_c$  is higher ( $\approx 1.74 \times 10^{-8} \text{ m}^2 \text{ yr}^{-1}$ ), and the floor shoots through the fully-corrected  $D_{F2}$  values even though their level is not a fitting target;  $D(t)$  also lies slightly below their trend, as anticipated. Thus, this  $D(t)$  profile (Fig. 8b) explains the mean absolute gradient data as well as the peak-amplitude data and yields the better reconstruction of the two experiments. It also gives a more plausible estimate of the true diffusivity than the opposite conversion from  $D_R$  to  $D$  (Sect. 3.1), which reconstructed negative  $D$  intervals. Its steep initial drop is mainly constrained by the  $D_R$  decay in 0–50 ka, and its inclined-floor level by the



530 Figure 8. Forward modelling of the effective diffusivity profile  $D_R(t)$  from the true diffusivity profile  $D(t)$ , and least-squares fitting to constrain  $D(t)$ . As described in Sect. 3.4, panels (a) and (c) report an experiment assuming a flat floor for  $D$ ; and panels (b) and (d), an inclined floor. (a, b) Plot of log diffusivity versus age, showing  $D(t)$  (dashed), the predicted  $D_R(t)$  profile (solid curve), and  $D_R$  data from peak-amplitude inversion (points). Panel (b) includes the fully-corrected  $D_{F2}$  results of Fig. 7b for comparison. Grey shading about  $D(t)$  shows its maximal variation as found from the confidence intervals of the best-fit parameters,  $t_c$  and  $D_c$ . (c, d) Root mean square (RMS) mismatch in log-10 scale between predicted and estimated  $D_R$  values, as a function of the corner age  $t_c$  and corner diffusivity  $D_c$  of the  $D(t)$  profile. White crosses locate the optimal  $t_c$  and  $D_c$  values in (a) and (b), which yield RMS mismatches of 7.16 and 6.70, respectively.

535

deeper  $D_R$  values. Importantly, the corner age (2.8 ka) confirms our finding from Sect. 3.1 that the high  $D$  decaying through the upper column does not extend far below the firm-ice transition. Note that  $D(t)$  in Fig. 8b is reliable to a maximum age of only  $\approx 390$  ka ( $\approx 2700$  m) because the deepest  $D_R$  and fully-corrected  $D_{F2}$  data constraining the fit are interval-based results.

540 In these experiments, the long tails on  $D_R$  caused by the high initial  $D$  values confirm the memory effect, and the  $D(t)$  profiles are broadly consistent with the Holocene  $D_{\text{eff}}$  estimate of Barnes et al. (2003),  $\approx 1.3 \pm 0.6 \times 10^{-7} \text{ m}^2 \text{yr}^{-1}$  after applying the  $k^*$ -correction (Sect. 2.3). That  $D(t)$  in Fig. 8b lies below the  $D_R$ ,  $D_{F1}$  and  $D_{F2}$  estimates of R2024 and F2024 by up to 1–2 orders of magnitude confirms that these effective diffusivities approximate  $D$  crudely, and that the discrepancy between them

stems from the underlying averaging, the different intervals used to evaluate them, and errors in the mean absolute gradient  
 545 method.

Finally, the  $D_R$  estimates being fitted depend on the assumed 3-year FWTM duration for the surface peaks (Sect. 2.1). To gauge the impact of this assumption, we conducted an ensemble of  $10^5$  best-fit forward model runs, where each of the 537  $D_R$  estimates serving as fitting target in each run was picked randomly from its three values based on FWTMs of 1, 3, and 5 years. The maximal ranges found for  $t_c$  and  $D_c$  are 2.3–2.9 ka and  $1.70\text{--}1.78 \times 10^{-8} \text{ m}^2 \text{ yr}^{-1}$ , respectively, narrowly bracketing the  
 550 results in Fig. 8b. This is not surprising as  $D_R$  is weakly sensitive to the FWTM, as found by R2024.

### 3.5 Diffusivity inversion in the firn

The preceding inversions highlight the firn diffusivity as a key interest, but their methods ignore firn densification and assume an EDC column consisting of ice only. Might the high  $D$  found for the firn be an artefact of this neglect? Should the methods be adjusted to account for firn density change? The  $D_R$  inversion is especially relevant in this regard, as it involves signals  
 555 descending through the firn layer; its results are also used in the estimation of  $D(t)$  (Sect. 3.1 and 3.4). Here we show that because of the way the bulk concentration  $C$  is defined and used, Eq. (1) correctly describes signal evolution in the firn as well as in the ice, so that the  $D_R$  inversion and our findings for  $D$  are valid.

The concerns are two-fold. R2024’s reconstruction of the original surface peaks, which provides input data for the  $D_R$  inversion and takes each peak’s width (FWTM) to be  $3a$ , uses the ice-equivalent thickness and assumes surface material with  
 560 the ice density  $\rho_i$  ( $917 \text{ kg m}^{-3}$ ) throughout calculation (Sect. 2.2.1). If the firn surface density  $\rho_0$  ( $< \rho_i$ ) is used in the reconstruction, each original peak would be wider ( $3a\rho_i/\rho_0$ ), its height proportionally less, so  $\alpha$  may have been underestimated and  $D_R$  overestimated. A second concern is that Eq. (1) might not conserve the amount of impurity in densifying firn. With  $D$  defined as the diffusivity of the bulk material (ice–air composite in the case of firn),  $D\partial^2 C/\partial z^2$  in Eq. (1) describes impurity flux divergence only if  $C$  is the impurity amount *per unit volume* of bulk material, not if  $C$  is impurity amount *per unit mass* –  
 565 as used by us and R2024 in the  $D_R$  inversions. Consequently, one fears that Eq. (1) might be the wrong model, and it is unclear whether  $D$  presently retrieved for the firn describes its bulk diffusivity or some other quantity.

We dispel these concerns in the following by deriving Eq. (1) from first principles. Consider the firn layer in the Cartesian coordinates  $(X, Y, Z)$ , with depth  $Z$  measuring down from the surface. Let  $\mathbf{U} = (U, V, W)$  be the firn velocity, and  $\rho = \rho(Z)$  be the firn density profile, assumed time-invariant. We define the bulk concentration  $c_B$  as the impurity amount *per volume*, i.e.,  
 570  $c_B = \rho C$ . Then, impurity conservation obeys

$$\frac{\partial c_B}{\partial t} + \nabla \cdot (\mathbf{U} c_B) = \nabla \cdot (D \nabla c_B), \quad (32)$$

in which  $D = D(Z)$  describes the vertical diffusivity profile, and the equation for water mass conservation is

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{U}) = 0 . \quad (33)$$

At ice-sheet divide or summit locations,  $\rho$ ,  $c_B$  and  $W$  have negligible horizontal variations (they are functions of  $Z$  only) so the

575 above equations become

$$\frac{\partial \rho}{\partial t} + W \frac{\partial \rho}{\partial Z} + \rho \nabla \cdot \mathbf{U} = 0 , \quad (34)$$

$$\frac{\partial c_B}{\partial t} + W \frac{\partial c_B}{\partial Z} + c_B \nabla \cdot \mathbf{U} = \frac{\partial}{\partial Z} \left( D \frac{\partial c_B}{\partial Z} \right) , \quad (35)$$

where  $W = W(Z)$  is the submergence velocity profile in the column.

Now suppose the depth–age scale  $Z = g(t)$ , with the function  $g$  given by

$$580 \quad t = g^{-1}(Z) = \int_0^Z \frac{d\eta}{W(\eta)} . \quad (36)$$

We define  $z = Z - g(t)$  in order to use the reference frame of Eq. (1), which follows the material as it descends. The variable change from  $Z$  to  $z$  gives  $\partial/\partial Z \rightarrow \partial/\partial z$  and  $\partial/\partial t \rightarrow \partial/\partial t - W(g(t))\partial/\partial z$ , and Eqs. (34) and (35) become

$$\frac{\partial \rho}{\partial t} + \tilde{w} \frac{\partial \rho}{\partial z} + \rho \left( \frac{\partial U}{\partial X} + \frac{\partial V}{\partial Y} + \frac{\partial W}{\partial z} \right) = 0 , \quad (37)$$

$$\frac{\partial c_B}{\partial t} + \tilde{w} \frac{\partial c_B}{\partial z} + c_B \left( \frac{\partial U}{\partial X} + \frac{\partial V}{\partial Y} + \frac{\partial W}{\partial z} \right) = \frac{\partial}{\partial z} \left( D \frac{\partial c_B}{\partial z} \right) . \quad (38)$$

585 In this reference frame, material seen from the horizon with age  $t$  has the velocity

$$\tilde{w}(z, t) = W(g(t) + z) - W(g(t)) . \quad (39)$$

On the short length scale of the signals ( $\sim 10^{-1}$ – $10^0$  m), the vertical gradient of velocity  $W$  can be approximated by the strain rate, so  $\tilde{w} \approx \dot{\epsilon}_z(t)z$ . Density and diffusivity variations across individual signals can be assumed to be small on this scale, so we take  $\partial \rho / \partial z \approx 0$  and  $\partial(D \partial c_B / \partial z) / \partial z \approx D \partial^2 c_B / \partial z^2$ . Applying the first of these approximations in Eq. (37) yields the

590 compaction relation  $\partial U / \partial X + \partial V / \partial Y + \partial W / \partial z = -(\partial \rho / \partial t) / \rho$ , which, when used in Eq. (38), converts it to

$$\frac{\partial c_B}{\partial t} - \frac{c_B}{\rho} \frac{\partial \rho}{\partial t} = D \frac{\partial^2 c_B}{\partial z^2} - \dot{\epsilon}_z(t)z \frac{\partial c_B}{\partial z} . \quad (40)$$

This is an approximate general evolution model for signals on  $c_B$  in firm or ice.

In the ice, where  $\rho \equiv \rho_i$  (constant), Eq. (40) loses the compaction term and reduces to the same form as Eq. (1). This means that Eq. (1) is valid in the ice whether the bulk impurity concentration is defined in per mass or volume terms.

595 In the firm, Eq. (1) is missing the compaction term of Eq. (40) so it cannot be used to track  $c_B$ . But by substituting  $c_B = \rho C$  into Eq. (40), we recover Eq. (1) exactly after some algebra. This means that Eq. (1) is valid in the firm and is the right model for formulating the diffusivity inversion, provided that  $C$  measures the bulk impurity concentration in per mass terms, as done by R2024 and us here. Inversions with the impurity concentration in per volume terms must use Eq. (40) instead.

It follows that R2024's reconstruction of the original peaks gives the right inputs, and the  $D_R$  inversion is valid for both  
600 peaks in the firm (which experienced diffusion in a densifying material) and peaks in the ice (which experienced diffusion in a densifying material and then diffusion under constant density). A further realisation unknown to the earlier studies is that  $D$  retrieved for the firm by inversions based on Eq. (1) automatically quantifies its bulk diffusivity. It thus turns out fortunate that R2024 used the chemical measurements expressed as sulphate concentration in per mass terms directly as  $C$  in Eq. (1).

#### 4 Physical controls on sulphate diffusion at EDC

605 Armed with  $D(t)$  in Fig. 8b, we discuss the mechanisms of sulphate transport in the EDC column, going beyond the interpretations made by R2024 and F2024 from their effective diffusivities.  $D$  drops steeply from its surface value  $\approx 10^{-6} \text{ m}^2 \text{ yr}^{-1}$  to  $\approx 1.7 \times 10^{-8} \text{ m}^2 \text{ yr}^{-1}$  at 2.8 ka, an age coinciding roughly with the firm base ( $\approx 2.5$  ka at 100 m depth); this drop is much shorter in duration than the initial decay in  $D_R$  (Figs. 1c and 4). A slower decay in  $D$  to  $\sim 10^{-10} \text{ m}^2 \text{ yr}^{-1}$  follows from 2.8–390 ka, although its real form may not be exactly log-linear as posited in our forward model;  $D$  is similar at  $\approx 125$  ka to the  $D_{F1}$  and  
610  $D_{F2}$  estimates of F2024 ( $1.6\text{--}6.1 \times 10^{-9} \text{ m}^2 \text{ yr}^{-1}$ ) but much lower in deeper ice. We consider these intervals in turn.

##### 4.1 Vapour diffusion in the firm

Recall that  $D$  retrieved for the firm reflects its bulk diffusivity (Sect. 3.5). We interpret the high  $D$  on the steep drop as being due to diffusion of  $\text{H}_2\text{SO}_4$  vapour through interconnecting air pores in the firm. This mechanism is plausible because  $\text{H}_2\text{SO}_4$ , though often viewed as nearly non-volatile, does have a vapour pressure (Tsagkogeorgas et al., 2017).

615 A back-of-the-envelope calculation of the diffusion rate involving the  $\text{H}_2\text{SO}_4$  vapour pressure  $p_v$  and  $\text{H}_2\text{SO}_4$  diffusion coefficient  $\Omega_a$  in firm air supports the interpretation. We assume  $\text{H}_2\text{SO}_4$  transport by vapour diffusion to be much faster than solid-state diffusion of sulphate through ice grains, but slow compared to sulphate exchange between ice and air, such that vapour diffusion is rate limiting. This assumption, which is justified by the time scales found below, features also in the Whillans and Grootes (1985) model for water isotope diffusion in firm, except evaporation replaces fractionation of the species  
620 here. To estimate  $p_v$ , we assume sulphuric acid to be available on firm grain surfaces to exchange with vapour; then, Eq. (11) of Tsagkogeorgas et al. (2017) gives  $p_v \sim 5 \times 10^{-9} \text{ Pa}$  at  $-53^\circ\text{C}$ . To estimate  $\Omega_a$ , we extrapolate the  $\text{H}_2\text{SO}_4$  diffusion coefficients measured by Brus et al. (2017) at 278–298 K under laminar conditions to  $\approx -50^\circ\text{C}$ , finding  $\Omega_a \sim 0.015$  to  $0.05 \text{ cm}^2 \text{ s}^{-1}$  or  $\sim 45$  to  $150 \text{ m}^2 \text{ yr}^{-1}$  when bearing in mind the uncertainty in its power-law temperature dependence noted by these authors (see their

Fig. 5 & Table 1). We adopt  $\Omega_a \sim 150 \text{ m}^2 \text{ yr}^{-1}$  from the top of the range, as it is based on a weaker temperature dependence (a power of 1.5) that is more consistent with the one (1.75) found across the literature on gas diffusion (e.g., Tang et al., 2014).

Now, if we focus on the top few metres of the firn and account for the relative density  $\rho_o/\rho_i \sim 0.4$  there, then the diffusion coefficient for the bulk firn would be less,  $\approx \Omega_a(1 - \rho_o/\rho_i)$ , but this correction is offset by a strong enhancement of diffusion by firn ventilation and wind pumping (e.g., Colbeck, 1989; Waddington et al., 1996). We therefore proceed by using the free-air diffusivity  $\Omega_a$  without correction. A ballpark estimate of  $D$  from vapour diffusion is found by scaling  $\Omega_a$  by the abundance ratio of  $\text{SO}_4^{2-}$  in the air to ice. The vapour pressure  $p_v$  converts via the ideal gas law to  $2.7 \times 10^{-12} \text{ mol m}^{-3}$ , whereas for a volcanic signal in the firn with bulk concentration peaking at 200 ppb ( $\approx 2 \text{ nmoles/g}$ ), the peak sulphate abundance is  $\approx 2 \text{ mmol m}^{-3}$  in the ice grains or  $\approx 0.8 \text{ mmol m}^{-3}$  in the bulk firn. The resulting abundance ratio,  $\approx 3 \times 10^{-9}$ , leads to the bulk diffusivity  $D \sim 4.5 \times 10^{-7} \text{ m}^2 \text{ yr}^{-1}$ , similar to the shallow high values on our  $D(t)$  profile.

The assumption regarding time scales may be checked. For signals on the decimetre scale  $l \sim 0.1 \text{ m}$ , the vapour-diffusion time scale,  $l^2/D \sim 10^4 \text{ yr}$ , is much longer than the solid-diffusion time scale,  $d_g^2/D_s \sim 400 \text{ yr}$ . These values are based on the mean grain diameter  $d_g$  in the upper firn at Dome C ( $\approx 0.1\text{--}0.2 \text{ mm}$ ; Gay et al., 2002) and the assumption that the  $\text{H}_2\text{SO}_4$  diffusivity within ice grains,  $D_s$ , is similar to the  $\text{H}_2\text{O}$  self-diffusivity of monocrystalline ice ( $\sim 10^{-10} \text{ m}^2 \text{ yr}^{-1}$  at  $-53^\circ \text{C}$ ).

The vapour diffusion model also explains the steep drop of  $D$  in the range  $\approx 0\text{--}2.8 \text{ ka}$ , because firn metamorphism reduces the porosity and seals off interconnecting airways to lower the bulk diffusivity (Calonne et al., 2022) on descent through the firn layer, and because as grain growth occurs in the firn, larger grains slow the  $\text{H}_2\text{SO}_4$  diffusion from their interior to their surfaces, progressively limiting the bulk diffusion rate. At pore close-off ( $\rho \approx 845 \text{ kg m}^{-3}$  at Dome C; Calonne et al., 2002) vapour diffusion terminates, and other processes must control  $D$  thereafter.

## 4.2 Sulphate transport below the firn-ice transition

Below pore close-off at EDC, signal smoothing may result from (i) solid-state diffusion within ice grains, (ii) “Gibbs–Thomson diffusion” of vein signals (Ng, 2021; i.e., diffusion of the part of sulphate bulk concentration in liquid veins due to thermodynamic interactions including the Gibbs–Thomson effect and melting-point depression by dissolved ions), (iii) diffusion through the grain-boundary network, (iv) “residual diffusion” caused by the stochastic three-dimensional motion of veins and grain boundaries carrying impurities (Ng, 2021), and any combination of these processes. We expect suppression of Gibbs–Thomson diffusion where the veins are disconnected or blocked by microparticles or dust (Ng, 2021), and suppression of residual diffusion where such particles impede grain-boundary motion (Durand et al., 2006).

In terms of how sulphate is partitioned in EDC ice across crystal lattice, grain boundaries and liquid veins, direct observations are limited to a small number of shallow ice samples, but they indicate its presence at grain boundaries and triple junctions. Barnes and Wolff (2004) analysed 6 samples in the 140–501 m depth range with scanning electron microscopy, finding sulphur at grain-boundary sites, and at triple junctions only in samples with high sulphate concentration; they suggested that the veins could carry much impurity only when the grain boundaries were saturated. Recently, Bohleber et al. (2025) used

laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to map the abundances of S, Cl and Na at tens-of-microns resolution in samples from 281.6, 585.2 and 1000 m depth (9 ka, 27.3 ka, 64 ka), in places away with volcanic spikes. Their elemental maps show strong localisation of S at grain boundaries, with little of it in grain interiors, and no apparent trend in the partitioning with depth. They argued diffusion through grain boundaries (as well as veins) as potentially playing a key  
660 role in signal evolution. Measurements targeting triple junctions with a laser spot size of 1  $\mu\text{m}$  also revealed S there, but the ablated material volumes were too small for determining whether S was concentrated at the junctions – as was found for Na and Cl – and its abundance ratio between triple junctions and grain boundaries.

If  $D_s$ ,  $D_{vn}$ ,  $D_{bn}$  and  $D_{res}$  symbolise the respective “component diffusivities” contributing to  $D$  from processes (i) to (iv) above, then one might regard  $D$  as their signal-partitioning weighted sum. In the following, we assess how they conspire with  
665 signal partitioning to different impurity sites to govern  $D(t)$  in  $2.5 \leq t \leq 390$  ka, by estimating their profiles down column. For reasons given below, we evaluate  $D_{bn}$  only qualitatively.

We calculate  $D_s$ ,  $D_{vn}$  and  $D_{res}$  by using published equations (Appendix C) and temperature and grain-size data from EDC as input (Fig. S1). These diffusivities increase with temperature. The Gibbs–Thomson diffusivity  $D_{vn}$  decreases with the mean grain size and sulphate bulk concentration  $c_B$  (Eq. (C2)). We calculate it for  $c_B$  from 1  $\mu\text{M}$  (the typical background concentration  
670 at EDC) to 10  $\mu\text{M}$  (order of magnitude of large volcanic peaks), noting that this range constrains a lower-bound  $D_{vn}$  because not all of  $c_B$  may reside in veins. For finding  $D_s$  and  $D_{vn}$ , empirical estimates of the molecular diffusivities of sulphate in ice single crystals and water are desired but lacking; we approximate them by the  $\text{H}_2\text{O}$  self-diffusivities in those materials.

Turning to the grain-boundary network diffusivity  $D_{bn}$ , we note that grain boundaries, each bounded by triple junctions, must form a discontinuous transport network that is interrupted repeatedly by triple junctions, where we envisage liquid veins  
675 to exist. Sulphate can diffuse within each grain boundary according to its molecular diffusivity,  $D_{gb}$ ; this is probably several orders of magnitude larger than the solid-state/lattice diffusivity,  $D_s$  (Lu et al., 2009; Ng, 2024). But on the centimetre or longer scale of signals of interest (over multiple grains), the veins intersect and strongly short-circuit the grain-boundary transport; the vein-water molecular diffusivity is several orders of magnitude above  $D_{gb}$  (Lu et al., 2009; Ng, 2024). Consequently, grain-boundary signal diffusion is inherently coupled to vein-signal diffusion. With  $D_{bn}$  representing diffusion of only the part of the  
680 bulk signal in grain boundaries, we expect  $D_{bn} < D_{vn}$  because signal evolution involves sulphate diffusing along them (to and from the veins) in series with the vein short-circuiting.<sup>2</sup> Any impurity segregation where grain boundaries meet vein apices might further limit  $D_{bn}$ . In this way, grain boundaries are slow (diffusive) extensions of the veins. Both the coupling and

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<sup>2</sup> Research on polycrystalline diffusion has also considered the effect of grain boundaries on  $D$ , but mainly for systems below the eutectic, without triple-junction melt. The focus there is different: how grain-boundary diffusion short-circuits lattice diffusion. For coupled diffusion in the long time (Harrison Type-A) regime, it is estimated that  $D_{bn} \approx sfD_{gb}$ , where  $f$  is the volume fraction of grain boundaries and  $s$  is the impurity segregation coefficient (e.g., Kaur et al., 1995; Dohmen & Milke, 2010). We cannot use this result when liquid veins are present.

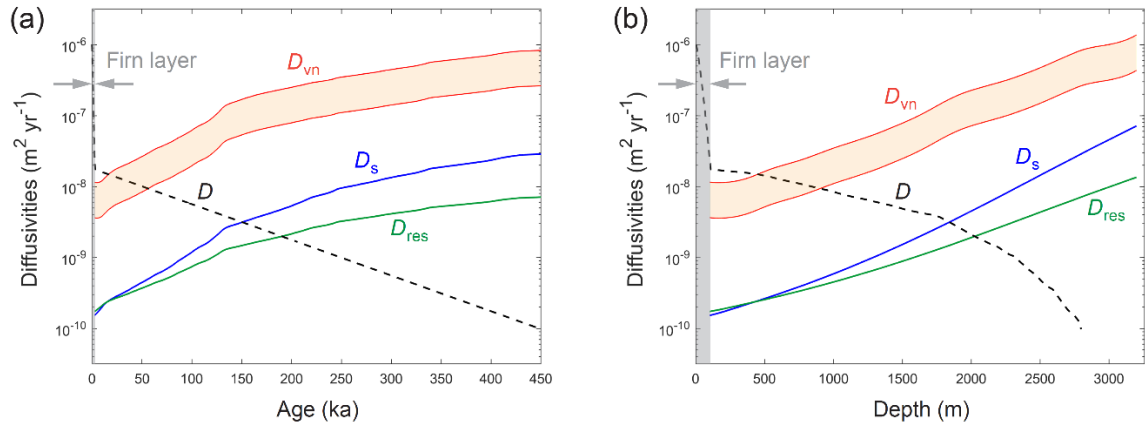


Figure 9. Estimated contributions to the sulphate signal diffusivity  $D$  in the EDC ice column (below the firn) from Gibbs–Thomson diffusion in the vein network ( $D_{vn}$ ), solid-state diffusion within ice crystals ( $D_s$ ), and residual diffusion ( $D_{res}$ ), as functions of (a) age and (b) depth. Dashed curves plot our inversion result for  $D$  from Fig. 8b. Red shading indicates the range in  $D_{vn}$  described in the text.

segregation are poorly understood so a precise estimation of  $D_{bn}$  is presently out of reach.

Figure 9 shows the computed profiles of  $D_s$ ,  $D_{vn}$ , and  $D_{res}$ , including  $D$  from Fig. 8b for comparison.  $D_{vn}$  is the highest component diffusivity. From pore close-off to  $\approx 1700$  m depth ( $\approx 130$  ka), some sulphate diffusion must occur in a connected vein network because  $D_s$  and  $D_{res}$  are too small to account for  $D$  and because we expect  $D_{bn}$  to be much less than  $D_{vn}$  (possibly by one to several orders of magnitude). In the upper part of this interval, a sizeable fraction of sulphate signals must lie in veins, because the similarity of  $D_{vn}$  and  $D$  suggests that Gibbs–Thomson diffusion dominates signal smoothing, although grain-boundary diffusion in series with vein short-circuiting – as described earlier – may supplement transport. This interpretation tallies with our vapour diffusion model (Sect. 4.1), which envisages sulphuric acid present on firn grain surfaces. When the grains cross the firn-ice transition, some sulphate should end up at crystal junctions (grain boundaries and veins). Below the transition, grain boundaries may supply veins continually with sulphate, as grain growth reduces their area density. These ideas are broadly compatible with the microscale observations of Barnes and Wolff (2004) and Bohleber et al. (2025).

On descending the interval towards 1700 m,  $D_{vn}$  and  $D$  diverge (Fig. 9). Despite enhancement of  $D_{vn}$  by rising temperature (grain growth offsets this only partially, according to Eq. (C2)),  $D$  decreases. This decrease can be explained by a shift in signal partitioning away from veins. That is, each signal peak may be thought of generally consisting of a vein component, a grain-boundary component, and a crystal-interior component. The last component contributes minimally to signal evolution *if* we assume that the low abundance of sulphate within grains and its localisation at grain boundaries inferred by Bohleber et al. (2025) apply at all depths to 1000 m (depth of their deepest sample) and further below. As the vein component smooths by Gibbs–Thomson diffusion, the less it contributes to the peak form, so an increasing fraction of surviving signals comes from sulphate at grain boundaries, so  $D$  tends towards  $D_{res}$  and  $D_{bn}$  (note the focus on signals rather than concentration; the veins are not necessarily losing sulphate, and grain boundaries not necessarily gaining sulphate). That  $D$  has dropped to less than a

tenth of  $D_{\text{vn}}$  at  $\approx 1700\text{--}2100$  m suggests that by then, most vein signals have been eliminated and grain-boundary network diffusion and residual diffusion dominantly control signal smoothing. The large decrease in  $D$  through  $\approx 100\text{--}1700$  m is  
710 consistent with the modelling results of Ng (2021; his Fig. 8) showing that Gibbs–Thomson diffusion rapidly damps vein sulphate signals in the upper EDC column if the veins are fully connected. In this “signal partitioning shift” mechanism,  $D_{\text{vn}}$  is unchanged from its estimated trajectory in Fig. 9 unless the veins are blocked or disconnected.

Progressive blockage of veins by dust that lowers their connectivity – and thus  $D_{\text{vn}}$  – may explain part, but not all, of the decrease in  $D$  through the interval, because Gibbs–Thomson diffusion will occur in a partially-connected vein network to cause  
715 signal partitioning shift. Consequently, signal partitioning shift with or without vein-blockage/disconnection can explain the decrease. According to R2024, vein blocking is not clearly evidenced by the EDC dust-flux record, which does not increase overall through the interval (their Fig. 5), but it cannot be ruled out while the precise microstructural distribution of dust in the ice is uncertain.

Our foregoing inferences revise the ones by R2024, who attributed the decay of  $D_{\text{R}}$  in 0–50 ka to a switch in diffusion  
720 mechanism due to changing location of sulphate in the microstructure and/or changing connectivity of the grain interfacial network (factors related to those identified by us above) and who interpreted the high  $D_{\text{R}}$  values on the decay for active diffusion through interconnected veins in ice dating to the Holocene and reaching into the last glacial. The  $D(t)$  decay analysed by us has much lower diffusivities than  $D_{\text{R}}$  (Fig. 8b) and extends to  $\approx 130$  ka, implying vein-network connectivity to greater depths. Our interpretation emphasises changing partitioning of signals (depth variations in concentration) over changing  
725 partitioning of bulk concentration (sulphate location). We also showed in Sect. 3 that the  $D_{\text{R}}$  decay originates from memory of very fast diffusion in the firn lasting only a few kiloyears, rather than from processes beneath the firn-ice transition.

In the  $\approx 2100\text{--}2700$  m interval,  $D$  continues to plunge below  $D_{\text{s}}$  and  $D_{\text{res}}$ . A plausible interpretation of this focusses on grain-boundary signals, as there is no obvious mechanism of lowering  $D_{\text{s}}$  substantially, and our earlier inference suggests limited vein signals surviving to these depths. The observed  $D$  may result from suppressed residual diffusion due to dust-  
730 particle drag on grain boundaries, together with grain-boundary network diffusion rates  $D_{\text{bn}}$  not exceeding  $\sim 10^{-10}\text{--}10^{-9} \text{ m}^2 \text{ yr}^{-1}$ . As  $D_{\text{bn}} \ll D_{\text{s}}$  then, this interpretation suggests potential bottlenecks (e.g., segregation effects) where grain boundaries connect with veins. We emphasise that our analysis for this interval does not address the deep anomalous sulphate peaks described in Sect. 1.

These inferences from order-of-magnitude comparisons in Fig. 9 are preliminary, given the approximations for the  
735 molecular diffusivities, the uncertain size of  $D_{\text{bn}}$ , our use of simple models (Appendix C) that ignore other ionic impurities besides sulphate (which may impact  $D_{\text{vn}}$ ) and potential anisotropy in grain-boundary motion and orientation (which may impact  $D_{\text{res}}$ ) and that does not capture the coupled diffusion in grain boundaries and veins (as modelled by Ng (2024) for water stable isotopes), and given the assumptions made from the Bohleber et al. (2025) findings, which themselves are based on a few samples not carrying sulphate peak signals. Our most robust interpretation is the shift of sulphate signals away from veins and  
740 increasing dominance of grain boundaries in carrying them as we descend the upper half column.

## 5 Conclusions and outlook

In this paper, we advanced a theory of diffusivity inversion for impurity signals in ice cores and applied it to the sulphate datasets of F2024 and R2024 to estimate the diffusivity ( $D$ ) profile at the EDC core site, gaining new insights on sulphate transport in the ice column there to  $\approx 2700$  m depth. Our framework unifies and extends the methods of F2024 and R2024 for finding the effective diffusivities ( $D_R$ ,  $D_{F1}$ ,  $D_{F2}$ ) and reconciles their results. The effective diffusivities differ significantly from the local diffusivity  $D$  because they are nonuniform-weighted averages of  $D$  over large, finite age intervals. The “memory effect” from this averaging explains how the decay in  $D_R$  in  $\sim 0$ –50 ka found by R2024 originates from high diffusivity in the thin ( $\approx 0$ –100 m equating to  $\approx 0$ –2.5 ka) firn layer atop the column. By incorporating firn densification in the model, we show that  $D$  retrieved in the firn by the inversion measures the impurity diffusivity of bulk firn material. Our theory can be used on other ice cores and other chemical impurities to estimate the corresponding diffusivity profiles.

The EDC sulphate diffusivity profile (Fig. 8b) shows high, sharply decreasing  $D$  in the firn layer ( $\approx 0$ –100 m depth), followed by a gradual decline from  $\sim 10^{-8}$  to  $\sim 10^{-10}$  m<sup>2</sup> yr<sup>-1</sup> through  $\approx 110$ –2700 m ( $\approx 2.8$ –390 ka). We propose vapour diffusion of sulphuric acid in firn air as the cause of the high firn diffusivity. By studying how the profile is controlled by the component impurity transport mechanisms (i.e., diffusion through crystal lattice, veins, and grain boundaries, and residual diffusion due to interfacial motion), we interpret the decline in  $D$  in  $\approx 110$ –2000 m for a progressive removal of vein sulphate signals by Gibbs–Thomson diffusion, which leaves more and more of the remaining signals to grain boundaries, and the further decline in  $D$  in  $\approx 2000$ –2700 m for slow diffusion through the grain-boundary network and potential slowing of grain-boundary motion by dust/microparticle drag. These factors can explain why  $D$  decreases with depth despite rising temperature. Our findings broadly agree with F2024 and R2024’s interpretation (from their effective diffusivities) of limited vein-signal diffusion at depth, but yield more precise and reliable information about changing signal partitioning in the upper half column.

### 5.1 Implications

What of the fate of sulphate signals deposited on the surface of Dome C? Our diffusivity profile implies that if they survive the initial fast diffusion in the firn layer to “punch through” to its base, then afterwards they enjoy much slower diffusive smoothing and might survive into deep ice. For sulphate signals generally, not only volcanically-sourced spikes, we study this in Fig. 10 by computing the vertical variation of diffusion length  $\sigma$  (using Eq. (24) with our  $D$  profile) and using  $\sigma$  to predict the amplitude attenuation ratio for peak signals with annual, 3-year, decadal and centennial durations, i.e., peaks whose depositional widths at the surface are 1, 3, 10 and 100 times the mean annual layer thickness ( $\approx 53$  mm after accounting for the surface firn density, taken as 400 kg m<sup>-3</sup>). The 3-year long signal is akin to the original surface peaks assumed in our inversion method, so its predicted attenuation trajectory resembles the trajectory of the  $\alpha$ -data (Fig. 10a; cf. Fig. 4a).

As shown in Fig. 10, the initial rise in  $\sigma$  reflecting fast diffusion in the firn gives a total firn diffusion length of 3.6 cm. Annual signals attenuate drastically and struggle to punch through, although those with high starting amplitudes may remain

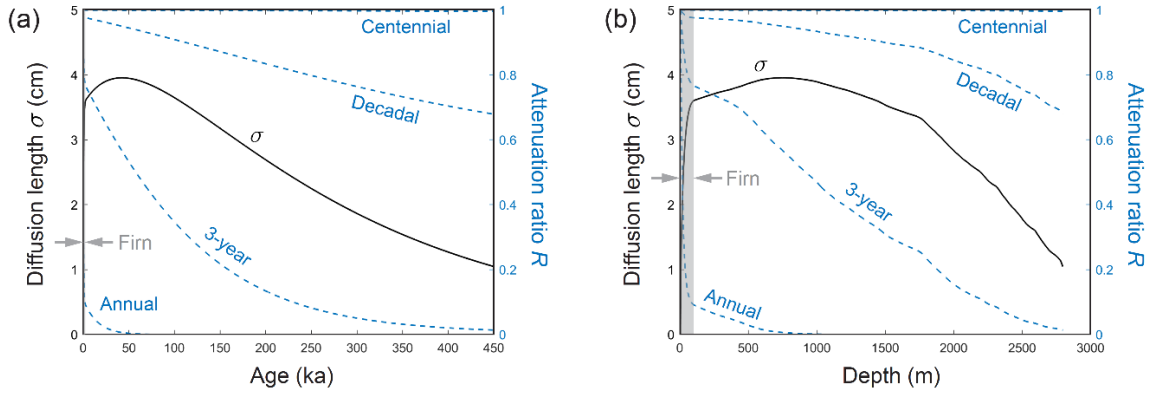


Figure 10. Diffusion length  $\sigma$  at the EDC core site (solid curves, left axes) against (a) age and (b) depth, calculated with Eq. (24) using the diffusivity profile  $D(t)$  from the inversion in Fig. 8b. Grey shading indicates the firn layer. Dashed curves (right axes) plot the amplitude attenuation ratio  $R = \exp(-2\pi^2\sigma^2/(\lambda_0 S)^2)$  (equivalent to the right-hand side of Eq. (22)) for signal peaks that are annual, 3-year, decadal and centennial in duration. As these signals are not sinusoidal, we estimate  $R$  by approximating the wavelength  $\lambda_0$  to be twice their widths.

detectable for some distance below the firn. Decadal and longer signals attenuate significantly less. The attenuation amount depends sensitively on the width of signals that are annual to decadal. Notably, since volcanic events vary widely in duration, their sulphate spikes in the ice have marginal survivability, in the sense that 3-year long spikes could reach  $\approx 1500$  m depth with 1/3 of their original amplitude, but slightly shorter spikes perish much faster. This means that the FIC sulphate record presents a filtered history of volcanic forcing with short (as well as low magnitude) eruptions severely underrepresented. For non-volcanic forcings, similar low-pass filtering suppresses sub-decadal signals. Note that the sulphate diffusion lengths in Fig. 10 do not apply to water stable isotopes, and, across the depth range considered here, they are less than or similar to modelled diffusion lengths for  $\delta D$  in the same core (Fig. 6 of Pol et al., 2010), indicating slightly better signal preservation for sulphate compared to water isotopes.

For the ongoing Beyond EPICA – Oldest Ice (BE-OI) project and the Million Year Ice Core (MYIC) project at nearby Little Dome C, a key interest is the resolution of recoverable climate signals in ice 1–1.5 Myr old. The extreme layer thinning experienced by that ice, whose age density is expected to reach  $20 \text{ kyr m}^{-1}$  or more at 1.5 Ma (Chung et al., 2023), will limit the retrieval and interpretation of signals of shorter than millennial time scale; e.g., centennial signals may be contained in sections  $\sim 1$  cm long, similar to individual grain diameter. Still, it is useful to know the diffusion length  $\sigma$  of (potentially observable) longer-scale signals. Here we estimate  $\sigma$  for sulphate in deep ice at Little Dome C, by assuming that the diffusivity profile there has the same form as found for EDC back to 450 ka and is, beyond that age, capped at  $10^{-10} \text{ m}^2 \text{ yr}^{-1}$ , the value on our  $D$ -profile at 450 ka (Fig. S2). A first calculation, made by integrating Eq. (24) again but with the thinning function  $S(t)$  derived from the modelled age–depth scales at the BE-OI and MYIC core sites (Chung et al., 2023), predicts  $\sigma = 0.5\text{--}0.9$  cm

from 500 ka to 2 Ma (Fig. S3), with  $\sigma$  variations in 0–450 ka very similar to the EDC result. Separately, we then make a bounded estimate that does not depend on the age-depth scales at those sites. We use the property that the squared-diffusion lengths  $\sigma^2$  from two contiguous parts of an ice column are additive after applying the respective vertical thinning (Gkinis et al., 2014; Ng, 2023). Thus, the value of  $\sigma^2$  at 1.5 Ma can be found by taking  $\sigma^2$  at 450 ka from Fig. 10 (where  $\sigma \approx 1$  cm) and adding a  $\sigma^2$  contribution from an extra 1.05 Myr ( $\Delta t$ ) of signal diffusion at constant diffusivity  $10^{-10} \text{ m}^2 \text{ yr}^{-1}$ ; we deliberately ignore the effect of layer thinning on this contribution, taking it as  $2D\Delta t$ , to overestimate the total  $\sigma$ . This second calculation conservatively constrains the maximum sulphate diffusion length to be 1.8 cm at 1.5 Ma (2 cm if made for 2 Ma).

These diffusion length results for EDC and Little Dome C (Figs. 10 and S3) pertain only to sulphate signals that entered the ice column at the top and underwent diffusion and shortening, not to signals produced or modified by other processes (e.g. the anomalous deep peaks described in Sect. 1), to which the concept of diffusion length may not apply.

Estimating the sulphate signal survival for ice-core sites outside the Dome C region is not attempted, as it requires specific knowledge about their diffusivity profiles or bolder assumptions (than for Little Dome C) to be made for those profiles.

## 5.2 Future research

The fast sulphate diffusion in EDC firn discovered by us, which has not been recognised before, motivates enquiry into its origin and a wider study at multiple locations. Inversions should be made with high-resolution sulphate records from other ice cores from Antarctica and Greenland to see if they show rapid firn diffusion, and to study the factors behind the diffusivity, e.g., temperature and accumulation rate. In some of those exercises, signal diffusion in the firn might not be apparent from visual inspection of the observed firn peaks (e.g., our EDC record features only 8 major sulphate peaks in the firn, amidst diverse background fluctuations, that do not show a clear trend of amplitude decay); then, as in our study, the peaks far below the firn layer may prove to be instrumental for constraining the firn diffusivity via the memory effect. Also, our proposed mechanism for the firn – involving both  $\text{H}_2\text{SO}_4$  vapour diffusion in firn air and the assumed availability of sulphuric acid on grain surfaces (Sect. 4.1) – needs to be tested by in-situ chemical analysis in the field or laboratory experiments on firn samples. The inversion and measurement results will help us model the depth variation of  $D$  in the firn at a level of sophistication like in the Whillans and Grootes (1985) isotope diffusion model.

Another avenue concerns the grain-scale mechanisms of ionic impurity transport in polycrystalline ice, which are critical for understanding post-depositional signal alteration on ice-core records and are a known stumbling block (Stoll et al., 2021; Ng, 2021; R2024 and F2024). Although our work in Sect. 4.2 shows that we can begin to estimate the diffusivity contributions of component transport mechanisms, the partitioning of impurity to different sites and how impurity transfer between them occurs and alters the partitioning – and thus the bulk-signal diffusivity – remain poorly understood. There is also possibility for signal modification by mechanisms involving more than just diffusion, e.g., reactions between different compounds or between dissolved ions and dust particles. It is enticing to build theoretical models for all these processes, but we need abundant

microscale observations of the impurity distribution to inform the effort. For sulphate, it is hoped that the LA-ICP-MS mapping of S (Bohleber et al., 2025) will soon be used to analyse much more of the length of the EDC core with dense sampling, including stretches across peak signals. The results will yield high-resolution data on dust distribution and grain size as well, which can help us understand what governs the decay on the  $D$  profile and refine our interpretation in Sect. 4.2. Accurate experimental data on the low-temperature molecular diffusivities of different ions (not limited to sulphate) in monocrystalline ice, in water and at grain boundaries are also highly desirable.

A separate challenge is to extend our inversion theory to non-steady state conditions, where the vertical profiles of  $D$  and  $\dot{\epsilon}_z$  evolve with time (over glacial–interglacial time scales) as a result of climatic forcing that influences the physical properties of the ice from different periods. Such work can shed light on which of the shorter fluctuations in the effective diffusivity  $D_R$  (as discussed by R2024) reflect true diffusivity variations and how to retrieve them by inversion.

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## Code and data availability

The EDC sulphate signal data used by us come from Fudge et al. (2024) and Rhodes et al. (2024). Our computed results in Figs. 4, 6–10, and S3 are archived at <https://doi.org/10.15131/shef.data.29015291> (Ng, 2025).

## Author contribution

FSLN formulated the theory, performed the calculations with data provided by the other authors, and wrote the manuscript. RHR, TJF, and EWW contributed knowledge and ideas to the analyses and interpretations and helped shape the paper’s messages.

## Competing interests

TJF is an editorial board member of The Cryosphere.

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975 **Appendix A**

Table A1: Key mathematical symbols in our model.

| Symbol | Meaning                                                                                     |
|--------|---------------------------------------------------------------------------------------------|
| $a$    | Ice-equivalent accumulation rate (m/yr)                                                     |
| $c_B$  | Impurity bulk concentration (amount per volume), i.e., $c_B = \rho C$                       |
| $C$    | Impurity bulk concentration ( $\mu\text{g kg}^{-1}$ , or $\mu\text{g L}^{-1}$ of meltwater) |
| $d_g$  | Mean grain diameter                                                                         |
| $D$    | Local or true diffusivity of sulphate signals ( $\text{m}^2 \text{yr}^{-1}$ )               |

|                     |                                                                                         |
|---------------------|-----------------------------------------------------------------------------------------|
| $D_{\text{bn}}$     | Signal diffusivity in the grain-boundary network                                        |
| $D_{\text{c}}$      | Corner diffusivity value on $D(t)$ profile                                              |
| $D_{\text{eff}}$    | Effective diffusivity                                                                   |
| $D_{\text{gb}}$     | Molecular diffusivity i grain boundaries                                                |
| $D_{\text{E}}$      | Effective diffusivity from signal-gradient based inversion (corrected value)            |
| $D_{\text{F1}}$     | Effective diffusivity from peak-width based inversion                                   |
| $D_{\text{F2}}$     | Effective diffusivity from signal-gradient based inversion (Barnes et al., 2003)        |
| $D_{\text{R}}$      | Effective diffusivity from peak-amplitude based inversion                               |
| $D_{\text{res}}$    | Residual diffusivity from stochastic motion of veins and grain boundaries               |
| $D_{\text{s}}$      | Solid-state diffusivity in ice grains                                                   |
| $D_{\text{vn}}$     | Diffusivity of vein impurity signals (“Gibbs–Thomson diffusivity”)                      |
| $k^*$               | Signal wavenumber                                                                       |
| $\bar{m}$           | Signal mean absolute gradient                                                           |
| $p_{\text{v}}$      | H <sub>2</sub> SO <sub>4</sub> vapour pressure in firn air                              |
| $S$                 | Thinning factor in the ice column                                                       |
| $t$                 | Age                                                                                     |
| $t_{\text{c}}$      | Corner age value on $D(t)$ profile                                                      |
| $\mathbf{U}$        | Firn velocity vector, = ( $U$ , $V$ , $W$ )                                             |
| $\bar{W}$           | Mean destrained wavelength of signals                                                   |
| $z$                 | Depth below a material horizon                                                          |
| $Z$                 | Depth below the ice-sheet surface                                                       |
| $\alpha$            | Relative signal peak amplitude (ratio of observed amplitude to reconstructed amplitude) |
| $\beta$             | Relative signal peak width (ratio of observed width to original width)                  |
| $\dot{\epsilon}_z$  | Vertical strain rate                                                                    |
| $\zeta$             | Destrained or unthinned thickness                                                       |
| $\eta$              | Variable of integration                                                                 |
| $\rho$              | Firn density (surface value $\rho_0$ , where $\rho_0/\rho_i \sim 0.4$ )                 |
| $\rho_i$            | Ice density (917 kg m <sup>-3</sup> )                                                   |
| $\sigma$            | Standard deviation of Gaussian signal or Johnsen’s (1977) diffusion length              |
| $\tau$              | Transformed variable in Sect. 2 (proxy of age or time)                                  |
| $\psi$              | Dilated age                                                                             |
| $\Omega_{\text{a}}$ | H <sub>2</sub> SO <sub>4</sub> diffusion coefficient in firn air                        |

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## Appendix B: Estimating the wavenumber $k^*$

Barnes et al.'s (2003) formula for  $k^*$  uses the mean absolute variation  $V$  of the demeaned, preprocessed and unthinned signal:

$$V = \frac{1}{L} \sum_{i=1}^n |C_{p,i} - \bar{C}_p| \Delta \zeta. \quad (\text{B1})$$

For a triangular signal of height  $h$  (Fig. B1), they state the result in Eq. (31), which is equivalent to  $\bar{w} = 4V/\bar{m}$ , where  $\bar{w}$  is the (mean) signal wavelength. Then they calculate the wavenumber with  $k^* = 2\pi/\bar{w}$ . In contrast, our study of this signal gives  $V = h/4$  and mean absolute gradient  $\bar{m} = 2h/\bar{w}$  and hence a different result:  $\bar{w} = 8V/\bar{m}$  – this finding holds also for an asymmetric triangular signal. A sinusoidal signal may also be considered, e.g.  $A \sin(2\pi\zeta/\bar{w})$  (Fig. B1). In this case, we find  $V = 2A/\pi$  and  $\bar{m} = (2\pi A/\bar{w}) |\cos(2\pi\zeta/\bar{w})| = 4A/\bar{w}$ , so  $\bar{w} = 2\pi V/\bar{m}$ . Consequently, Barnes et al.'s  $\bar{w}$  is too small – and their  $k^*$  too large – by 2 times for a triangular signal and  $\pi/2$  times for a sinusoidal signal. Real signals are typically non-periodic and different from these idealised waveforms, so  $k^*$  is overestimated by  $\approx 1.57$ –2 times and  $D_{\text{eff}}$  underestimated by  $\approx 2.47$ –4 times in the Barnes et al. (2003) method.

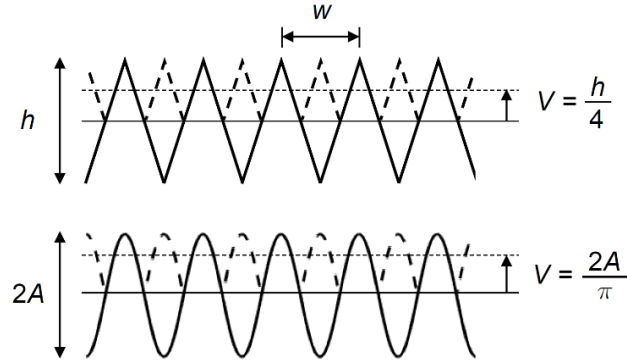


Figure B1. Test waveforms for deducing the relationship between signal height, wavenumber and mean absolute gradient.

### Appendix C: Models of solid-state diffusivity $D_s$ , vein-signal diffusivity $D_{vn}$ , and residual diffusivity $D_{res}$

995 The sulphate diffusivity in monocrystalline ice has not been determined experimentally, as far as our literature search suggests. As described in the text, we approximate it by the  $H_2O$  self-diffusivity in monocrystalline ice and use Ramseier's (1967) empirical formula,

$$D_s = 9.1 \times 10^{-4} \exp\left(-\frac{7.2 \times 10^3}{T}\right) \text{ m}^2 \text{ s}^{-1}, \quad (C1)$$

where  $T$  is temperature in Kelvin. F2024 referred to the same approximation when qualitatively comparing their effective  
1000 diffusivities to the solid-state diffusivity.

According to Eq. (23) of Ng (2021), the bulk diffusivity of ionic signals in a connected vein network in ice is given by

$$D_{vn} = \frac{D_l \gamma T_0}{6 \rho_i L d_g} \sqrt{\frac{3 \alpha_0}{c_B \Gamma (T_0 - T)}}, \quad (C2)$$

where  $D_l$  is the sulphate molecular diffusivity in water,  $c_B$  is the sulphate bulk concentration (by volume) in the ice, and  $d_g$  is the mean grain diameter. Equation (C2) includes a factor of 1/3 to account for random orientation of the veins in three  
1005 dimensions. As described in Sect. 4.2, we evaluate Eq. (C2) for  $c_B$  from 1 to 10  $\mu\text{M}$ , using temperature and grain size data from EDC (Fig. S1). The following parameters from Ng (2021) are used: the reference melting point  $T_0 = 273.15$  K, Gibbs–Thomson coefficient  $\gamma = 0.034$  J  $\text{m}^{-2}$ , latent heat of melting  $L = 333.5$  J  $\text{kg}^{-1}$ , vein cross-section geometrical factor  $\alpha_0 = 0.0725$ , and liquidus slope  $\Gamma = 4.53$  K  $\text{M}^{-1}$  for the sulphate– $H_2O$  system. Since empirical data for  $D_l$  below 0 °C are lacking, we approximate it with the molecular diffusivity of water by using Eq. (A1) of Ng (2023), which is valid down to –60 °C and  
1010 agrees with the laboratory measurements of  $D_l$  for sulphuric acid in water from 0 to 35 °C (Umino and Newman, 1997) to within a multiplicative factor of  $\approx \pm 2$ .

Finally, for the “residual diffusivity” due to stochastic vein and grain-boundary motion, we use Eq. (9) of Ng (2021),

$$D_{res} = K_0 \exp(-Q/RT) / 3c_1, \quad (C3)$$

taking (as he did)  $c_1 = 2.5$ , the grain-growth rate coefficient  $K_0 = 1.68 \times 10^7$   $\text{mm}^2 \text{ yr}^{-1}$ , activation energy  $Q = 42.4$  kJ  $\text{mol}^{-1}$ ,  
1015 and the gas constant  $R = 8.314$  J  $\text{K}^{-1} \text{ mol}^{-1}$ . Our models for the Gibbs–Thomson diffusion and residual diffusion encompass the two earlier grain-growth dependent models of ionic impurity diffusion by Barnes et al. (2003).