New estimates of sulfate diffusion rates in the EPICA Dome C ice core

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The manuscript reports on a detailed examination of volcanic sulfate peaks through a 450 kyr record from the EPICA Dome C ice core. Such compositional inputs are characterized as relatively high amplitude, short duration events; yet in older, deeper ice the amplitudes of recovered signals are observed to decrease and their apparent durations are extended by post-depositional processes. The authors' analysis points to a median effective diffusivity in Holocene ice that is somewhat higher than that found in early work by Barnes et al. (2003), but the median diffusivity in older ice is considerably lower and interpreted by the authors to possibly be caused by a switch in diffusion mechanisms, as might be expected from a change in impurity locations within the polycrystalline microstructure. This careful and interesting study will be of considerable interest for its importance in cataloging the post-depositional alteration of soluble impurity anomalies, thereby influencing future interpretations of soluble impurity records in older ice cores. The scientific approach and applied methods appear to be well-considered and the results and conclusions are presented in a balanced and clear manner. Following minor revisions, I anticipate that the manuscript will be ready for publication. I offer several comments below for the authors' consideration, with a view to clarifying some of their reasoning and encouraging firmer connections to the physical processes involved.

The discussion of previous theoretical results in the introduction is appropriately concise, but might be altered slightly to some benefit. On line 45, the 50 cm displacement noted in the abstract of the paper by Rempel et al. (2001) is quoted without sufficient context to enable the reader to understand the conditions that led to that particular figure, which applied to ice of Eemian age in the GRIP ice core. Since that theory would predict different displacements in the EPICA Dome C core at different depths, I'd suggest rewording to something like: "The implication was that a chemical signal of Eemian age in the GRIP ice core ...". Regarding the following sentence, a half meter doesn't seem like much in a >2 km deep core, so it isn't clear whether the consequences for cross-matching events between ice cores for stratigraphic purposes would in fact be "major", or typically quite minor – perhaps the adjective should be removed. On line 50, the claim is made that Ng's (2021) modified theory would prevent such compositional displacement, but destroy the chemical signals over time. This would be somewhat unsatisfying given that chemical

signals clearly persist for long durations, but Ng does show that deep signals can remain intact if the effective diffusivity is reduced or if spatial variations in grain size are invoked. I'd suggest appending the sentence with something like: "… they will be destroyed over time if they are free to diffuse unimpeded through connected veins into adjacent low concentration regions."

The differences between the Rempel and Ng treatments are not central to this manuscript, but as the former model is disregarded following the opening sentences of this paragraph, for further context I think it worth clarifying my own understanding of the primary difference between these formulations. Rempel et al. (2001) did not, in fact, ignore the Gibbs–Thomson effect, but instead made a particular (possibly naive) assumption regarding the relationship between impurity loading and grain size, or more precisely vein density (length of veins per unit volume). Citing the laboratory work of Mader (1992) and the theoretical treatment of Nye (1989), they reasoned that surface energy (i.e. the Gibbs–Thomson effect) would cause vein radii to evolve quickly towards a uniform value and that reported anti-correlations between grain size and impurity loading at GRIP are consistent with expectations if vein radii vary only over length scales that are much greater than those over which the bulk concentration of dissolved solutes vary. Notably, they did not explicitly treat the evolution of vein density (or crystal size) in their model, but application of their key uniform-vein-radius assumption would imply that the slow temporal variations in liquid fraction associated with the gradual displacement of bulk impurity signals that they predict requires vein density (and likely crystal size) to evolve at commensurate rates. In contrast, Ng (2021) argued that a physical mechanism for producing variations in vein density with impurity loading of the particular type assumed by Rempel et al. (2001) is both lacking and unlikely (for example, the cited study by Durand et al, 2006 argues against a causal relationship between grain size and soluble impurity content; I'm not aware of published empirical efforts to systematically quantify vein density as a function of bulk concentration at the scale of volcanic anomalies). In his preliminary model development, Ng (2021) assumes that vein density is effectively uniform or varies only much more gradually with depth than do compositional signals (i.e. the opposite assumption to that made by Rempel and coauthors). With bulk composition and vein density controlled by separate mechanisms in Ng's model (e.g. in illustrative calculations vein density is almost spatially uniform, with only extremely gradual changes promoted by grain growth over time), bulk concentration gradients lead to signal diffusion and destruction over time, as you note. This happens because the larger vein radii that are present where bulk concentration is higher gradually diminish in size as solute diffuses and enlarges vein radii in adjacent ice – evolving towards the uniform value for vein radius that Rempel et al. (2001) had assumed to be maintained instead through vein density (e.g. crystal size) changes. Ng also demonstrates the effects of alternative patterns of imposed crystal size (i.e. vein density) variation that can produce spurious peaks in bulk concentration. Importantly, since no feedback between vein density and bulk concentration changes is contained in Ng's model, impurity anomalies are effectively constrained to remain in high vein-density regions without a tendency

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for the post-depositional translation that the Rempel et al. (2001) model predicts. To summarize: if vein density were to evolve in such a way as to keep vein radius constant, Ng's model would predict the same result as Rempel et al. (2001) – translation with negligible signal diffusion. Absent such fortuitous changes, Ng's model predicts ongoing signal diminishment and their evident resilience in ancient ice requires some other mechanism for retarding such changes – like disconnected veins or significant impurity loading within crystal interiors.

This has been a rather verbose digression. Perhaps rather than saying that the Gibbs–Thomson effect was neglected, it would be more correct to say something along the lines of: "... challenged the impact of this phenomenon by noting that since soluble impurity content appears not to exert a dominant control on ice grain size (e.g. Durand et al., 2006) and by extension, vein density, the Gibbs-Thomson effect should cause vein radii to adjust by producing solute concentration gradients that diminish bulk concentration anomalies."

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

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

I found the theoretical development in sections 3.2 and 3.3 somewhat confusing. The standard convention in the modeling literature with which I am most familiar is to treat equations as portions of sentences, with appropriate punctuation (e.g. see Ng's 2021 paper). Instead, here you refer to the equations by number, and subsequently separate them out from the text. To me, this seems disjointed. For example, I would favor a modification of the beginning of 3.2 to something like: "For a Gaussian function with standard deviation σ, the Full Width at Tenth Maximum is given by

$$FWTM \approx 4.292 \times \sigma \;, \tag{1}$$

while the area under a peak of height h is

$$A \approx (h \times \sigma)\,/0.3989 \;, \tag{2}$$

so that

$$A \approx h \times FWTM/1.712 \ . \tag{3}$$

In equations (6) and (7) you note that the effective diffusivity is expected to be a function of time. However, my understanding is that your model calculations in fact treat the diffusivity as constant through time – is this correct? It wasn't immediately obvious to me how equation (12) came about and why there is no explicit dependence on time. Indeed, a is really a rate, so I believe at/H is needed in the argument of the exponential to ensure dimensional correctness, and integration of (9) would produces this result following correction of a sign error.

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

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

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

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