Interactive comment on “Methanesulfonic acid (MSA) migration in polar ice: Data synthesis and theory” by Matthew Osman et al.

Anonymous Referee #2

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Dear Anonymous Referee #2,

We thank you for your valuable feedback. We have reviewed all your comments/suggestions, and have attempted to address each to the best of our ability below. For convenience, your comments are reproduced below, our replies to them are in italics, and revised excerpts from the manuscript are noted between double quotes.

The manuscript by Osman et al describes a very detailed study on the migration of MSA in ice cores. A crucial finding is correlation between the depth at which migration is observed and the accumulation site, asking for caution when concluding the absence of MSA migration in short cores. Further, the role of a number of physical parameters and processes on MSA migration is discussed in detail, it turns out that accumulation rate is an important one. Last but not least, diffusivity coefficients are suggested based on detailed modelling work on a high resolution ice core. I’m impressed how the study combines expertise in ice core analysis with fundamental physical chemistry. Therefore, it is of paramount interest to a wide scientific audience. The manuscript is very long due to the wealth of information and the careful and precise description of the analysis. It reads very charming, the conclusions are well justified, and assumptions and uncertainties in the analysis are openly mentioned. I refrain from recommending immediate publication, because I need clarification regarding the fundamental aspect in discussing and applying the phase diagrams. These fundamental details are directly linked to the conclusion of the manuscript and one of the questions raised in the introduction “Why should MSA in particular exhibit migrations, while associated soluble impurities and acids do not?”.

My concern comes down to the point, that I can’t follow how the impurity transport model by Rempel as presented in the manuscript leads to a transport from summer to winter layers via concentration driven diffusion. I can think of two scenarios:

(C1) At T above -20°C, isolated patches of NaCl (winter) and NaCl/MSA (summer) solution form. If temperature increases, volume of the liquid brine increases. At a specific T the two patches might meet. If they do not mix, MSA will diffuse from summer to winter resulting in a constant concentration. On first approximation NaCl might have the same concentration in both patches, so it does not diffuse. This scenario will not build up a new peak at the winter location in the core, but rather smooth the MSA over the whole year.

As per the model by Rempel et al. (2002) and its linearized form presented in the manuscript, the movement of MSA is not only driven by its own concentration gradient but also by the concentration gradients of other species, such as Na^+. This is particularly clear in the linearized model, where MSA migration is shown to be the sum of (i) Fickian diffusion along the MS^- concentration gradient and (ii) an effective advection driven by the vertical variations in Na^+ concentration (eq. 13). As shown by the formal development in Section 4.3 of the manuscript (eq. 13 in particular; Page 23, line 4) and illustrated in figure 11 of the manuscript, any local maxima present in a layer where Na^+ shows a *unique maximum will be carried to the level of the [Na$^+$] maximum. It is an advective effect, fundamentally different from the smoothing effect expected from Fickian diffusion with constant diffusivity.*

If [Na$^+$] is uniform over the thickness of an annual layer, then the advective effect on MSA migration will vanish, and MS$^-$ will simply diffuse along its own concentration gradient and not show concentration peaks, as correctly pointed out for the Reviewer. However, [Na$^+$] is not observed to be uniform over an annual layer in ice cores (as illustrated in this study as well as in many others), most likely because of the high-frequency (i.e., sub-annual) variability of Na$^+$ deposition. As such, this scenario is currently untested.

(C2) At T between -75 and -30_C (MSA is still in solution, but NaCl and NaMS are solid). Thus a liquid patch at summer location holding only MSA will form. If that spreads or moves it might meet NaCl crystals. There, crystallisation of NaMS could occur, which will built up a concentration gradient and lead to diffusion of more and more MSA towards the winter layer. This might indeed lead to a complete shift of the MSA peak from summer to winter. But, is the diffusion of MSA in liquid rate determining, or the spreading/movement of the film, or the solution of NaCl, or the precipitation of NaMS? I attached a graph for illustration. It is very likely that I miss an important point here, but may I ask you to clarify the ultimate process in more detail?

We deeply appreciate your comment, in particular your taking the time to illustrate your point in a graph. As noted in the manuscript (Sect. 2.3), the hypothesis referred to in the comment was indeed initially speculated early on by Mulvaney et al. (1992) in their original study on the migration phenomenon, though these authors lacked empirical constraints on the eutectic temperature of the $CH_3SO_3Na{\cdot}nH_2O$ – H_2O system. We again agree with the Reviewer's intuition here, and thank him/her for turning us to this point, and particularly so as the comment cued us to a typo in the original document where we aimed to address (albeit less extensively) such a scenario. The typo was corrected, and a more explicit discussion on the matter was added to Sect. 5.1 of the manuscript (Page 27, lines 6-21 and page 28, lines 10-23):

(Page 27, Lines 6-21)

"In section 2.3, we tested the hypothesis that post-depositional formation of winter [MS$^-$] maxima occurs solely as a result of the precipitation of MS$^-$-salts from their grain boundary solutions in sea-salt rich winter layers (Mulvaney et al., 1992; Wolff et al., 1996; Kreutz et al., 1998, Pasteur and Mulvaney, 2000; Curran et al., 2002). This hypothesis, denoted below as the "Mulvaney model", suggests that MS$^-$ in under-cooled solutions should migrate along its concentration gradient via Fickian diffusion until reaching Na$^+$-rich layers, where crystallization of CH_3SO_3Na removes MS$^-$ from the premelt solution, thereby perpetuating a [MS$^-$] gradient between summer and winter layers in the residual premelt. Importantly, it suggests MSA migration would be inhibited at sites where in situ temperatures are greater than the eutectic temperature of $CH_3SO_3Na{\cdot}nH_2O$ – H_2O (-29.3˚C), since CH_3SO_3Na would not be precipitated from the premelt liquid. However, such an inhibition is not apparent in our data compilation (Sect. 2.3).

The RWW model (Sect. 4) is fundamentally different than the Mulvaney model. The RWW model does not represent crystallization and metathetic removal of constituents from the liquid phase (Sect. 2). Rather, in the RWW model, MS$^-$ is implicitly assumed to remain dissolved in the premelt liquid following migration from the summer to winter layers, provided in situ temperatures exceed the eutectic temperature of the binary system $CH_3SO_3Na{\cdot}nH_2O$ – H_2O.

…

(Page 28, Lines 10-23)

A currently poorly constrained situation arises for sites characterized by in situ temperatures less than ~ -30˚C and greater than -75˚C (Table 2) In this temperature regime, MSA remains in solution while Na^+ is presumably immobile, either as solid state NaCl, CH_3SO_3Na, or Na_2SO_4 (Table 2). MSA migration as envisioned in the Mulvaney model, but not in the RWW model, may operate under such conditions. On the other hand, the Mulvaney model may not apply should summer concentrations of Na^+ be high enough to sequester a large fraction of the $[MS^-]$ as CH_3SO_3Na (s) in summer layers. This sequestration process appears supported by the lack of discernable MSA migration in the subannually-resolved portion (i.e., down to ~ 10.5 m) of the $[MS^-]$ record from South Pole (SP-95), where annual mean SAT is -51˚C (Meyerson et al., 2002). While SP-95 is not considered in our data compilation due to the site's low $\dot{b}$ (0.08 m w.eq. yr^{-1}), the lack of clear MSA migration at SP-95 departs from the expected relationship found between $\dot{b}$ and z_{f0} in Antarctica (Sect. 2.1; Fig. 2). This observation leads us to speculate that MS^- at SP-95 may be immobilized in the summer layers through a metathesis reaction with Na^+ allocated to the grain boundaries."

(C3) As a third option, could MSA also be pushed into the gas phase from solution and be transported by gas-phase diffusion? May I ask you to comment on this aspect. (M. H. Kuo, S. G. Moussa and V. F. McNeill, Atmos. Chem. Phys., 2011, 11, 9971–9982.)

The model presented by Kuo et al. (2011) contrasts loss processes of soluble and volatile impurities by modeling the solubility of the impurities in the solid (ice crystal) water phase and (or) their release to the gas phase during surface melting (i.e., at the grain boundary-vapor interface). We envisage that these processes may be relevant in near-surface (nominally, <1-2 m depth) layers of the polar firn pack, where snow-density is low (effective porosity is high, allowing increased volatile loss through the interconnected pore space of ice grains; Wolff et al., 1996; Domine et al., 2008; Bartels-Rausch et al., 2013) and thermal fluctuations rather extreme (via diurnal, seasonal cycles). These surficial processes thus appear to be useful in predicting the mass conservation of originally-deposited MS^- at some sites. However, as the mechanism of MSA migration explored here appears to be primarily limited to depths deeper than 2 m (Sect. 2), we assume in the manuscript that this volatile post-depositional redistribution plays a negligible role in MSA migration below 2 m. Indeed, empirical evidence by Weller et al. (2004) suggests that, whereas volatile losses of MS_- (as well as NO_3^-) can be severe in the upper 1.2-1.4 m of the snow and (or) firn layer at low accumulation sites (<0.10 m w.eq. yr^{-1}), such losses (and gaseous-redistribution) are found to be negligible below this depth. These authors attributed the losses in the upper layers jointly to volatile acid formation in acidic (summer) snow layers that can be partially remitted to the atmosphere, a process akin to that described in depth by Kuo et al. (2011). We have included the following text (Page 5, Lines 10-15) making it explicit that we assume no vertical volatile redistribution of MSA:

"Post-depositional surficial losses of MSA may occur via gaseous diffusion in the top 1-2 meters of the firn at low accumulation sites (Wagnon et al., 1999, Delmas et al., 2003, Weller et al., 2004). As a result, we exclude records from sites where annual mean accumulation rate is less than 100 kg m^{-2} yr^{-1}, and assume that vertical redistribution of MSA via gas-phase diffusion (Kuo et al., 2011) is negligible at all considered sites and depths"

(C4) Second, I would like to read more about the grain boundary network along which migration

of the MSA takes place. A) What is the crystal size, grain boundary density at the position where MSA migration is observed? B) The diffusivity that is discussed is then an effective diffusivity in a porous medium like water/sand or air/snow. When comparing diffusivity between different ice cores or between single crystals and ice cores the grain boundary density (or its volume fraction) needs to be taken into account. I acknowledge that –taken the missing data- this is not possible, but would encourage a more detailed discussion on this issue (F. Dominé, M. R. Albert, T. Huthwelker, H.-W. Jacobi, A. A. Kokhanovsky, M. Lehning, G. Picard and W. R. Simpson, Atmos. Chem. Phys., 2008, 8, 171–208.)

Question A) To our knowledge, there is little empirical knowledge on the grain boundary density and crystal size at locations where MSA migration takes place. Thus while we acknowledge the importance of both parameters in acquiring an improved understanding of the migration process, we are severely limited in our ability to investigate this process more fully in this present study, and thus do not discuss further. We have now extended the discussion of Sect. 4.4 to make these points more explicit, namely with respect to constraining the MS^- diffusivity (Pg. 26, Lines 21-26; see Question B for denoted text).

Question B) We agree with the Reviewer that the MS^- diffusivity that is discussed in our manuscript should be regarded as an effective diffusivity. The revised manuscript includes a paragraph where this point is elaborated (Pages 26-27, Lines 17-29 and 1- 3):

"While the D_{MS} range estimated by a comparison to DIV2010 data is instructive, we note it is not necessarily universal, as diffusivities in polar ice are expected to vary in response to multiple glaciological factors. For example, the experimental results of Kim et al. (2008) show that the diffusion coefficients of ions in under-cooled mixtures are a function of both ionic concentration and temperature. Additionally, physical properties of the firn and ice, including porosity, grain-boundary density, and crystal size, may affect the partitioning of chemical impurities between the liquid premelt and the ice lattice (Dominé et al., 2008; Spaulding et al., 2011), thereby affecting the amount of impurities subjected to anomalous diffusion as well as the interconnectivity of the liquid premelt/vein network. While the RWW model can account for this partitioning (Rempel et al., 2002), the proportions of total MS^- and Na^+ that are present in liquid form remain poorly constrained (Sakurai et al., 2010). Even at a given site, seasonal and interannual variations in impurity concentrations may lead to down-core changes in D_{MS}. Finally, D_{MS} does not take into account whether MS^- migration is dominated by diffusion at two-grain boundaries, or at triple junctures and node networks (Wettlaufer and Worster, 2006, Riche et al., 2012). As a result of all these complicating factors, D_{MS}, as defined in the RWW model and constrained here, should probably be viewed as an effective diffusivity."

We thank the reviewer pointing us towards the study of Domine et al. (2008), which is now discussed/cited in the revised manuscript, shown above.

Minor comments

C5) Page 7 line 10 ff: Here I wonder, if the observation of MSA migration at these depths is a matter of time rather than ice density at that depth. Time is mentioned in the intro to this 2.1 but then I miss a discussion or final conclusion on time.

We have removed the mention of "time" in the introduction to Section 2.1 (Pg 6, line 15).

We consider the depth of first migration occurrence (z_{fo}), as opposed to the timing of first migration occurrence (t_{fo}), in Section 2 due to the relatively fewer assumptions and ambiguities associated with z_{fo} as opposed to t_{fo}. For example, t_{fo} could be reasonably defined either as the difference between the *surface age and the prescribed age at z_{fo}, or as the difference between the age at the threshold migration onset density (Sect. 2.4) and t_{fo}. While the latter is preferable in that it suggests the "true" timespan required for MSA migration, it also would require a clear understanding of the migration onset density and corresponding depth, which remains poorly constrained (see expanded discussion in Sect. 2.4). Finally, z_{fo} is impervious to age-depth error, whereas t_{fo} is not. As a result of these limitations, the occurrence of MSA migration is defined in terms of depth, not of time, in our analysis.*

C6) Page 18 line 4 ff: "The RWW model as applied to the binary system containing MS and NA+". This confuses me. The binary system is water-NaMS. Or, do we have a ternary system water-NaCl-MSA?

We thank the reviewer for pointing out this potentially confusing wording. No, we do not have a ternary system water-NaCl-MSA. In Sect. 4.2.2, we arrive at the conclusion that the binary system being modeled is indeed the $CH_3SO_3Na \cdot nH_2O\text{-}H_2O$ binary system, though we acknowledge the ambiguity of "binary" prior to this conclusion. We have removed "binary" from the noted sentence (page 18, line 6), and changed all other wordings to explicitly denote the $CH_3SO_3Na \cdot nH_2O\text{-}H_2O$ binary system when "binary" is indeed implied (e.g., pg. 21 lines 1-2).

C7) Connected to this: Page 19 line 10: How can an ion have a liquidus curve? The phase diagram is different for each counter ion.

*The parameters Γ_{MS} and Γ_{Na} may be taken as shorthand notations for Γ_{MS*} and Γ_{Na*}, where * represents an unknown cationic – anionic pair, respectively. Indeed, exploration of the likely cationic – anionic pair for MS- and Na+, respectively, forms the remainder of 4.2.2's discussion. Text has been added to express this "shorthand" notation explicitly (page 19, lines 17-19):*

*"Knowledge of Γ requires knowledge of the dominant precursor (bonded) molecular state(s) of the MS^- and Na^+ ions present in the ice (thus, Γ_{MS} and Γ_{Na} should be viewed as shorthand notations for Γ_{MS*} and Γ_{Na*}, where * represents some unknown cationic – anionic pair)."*

C8) Page 18 line 18: I suggest to add and discuss the work of Domine on diffusion in single crystals (E. Thibert and F. Dominé, J. Phys. Chem. B, 1998, 102, 4432–4439; F. Dominé and E. Thibert, J. Phys. Chem. B, 1997, 101, 3554–3565.) and discuss the role of grain boundaries with respect to diffusion in porous media in more detail (last point hold throughout the text).

We thank the Reviewer for pointing us to these studies. In the revised manuscript, we now cite and briefly summarize these two studies (page 18, lines 19-23):

"Notably, this estimate is 1-3 orders of magnitude larger than that reported for solid-state diffusion of HCl (Thibert and Dominé, 1997), HNO_3 (Thibert and Dominé, 1998), HCHO (Barret et al., 2011), and deuteriorated water (Lu et al., 2009) determined in single ice crystals, despite the molecular radius of MSA greatly exceeding that of each of these species (Roberts et al., 2009)."

I hope you find these comments helpful and I'm looking forward to your revised manuscript. Please also note the supplement to this comment: https://www.the-cryosphere-discuss.net/tc-2017-84/tc-2017-84-RC2-supplement.pdf

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