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

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Dear Dr. Rempel,

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

General Comments

The concentrations of trace constituents measured in polar ice cores record changes in conditions at the time of deposition at the glacier surface. However, there is clear empirical evidence (e.g. from anomalies of volcanic origin that exhibit increasingly gradual onsets with age, changing seasonality of MSA peaks) that some degree of post-depositional redistribution can take place. The current manuscript examines the movement of MSA signals in considerable detail with a combination of empirical data and theoretical analysis applied primarily to a new high-resolution dataset from the DIV2010 core. The results of this effort include important new constraints on the environmental variables that are most important for determining the depth at which significant MSA migration can take place, an informative linearized model that predicts the evolution of MSA concentration in response to the changes in liquid content imparted by seasonal variations in the impurity loading that are gauged by Na concentrations, and a new determination of the effective diffusivity of MSA that is held responsible for the concentration changes observed in the DIV2010 core. This represents substantial progress beyond previous understanding of impurity migration in polar ice, and will help in the interpretation and design of future sampling efforts.

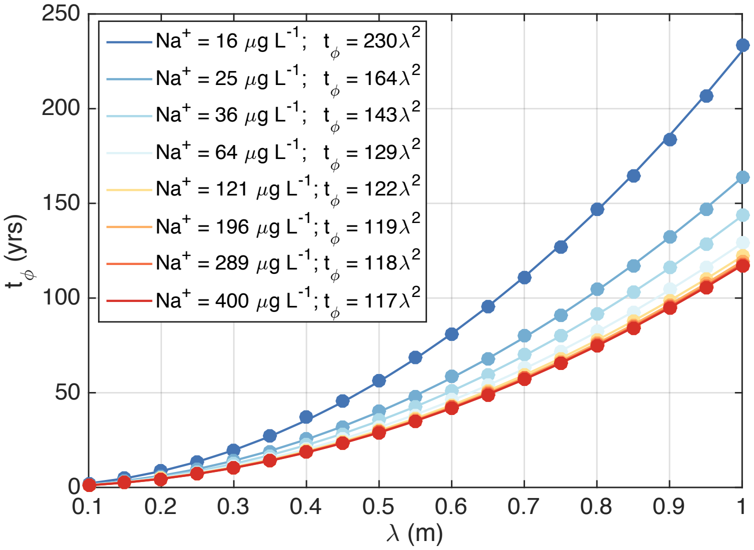
Specific Comments

C1) The manuscript is well organized and clearly written. I appreciated the examination of site-specific variables contributing to MSA migration, including regression analyses leading to best-fit relationships (figs. 2-4) with the depth at which migration is evident. If the authors could provide some further intuition for the source of the exponents in these power laws, this would be a useful addition to the synthesis subsection (2.5).

The power law $z_{fo} \propto \dot{b}^E$ *with E = 1.77 > 1 (Fig. 2) implies that the depth of first occurrence of MSA migration,* z_{fo}*, is more sensitive to annual mean accumulation rate,* $\dot{b}$*, for small* $\dot{b}$ *than for high* $\dot{b}$*. Interestingly, results from the model of Rempel et al. (2002) (section 5.3) leads to a power law between the time scale of MSA migration,* t_φ*, and the layer thickness over which the migration takes place,* λ *(see our new Figure 15, added to the main text and also appended below). That is,* $t_\varphi \propto= a\lambda^e$*, where* $e \approx 2$*. Thus, to the extent that* t_φ *and* λ *can be taken as surrogates for, respectively,* z_{fo} *and* $\dot{b}$*, the model results appear to be consistent with the data. The observed variation of the shallowest depth of MSA migration with accumulation rate would thus reflect the mere fat that, similarly to Fickian diffusion with constant diffusivity, the time scale for anomalous diffusion (*t_φ*) varies about quadratically with the thickness over which the diffusion takes place (*λ*). These points are now elaborated in the manuscript in Section 5.3 (Pages 31-32, Lines 27 and 1-5):*

"The nonlinear relationship found between z_{f0} and $\dot{b}$ (Section 2) is also worth further exploration. Results from the RWW model can be well-approximated by the power law $t_\varphi \propto \lambda^2$ (Fig. 15), which is reminiscent of the power law relationship $z_{f0} \propto \lambda^{1.77}$ derived from our data compilation (Fig. 2). The observed variation of the shallowest depth of MSA migration with accumulation rate would thus reflect the mere fact that, similarly to Fickian diffusion with constant diffusivity, the time scale for anomalous diffusion (t_φ) varies quadratically with the thickness over which the diffusion takes place (λ)."

(Page 52, Lines 1-6)



"Figure 15: The time required for approximate alignment of $[MS^-]$ and $[Na^+]$ maxima (t_φ) as a function of annual layer thickness (λ) for different layer averages of $[Na^+]$ and $D_{MS} = 10^{-11}$ m^2 s^{-1}. The various curves are the least-squares power law fit $t_\varphi = a\lambda^e$. The exponent e is estimated to about 2 for all values of layer-averaged $[Na^+]$ (note that the least squares power law fit for $D_{MS} = 10^{-12}$ m^2 s^{-1}, not shown, yields a value of a that is a factor of 10 higher than for $D_{MS} = 10^{-11}$ m^2 s^{-1})."

C2) The description of the DIV2010 MSA record and related variables in section 3 is succinct and informative. The mechanistic treatment of MSA migration is particularly clear and represents an important advance over earlier work, particularly by providing constraints on the effective diffusivity of MSA in the DIV2010 core. The value obtained for this key parameter is one or two orders of magnitude smaller than that typically used to describe compositional diffusion in pure water; this might suggest a significant role for motion along two-grain boundaries rather than only in the liquid veins that line triple-junctions and their associated nodes at 4-grain intersections. The authors appear to have made a conscious decision not to speculate on the details of the precise migration pathways, referring only to "grain-boundary" migration rather than specifying whether they expect the vein–node network or the two-grain boundaries to dominate. A brief comment on the distinctions between these possibilities might be of use for some readers.

We have added a clarifying statement along these lines to Sect. 4.4 (Pages 26-27, lines 28-29 and 1):

"…(our derived) D_{MS} does not take into account whether MS^- migration is dominated by diffusion at two-grain boundaries, or at the triple junctures and node networks (Wettlaufer and Worster, 2006, Riche et al., 2012)."

The paleoclimatic implications are well summarized in the final substantial section of the paper, prior to the conclusions.

Technical Corrections

C3) I didn't notice many typos or other technical issues requiring the authors' attention. The term "super-cooling" is used throughout, whereas previous authors have taken care to use "under-cooling" instead since super-cooling is most commonly used to refer to liquid in a transient, disequilibrium state.

All prior occurrences of "super-cooling" have now been changed to "under-cooling".

C4) Line 5 of page 27 repeats the word 'in' twice.

The typo has been corrected (pg. 27, line 19).

References

Riche, F., Bartels-Rausch, T., Schreiber, S., Ammann, M., and Schneebeli, M.: Temporal evolution of surface and grain boundary area in artificial ice beads and implications for snow chemistry, J. Glaciol., 58, 815–817, doi:10.3189/2012JoG12J058, 2012.

Wettlaufer, J. S., and Worster M. G.: Premelting Dynamics, Annu. Rev. Fluid Mech., 38(1), 427–452, doi:10.1146/annurev.fluid.37.061903.175758, 2006.