The Cryosphere
Discussions

Open Access

EGU

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

Anonymous Referee #2

Received and published: 27 July 2017

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 to the wealth of information and the carful 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:

(1) 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.

(2) 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 concertation 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? 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.)

Second, I would like to read more about the grain boundary net-work 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.)

Minor comments

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

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

Page 18 line 18: I suggest to add and discuss the work of Domine on diffusion in single crystals (E. Thibert, 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 througout the text).

I hope you find these comments helpful and I'm looking forward to your revised manuscript.