Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-1069-RC2, 2017

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Modeling the Physical Multi-Phase Interactions of HNO_3 Between Snow and Air on the Antarctic Plateau (Dome C) and coast (Halley)" *by* Hoi Ga Chan et al.

Anonymous Referee #2

Received and published: 20 February 2017

[Summary]

In this study, Chan et al. develop a set of process-oriented models in which the uptake and release of HNO3 from the surface "skin-layer" snowpack is simulated on the basis of "first principles" without employing additional tuning parameters from laboratory data. The reversible physical processes of surface adsorption/desorption, co-condensation with water vapor, solvation into the disordered interface (DI), solid-state diffusion into the core of ice grains and solvation into the micro-pockets of brine are formulated in the model, some of which are then turned on and off to identify the key process(es) involved in the incorporation of HNO3 into the surface snow in the Antarctic. By comparing their model results with observations of nitrate concentrations in the surface snow layer from

Dome C (high plateau) and Halley (coast) in the Antarctica, the authors conclude that the incorporation of HNO3 into the liquid-like DI is not a viable process. Although this appears to be one of the important results of the study, I have some difficulty in and/or objections to the rationale by the authors regarding the formulation of the HNO3 concentrations in the outermost layer of the snow grain, as detailed below. The authors also conclude that the incorporation of HNO3 at relatively warm temperatures (and yet below the freezing point) above the eutectic point(s) of the mixture(s) of ice and ionic impurities is accounted for largely by the micro-pockets of brine. This part of finding is quite convincing. I think the paper will merit publication in ACP once the authors have addressed the following concerns.

[Major comments]

1. Apparently, there is a loose interchange of what the grain-surface HNO3 concentration (HNO3 (surf)) represents while formulating the different processes involved/hypothesized in its determination. In Eq. (6) in Section 3.1.1, the authors simply take the sum of two terms, namely, the concentration due to surface adsorption (HNO3(ads)) and that due to co-condensation (HNO3(cc)). Although the unit of (HNO3(ads)) is carefully matched to allow this summation, I am not so sure if it is really legitimate to assume that all the surface-adsorbed HNO3 is automatically transferred into the bulk volume of the outermost solid-ice layer of the snow gain. It seems that the authors' claim for employing the first principles is partially broken here. Is it not more appropriate to assume that what happens on the surface stays on the surface and that [HNO3(ads)] is left out from Eq. (6)? I see the same problem in Eq. (12) in Section 3.1.2 where the authors assume that all the HNO3 dissolved in the liquid-like disordered interface (HNO3(DI)) is automatically transferred to the outermost solid-ice layer (HNO3(surf)). In my opinion, all these assumptions of automatic "phase" transfer (between the surface and the solid ice and between the liquid-like DI and the solid ice) should be adapted somehow to the one in compliance with the limitation of HNO3 solubility to the solid ice (Thibert et al., 1998). The authors run an alternative model by

calling it the “equilibrium approach”, which I think should be adopted as a base case except that kinetic aspects should be formulated into this version of the model.

2. The authors do not provide sufficient details about their model formulation of the disordered interface (DI) on the surface of the ice grain. How thick is the DI? Does the thickness of the DI change with temperature? Does it make sense to assume the fixed (constant) pH especially when the chemical composition of the DI is controlled predominantly by HNO3(gas) = H+(DI) + NO3-(DI) at Dome C? These are the critical points that should be discussed in detail before rejecting the hypothesis of the HNO3 incorporation into the DI.

3. It is not clear enough whether the kinetic limitation to the growth and decay of the snow grain HNO3 concentrations is caused mainly by mass transfer between the gas phase and the grain surface or by solid diffusion into the entire volume of the snow gain. This question should be discussed in some detail especially when contrasting the behavior of HNO3 between the “kinetic” and “equilibrium” approaches such as in Section 6.1. Also, the authors may want to refer to the work by Bock et al. (2016) on the matter of timescales due to various kinetic processes.

4. I am puzzled by the description of the rate of snow grain growth and shrinkage in Section 3.1.1. Eq. (9) implies that the change of the snow grain volume is calculated by the molecular diffusion of water vapor through its microscopic concentration gradient around the snow grain. But then the authors admit that this approach does not work owing to the input data limitation and instead “the macroscopic (few mm) water vapour gradient across the skin layer was used to estimate the condensation and sublimation processes”. Is the same equation still used for calculating dV/dt? In Sections 4.1 and 4.2, the authors state that meteorological input data have been obtained at 1.6 m and 1 m above the snow surface at Dome C and Halley, respectively. Is it then assumed that the water vapor concentrations are assumed to be constant with height between a few mm and 1-1.6 m above the snow surface? Please clarify. Also, is it possible to validate the authors’ macroscopic approach of calculating the water vapor flux by

field observations if any? This seems to be important as background information for discussing the role of co-condensation in Section 6.2. By the way, I think R_{eff} in Eq. (9) should be squared to be consistent in the physical dimension between LHS and RHS of the equation. Is it simply a typographic error?

5. The authors adopt the formulation of the α_0 (Hudson et al., 2002), N_{max} (Crowley et al., 2010) and K_{eq} (Burkholder et al., 2015) from different sources. In fact, all of these could have been adopted from Crowley et al. (2010). It seems appropriate to discuss why the authors pick their experimental values/formulae from the different sources and how much difference their choice would generate in the model behavior.

6. The quality of English needs to be improved significantly. There are so many grammatical and spelling errors, only a tiny part of which I can comment below as technical suggestions. This problem is really glaring but may be largely corrected by a copy-editor once the manuscript is accepted for publication. Nonetheless, there seems to be a room for improvement that should be addressed by the authors before that stage. I strongly recommend careful and diligent proofreading by the team of the authors (especially if the editor asks another round of review).

[Minor comments]

1. I think that “T – Tf” should be reversed to “Tf – T” in Eq. (4) to let $\phi_{H2O}(T)$ be the positive values. And I think that this inherits from what I believe is a typographic error in Cho et al. (2002) cited for Eq. (4). Am I wrong? Please double check.

2. The variable “z” refers to the distance from the snow grain surface in Eq. (9), whereas it refers to the depth in the snowpack in Eq. (11). Please adjust the notation to avoid confusion between the two.

3. On Line 92, it is stated that “thickness of the DI” is a tuning parameter in Toyota et al. (2014). In fact, they calculate the thickness of the DI on the basis of the Cho et al. formula, which is used by the present authors for calculating the volume of the micro-

pockets of brine. The difference from the present study is that Toyota et al. assume the brine covers the entire surface of the snow grain just like the DI.

4. On Line 255, it is stated that "Dg is the gas-phase diffusivity". It should be stated clearer that Dg is the gas-phase diffusivity of HNO3. It would also be nice to list how Dg is calculated in Table A1.

5. Lines 615-616: It appears to me in Figure 1 that the changes in pH of the order of 1 have a similar level of impact on the effective Henry's law coefficient to the changes in temperature of the order of 10 K. I don't quite understand what the authors try to point out here.

6. Lines 558-562, "…, which are 1-2 orders of magnitude higher than the averaged modelled temperature gradient (listed in Sect. 3.1.1)": It seems that this is not discussed/listed at all in Section 3.1.1. Please expand the discussion by referring to what the realistic range of the vertical temperature gradient should be.

7. Lines 625-631 and Figure 11: Please be more specific and detailed about what make up the "other ions".

8. Table A1: Sander (2015) is a compilation of Henry's law coefficients, but here it is cited for the temperature dependence of alpha. Please double check if it is the correct reference. Also, the "enthalpy of activation" is much too vague as terminology for $\Delta_{obs}H$. Please expand.

9. Table A1, values of $\Delta_{sol}H$ and $\Delta_{obs}H$: I think they should have been -72.3 and -44, respectively (the minus sign is missing). Please double check.

10. Table A1, footnote i: I suppose that the authors meant to formulate the temperature dependence of alpha somehow consistently with $d\ln[\alpha/(1-\alpha)]/d(1/T) = -\Delta_{obs}H/R$ (e.g., Jayne et al., 1991). But I cannot reconcile with the authors' formulation in this footnote. Am I wrong here? Please double check if it is formulated properly.

[Technical suggestions]

Line 216: d HNO3 / dt -> d [HNO3(ads)] / dt

Line 217: Substituting k_{ads} -> Substituting k_{des}

Line 321: organic -> inorganic (?)

Line 407: tough -> trough (?)

Line 414, Eq. (19): MM_{H2O} -> M_{H2O}

Line 603: … varying T_0 by 4 K up to 242 K and pH by ± 0.4 up and down between 5.2-6.4

Figure 1: Add the unit of temperature for the figure legends in (b): "T = 230 K", etc.

Figure 10: Is it not possible to use the same scaling in Y-axis for all the data shown here, for example, by using logarithmic scaling?

Table A1: Accommodation coefficient at standard temperature -> Accommodation coefficient at reference temperature (220 K)

Table A1, footnote ii: 258 K -> 298 K (?)

[Reference cited in my comments but not listed in the manuscript]

Jayne, J. T., Duan, S. X., Davidovits, P., Worsnop, D. R., Zahniser, M. S., and Kolb, C. E.: Uptake of gas-phase alcohol and organic acid molecules by water surfaces, J. Phys. Chem., 95, 6329-6336, 1991.

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