

## ***Interactive comment on “Modeling the Physical Multi-Phase Interactions of HNO<sub>3</sub> Between Snow and Air on the Antarctic Plateau (Dome C) and coast (Halley)” by Hoi Ga Chan et al.***

**Anonymous Referee #1**

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In this work, Chan et al examined the physical exchange of HNO<sub>3</sub> between the surface snow and the air above in the Antarctic Plateau, using a newly developed model framework. Snowpack is a complex multiphase system and to this day the air-snow interactions remain poorly understood (Domine et al 2013; etc). A better understanding of the physical and chemical processes in snow is in crucial need in order to evaluate the broader impacts of snowpack on the overlying atmosphere. Overall, I find the topic is of interest to the community and this study merits publication in Atmospheric Chemistry and Physics, once the following points have been addressed.

My main concern about this work is the lack of a clear description of the mass transfer between the atmospheric nitrate above snowpack and the nitrate concentration in the

C1

surface skin layer of snow.

(1) Atmospheric nitrate (gaseous HNO<sub>3</sub> + particulate nitrate) is assumed to be dominated by gaseous HNO<sub>3</sub> (which is supported by previous studies). In this work, the physical exchange of gaseous HNO<sub>3</sub> in the snow interstitial air (SIA) and the snow grains is described explicitly by different models. However, the mass exchange of HNO<sub>3</sub> between the SIA and air above snow (where the atmospheric nitrate is measured) is missing. Mass exchange between the SIA and air above snow is largely controlled by processes such as turbulent transport and wind pumping. How these processes would affect the bulk nitrate in the skin layer of snow needs to be clearly addressed.

(2) Model 2 incorporates the micro-liquid pocket. This topic is of great interest since the brine formed by impurities may not cover the entire grain surface due to limited wettability at cold temperatures. However, instantaneous air/micro-liquid pocket equilibrium is assumed. This seems to be oversimplified. For highly soluble species such as HNO<sub>3</sub> in liquid water (effective Henry's law constant > 10<sup>14</sup> M atm<sup>-1</sup>, Fig 1), interfacial transport or even gas diffusion (in this case, gas diffusion in the SIA) may well become the rate limiting steps. The timescale of the SIA/micropocket equilibrium needs to be examined before assuming equilibrium.

(3) From the model point of view, Model 2 does not really specify or depend on the location of liquid water, i.e. whether the liquid water is covering the whole/part of the grain surface as a thin layer, or is located in grooves at grain boundaries and triple junctions. It appears mathematically that, in Eq(4) + Eq(17), only the liquid water content matters while the location of liquid water does not.

(4) The authors claim that the physical exchange models are based on “first principles” (what exactly are first principles btw) and hence without requiring any tuning parameters. This seems not true: some parameters involved in the models are still somewhat adjustable and/or lack direct observational support, such as max number of adsorption

C2

sites, threshold temperature  $T_0$ , microscopic  $H_2O$  density gradient, eutectic temperature, etc.

(5) Comparison between models and measurements needs to be discussed in the context of their respective uncertainty ranges. What is the measurement uncertainty of skin layer nitrate concentration? What is the model uncertainty propagated from the inputs and parameters?

(6) The quality of English could use some polish.

In addition, the authors claim that the photochemistry of snow nitrate can be ignored due to slow photolysis in this region. Well, "what goes up must come down" and vice versa. What processes are then responsible for the loss of snow nitrate? And what is driving the seasonal variations of snow nitrate in this region? Snow nitrate can't always accumulate. This is perhaps not the main focus of this work, but the fact that only snow nitrate sources are included in the model may be quite confusing.

Specific comments:

Page 3, Line 61: the characteristic times of surface adsorption and solid-state diffusion for  $HNO_3$ ... please provide more details (either literature or point to later sections).

Page 3, Line 83: define skin layer. What is the thickness of this skin layer in the model and why this value is chosen? Or is it simply the layer in which the bulk ion concentrations are measured? Since the model is limited to the skin layer, it seems that there is no exchange between the skin layer and the deeper snow. However, previous studies (e.g. Traversi et al 2014) indicated that temperature gradients and wind pumping exist in the snowpack, therefore nitrate could be mobilized by physical processes reaching much deeper than the "skin layer" in this model (a few mm?).

Page 5, Line 141: the solid-state diffusivity is introduced here, and hence characteristic time can be calculated. Please compare to other processes, e.g. surface accommodation and gas-phase diffusion.

C3

Page 6, Line 178: what is the size of snow grain?

Page 7, Eq 7: both adsorption and co-condensation contribute to surface  $HNO_3$ . Is co-condensed  $HNO_3$  available for desorption? Judging from Eq 6 it seems the answer is yes, yet in Eq 7 it seems co-condensed  $HNO_3$  is not included. Also, will the co-condensed  $HNO_3$  molecules undergo solid diffusion?

Page 8, Line 248: what is the thickness of this DI covering the entire grain surface? Also, Eq 13 describes  $d[HNO_3(DI)]/dt$ , and there should be another equation for  $d[HNO_3(g)]/dt$  accordingly. Please provide this. Finally, I may be wrong but shouldn't mass transfer (Eq 13 and  $d[HNO_3(g)]/dt$ ) depend on liquid water content of some sort?

Page 8, Eq 8: this equation describes co-condensation. How about  $H_2O$  sublimation? Does  $HNO_3$  undergo co-sublimation (or whatever the term should be) as well?

Page 10, Line 294: again, for highly soluble species in liquid, interfacial transport or gas diffusion may be limiting (Schwartz, 1986). Please calculate the equilibrium timescale and discuss in the context of other mass transfer processes.

Page 13, Line 399: define winter (and other seasons too). The Northerners would appreciate this.

Page 14, Line 432: "However, Model 1... overestimated concentration by a factor of 1.5-5 in December". Which model 1? With 238 K or 242 K?

Page 15, Line 476: "the combination of larger temperatures and a larger diurnal temperature range" this sentence is confusing.

Page 16, Line 493: "it is possible that the snow  $NO_3^-$  concentration measured from Halley might be 'diluted' from deeper snow layer..." then can you extend your model to cover deeper layers, or simply increase the skin layer thickness? Also, as shown in Fig 11, Model 2 underestimated nitrate for the majority of the time (Line 458-459). If measured snow  $NO_3^-$  was indeed diluted, would this mean the model underestimates even more?

C4

Page 16, Line 497: what do you mean by "fixed by sea salt, ammonium or terrestrial dust"?

Page 16, Line 502: "the increase in sea salt concentration decreases the ratio of concentration of gaseous HNO<sub>3</sub> to total atmospheric nitrate". Please provide evidence.

Page 16, Line 503: "A possible explanation for the overestimation of NO<sub>3</sub>- concentration in both Model 1 and 2 in November at Dome C" this is not a complete sentence.

Page 17, Line 546: "In the summer, other processes are replaced..." this sentence is ill-formed. What are you trying to say?

Page 19, Line 605: there is no purple on Fig 7.

Page 19, Line 628: Again this is only true if gas diffusion and interfacial transport are not limiting. Also, Model 1 output is quite sensitive to T<sub>0</sub>. How sensitive is Model 2 to the eutectic temperature?

Fig 1: Please include units for the effective Henry's law constant. Also I feel this belongs in the Supplementary Information. The temperature and pH dependencies of effective Henry's law constant, although are important, do not deserve the spot of the very first figure of this particular paper.

Fig 4, Fig 6-11: dates on the bottom axis are difficult to read, i.e. it is hard to identify "early Feb" or "early May", ... Please set date tick labels to the first day of each month. If not enough space, rotate 90 degrees.

Fig 5: figure legend very unclear. What exactly are the scatter points? And what are "Head 1 1213", "Head 2, 1213", ...?

Fig 7 & Fig 8: I think these two figures can be combined. Easier to tell the difference between Model 1 and Model 2. Same for Fig 10 & Fig 11.

Table A1: temperature dependent Henry's law constant: standard temperature in 258K?

C5

## References

Domine, F., Bock, J., Voisin, D., and Donaldson, D. J.: Can We Model Snow Photochemistry? Problems with the Current Approaches, *The Journal of Physical Chemistry A*, 117, 4733-4749, 10.1021/jp3123314, 2013.

Schwartz, S. E.: Mass-transport considerations pertinent to aqueous phase reactions of gases in liquid-water clouds, in: *Chemistry of multiphase atmospheric systems*, Springer, 415-471, 1986.

Traversi, R., Udisti, R., Frosini, D., Becagli, S., Ciardini, V., Funke, B., Lanconelli, C., Petkov, B., Scarchilli, C., Severi, M., and Vitale, V.: Insights on nitrate sources at Dome C (East Antarctic Plateau) from multi-year aerosol and snow records, 2014, 10.3402/tellusb.v66.22550, 2014.

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C6