

We thank the reviewers for their reviews and recommendation to publish. We have considered every point and corrected the paper to include their points. The referees comments are in blue, responds from the authors are in black and revised text are in red.

Referee 2

[Major comments]

1. Apparently, there is a loose interchange of what the grain-surface HNO_3 concentration (HNO_3 (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 ($\text{HNO}_3(\text{ads})$) and that due to co-condensation ($\text{HNO}_3(\text{cc})$). Although the unit of ($\text{HNO}_3(\text{ads})$) is carefully matched to allow this summation, I am not so sure if it is really legitimate to assume that all the surface-adsorbed HNO_3 is automatically transferred into the bulk volume of the outermost solid-ice layer of the snow grain. 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 [$\text{HNO}_3(\text{ads})$] 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 HNO_3 dissolved in the liquid-like disordered interface ($\text{HNO}_3(\text{DI})$) is automatically transferred to the outermost solid-ice layer ($\text{HNO}_3(\text{surf})$). 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 HNO_3 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.

In the models, the solid-state diffusion into the grain is driven by the concentration gradient between the grain boundary and the centre of the grain and regulated by the solid-state diffusion coefficient (Thibert et al., 1998).

Abbatt, (1997), Huthwelker et al., (2004) and Cox et al., (2005) had observed a diffusion-like behaviour from flow tube study for trace gases uptake onto ice. The structure of the model presented in this paper is based on the suggestion from these references. References regarding the concurrence of surface adsorption and solid-state diffusion are now included in Sect. 2.2, Line 149- 151.

'A diffusion-like behaviour has been observed from flow tube studies for trace gas uptake onto ice (e.g. Abbatt, 1997; Huthwelker et al., 2004; Cox et al., 2005) and suggested the solid-state diffusion of nitrate molecules can occur concurrently with surface adsorption, such that ...'

The reasons for adopting a kinetic approach instead of an equilibrium approach are listed in Sect. 3.1.1 and Sect. 6.1. The ice solubility parameterisation by Thibert et al., (1998) was obtained after exposing the ice with gaseous HNO_3 for a period of 1-4 weeks, however, no information and no conclusion on the time taken to reach equilibrium was presented.

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 $\text{HNO}_3(\text{gas}) = \text{H}^+(\text{DI}) + \text{NO}_3^-(\text{DI})$ at Dome C?

These are the critical points that should be discussed in detail before rejecting the hypothesis of the HNO_3 incorporation into the DI.

The DI is treated as the boundary layer of the snow grain. The concentration of DI is used as the boundary condition for the solid-state diffusion of nitrate into the snow grain. Therefore, no thickness is assigned to the DI.

For clarification, the following lines (Page 9, line 275-277) are now included in the manuscript.

“Note that in this model the DI is treated as the boundary between the air and bulk ice. The concentration of the DI is used as the outermost boundary condition for solid-state diffusion within the grain, therefore, the DI has no arbitrary thickness.”

The sensitivity of Model 1 to the value of pH in the range of pH found in natural surface snow (5-6.5, Udisti et. al, 2004) is shown in Table 4. Changing the pH within this range does not have an impact on the model performance.

3. It is not clear enough whether the kinetic limitation to the growth and decay of the snow grain HNO_3 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 grain. This question should be discussed in some detail especially when contrasting the behavior of HNO_3 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.

A table of the characteristic times of various physical processes are listed in Table 1. At low partial pressures of HNO_3 , the characteristic time for surface adsorption to reach equilibrium is of the order of 10^3 s.

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 ?

For clarification now on Page 8, line 253-256 now read:

“For simplicity the macroscopic (few mm) water vapour gradient across the skin 240 layer was used to estimate the rate of volume change of snow grain due to condensation or sublimation, i.e. $(dp_v/dx)_{x=r}$ in Eq. 10 is replaced by $(dp_v/dz)_{z=4\text{mm}}$.”

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.

Information regarding the relative humidity used for calculation of water vapour gradient has been clarified in Sect 4.1, line 372-373

“Based on the assumption of a well mixed boundary layer, the RH above the snowpack surface was assumed to be the same as what measured at 1.6 m”

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. Reference to an observed temperature gradient across the top 2 cm of the snowpack at Dome C has been added to support the statement in Sect 3.1.1, Line 227-231

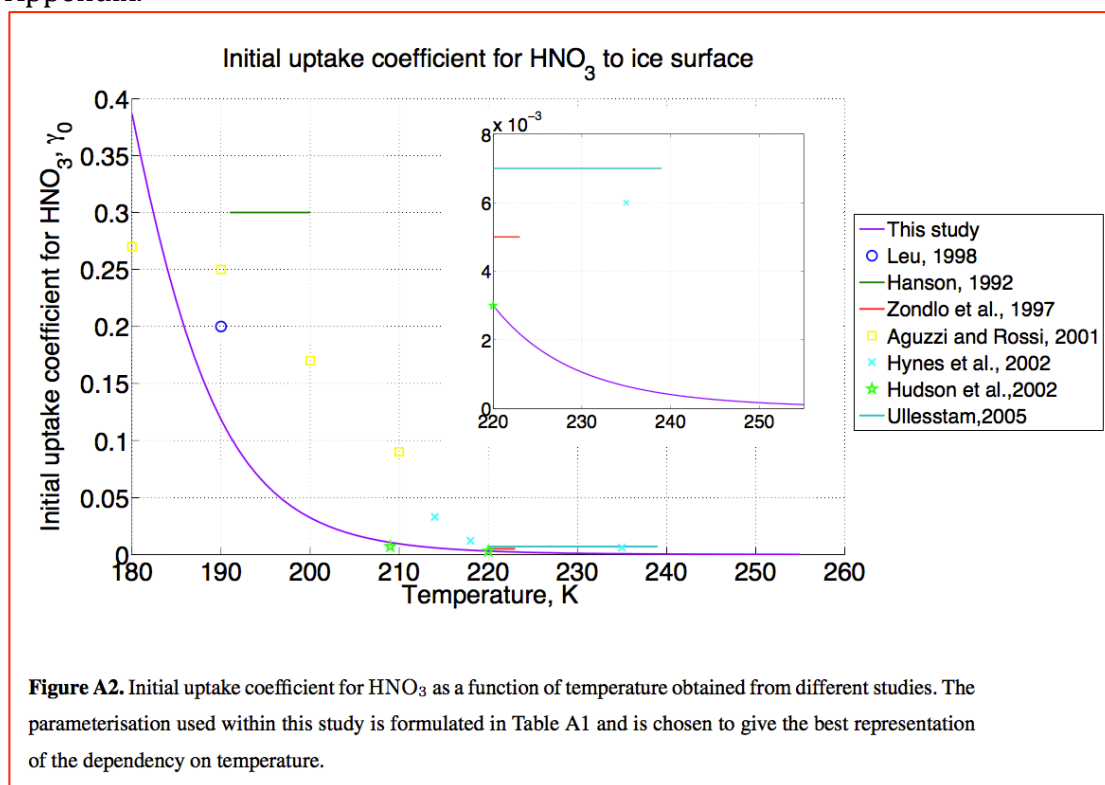
“Field observations (Frey et al., 2013) and the results from a heat transfer model (Hutterli et al., 2003) at Dome C in summer show absolute temperature gradients of 71 K m⁻¹ across the top 2 cm and 130 K m⁻¹ across the top 4 mm of the snowpack, respectively.”

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?

Yes, the error in Eq 9. is now fixed, thank you.

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.

Information and reasons for the choice of parameterisation are now listed in the Appendix.



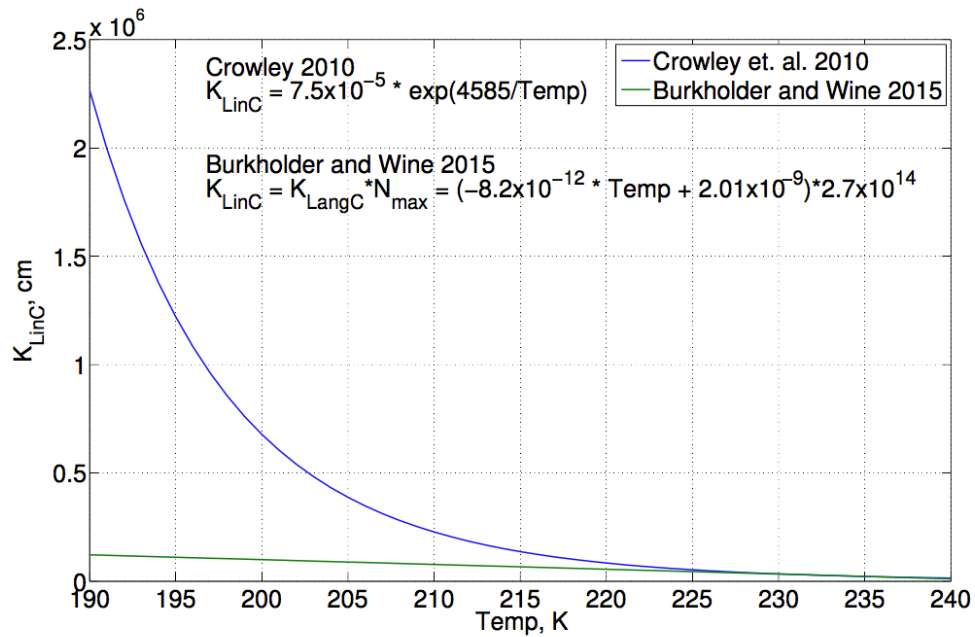


Figure A3. Langmuir adsorption equilibrium constant, $K_{LinC} = K_{eq} \times N_{max}$. The preferred temperature range for both parameterisation is 214–240 K and within this range the two parameterisations provide a comparable value. The Crowley et al. (2010) parameterisation deviate from the Burkholder and Wine (2015) parameterisation as temperature drop below 214 K due to the exponential temperature term. Here, the parameterisation from Burkholder and Wine (2015) was chosen based on the extreme cold temperature found in our validation sites.

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 copyeditor 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.

It is inherited from a typographic error in Cho et al (2002) and it is corrected now to “Tf - T”.

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.

The variable “z” is replaced by variable “x” to avoid confusion for representing the microscopic distance.

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.

Yes, sorry for incorrect information. The statement has been removed.

4. On Line 255, it is stated that “ D_g is the gas-phase diffusivity”. It should be stated clearer that D_g is the gas-phase diffusivity of HNO_3 . It would also be nice to list how D_g is calculated in Table A1.

The calculation of D_g is now listed in the footnote of Table 1.

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.

The sentence has been removed.

The sensitivity of Model 1 to pH is now on Page 21, line 677 – 682

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.

Reference to Frey et. al (2013) is included (Page 7, line 215 and Page 18, line 589).

Frey et. al (2013) measured a temperature gradient of 71 K m^{-1} across the top 2 cm of snowpack in Dome C.

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

Fig. 11 is now in Fig. 8B and the caption has been changed to

“...other ions, where other ions refers to the sum of $[\text{Na}^+]$ and $[\text{Cl}^-]$ ”

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 Δ_{obsH} . Please expand.

Δ_{obsH} is now referred to as the enthalpy of uptake. Reference to Thomas (2011) is used instead of Sander (2015).

9. Table A1, values of Δ_{solH} and Δ_{obsH} : I think they should have been -72.3 and -44 , respectively (the minus sign is missing). Please double check. 10.

Yes, has been corrected.

Table A1, footnote i: I suppose that the authors meant to formulate the temperature dependence of alpha somehow consistently with $d \ln[\alpha/(1 - \alpha)]/d(1/T) = -\Delta_{\text{obsH}}/R$ (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.

The listed formulation is the integrated form of the equation from Jayne et al., 1991

[Technical suggestions]

Line 216: $d \text{HNO}_3 / dt \rightarrow d [\text{HNO}_3(\text{ads})] / dt$

Yes, has been corrected.

Line 217: Substituting kads -> Substituting kdes

Yes, has been corrected.

Line 321: organic -> inorganic (?)

Yes, has been corrected.

Line 407: tough -> trough (?)

The sentence has been removed.

Line 414, Eq. (19): MM_{H_2O} -> M_{H_2O}

Yes, is now corrected.

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

The sentence is now removed.

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

The units have been added to the figure legend.

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)

Yes, has been corrected.

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

Yes, has been corrected.