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Atmospheric Chemistry and Physics
Discussions
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Interactive comment on "HO_2NO_2 and HNO_3 in the coastal Antarctic winter night: a "lab-in-the-field" experiment" *by* A. E. Jones et al.

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General comments

The paper reports gas phase measurements of HNO_3 and HNO_4 at the Antarctic coast. This is the first data set at this coastal site and during winter. Selected days were carefully chosen that allow to identify and to discuss the impact of adsorption/desorption from the snow surface on measured gas phase mixing ratio in the field. Taken that discussion of physical uptake to snow in field studies is often hampered by photochemistry dominating the fluxes, this study is highly valuable as it allows to link results from laboratory studies on the partitioning of trace gases to measurements in complex natural setting. This study thus tackles a key issue of atmospheric science.

Here,

- I'd like to comment on the use of the adsorption enthalpy that we have derived in Bartels-Rausch, 2002. I suggest to base your discussion on more recent data such as Ullerstam, 2005.

- I'd like to present an analysis of your data-set based on the air–ice/firn/snow partitioning that describes the physical interactions of trace gases with air, i.e. **Langmuir adsorption to the ice surface** and **solubility in ice forming a solid solution** : Equilibrium partitioning of HNO_3 and HNO_4 between the ice surface and the air (Langmuir) describes the data well supporting strongly that adsorption and desorption are the driving processes to explain the observed mixing ratio in the field. Calculations based on the solid solution – air partitioning do not reproduce the observations as well. In particular the amount of HNO_3 stored as solid-solution is too small to explain the observed mixing ratio.

Partitioning by Bartels-Rausch (2002)

Thank you for using results on the adsorption of HNO_3 to ice that we have derived in 2002. In that study, the partitioning of a number of nitrogen oxides was investigated and adsorption enthalpies were reported. On page 12782 of the manuscript, the adsorption enthalpy is compared to results based on your field measurements.

Since 2002, much more sophisticated approaches have been used to investigate the partitioning of HNO_3 to ice. May I kindly ask you to rather use results from those later studies for your discussion. I suggest to use the results from Ullerstam, as this was the first study done at relevant low concentrations of HNO_3. The Ullerstam (2005) are also preferred by the IUPAC. Key improvements to our study from 2002 are

- clear identification of HNO_3 by mass spectrometry
- more exact determination of the surface coverage
- more direct measure of the partitioning coefficient and of the adsorption enthalpy.

Literature:

- Bartels-Rausch, T., Eichler, B., Zimmermann, P., G‰, H. W., & Ammann, M. (2002). The adsorption enthalpy of nitrogen oxides on crystalline ice. Atmospheric Chemistry and Physics, 2(3), 235-247. doi:10.5194/acp-2-235-2002
- Ullerstam, M., Thornberry, T., & Abbatt, J. P. D. (2005). Uptake of gas-phase nitric acid to ice at low partial pressures: evidence for unsaturated surface coverage. Faraday Discussions, 130, 211-226. doi:10.1039/b417418f

- Crowley, J. N., Ammann, M., Cox, R. A., Hynes, R. G., Jenkin, M. E., Mellouki, A., et al. (2010). Evaluated kinetic and photochemical data for atmospheric chemistry: Volume V - heterogeneous reactions on solid substrates, 10(18), 9059-9223. doi:10.5194/acp-10-9059-2010

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Can the adsorption equilibrium explain gas phase mixing ratios?

Laboratory based studies have described the temperature dependent partitioning of HNO_3 and of HNO_4 between snow surface and air:

The Adsorption equilibrium

The temperature dependent partitioning is generally described as:

$$K_{\mathrm{LinC}} = \frac{n_{\mathrm{ads}}/a}{n_{\mathrm{gas}}/v}$$

with:

- K_{LinC}: linear Langmuir partitioning coefficient [cm]
- K_{LinC}^{HNO3} = 7.5e-5.*exp(4585./T) [cm]
- K_{LinC}^{HNO4} = 3.7e-12.*exp(7098./T) [cm]
- n_{ads}: number of molecules adsorbed
- n_{gas}: number of molecules in gas phase
- v: gas volume [cm^3]
- a: surface area of ice/snow [cm^2]

Literature:

- Crowley, J. N., Ammann, M., Cox, R. A., Hynes, R. G., Jenkin, M. E., Mellouki, A., et al. (2010). Evaluated kinetic and photochemical data for atmospheric chem-

istry: Volume V – heterogeneous reactions on solid substrates, 10(18), 9059-9223. doi:10.5194/acp-10-9059-2010

- Ulrich, T., Ammann, M., Leutwyler, S., & Bartels-Rausch, T. (2012). The adsorption of peroxynitric acid on ice between 230 K and 253 K. Atmospheric Chemistry and Physics, 12(4), 1833-1845. doi:10.5194/acp-12-1833-2012

Fractionation between ice and air

Knowledge of K_{LinC} allows to estimate the relative distribution of trace gases between the air and the ice phase for a specific surface to volume ratio: "The fraction (α) of a trace-gas with partition coefficient K_{LinC}(T) associated with the ice phase can be given by:"

$$\alpha = \frac{K_{LinC} \times A}{K_{LinC} \times A + 1}$$

with:

- K_{LinC}: linear Langmuir partitioning coefficient [cm]
- α: fraction of trace gas associated with snow surface [-]
- A: snow surface area per volume of interstitial air [cm^{-1}]

Literature:

- Pouvesle, N., Kippenberger, M., Kippenberger, M., Schuster, G., & Crowley, J. N. (2010). The interaction of H2O2 with ice surfaces between 203 and 233 K. Physical Chemistry Chemical Physics, 12(47), 15544-15550. doi:10.1039/C0cp01656j:

Fractionation in Antarctic snow

"In the firn the ratio of the surface area of snow to the volume of air is approximately 50-500 cm^{-1} (based on a density of snow of 0.3 and a specific surface area of 10 to 100 $\mathrm{m}^2\ \mathrm{kg}^{-1}$, Domine et al., 2008)" (Pers. Com. E. Wolff).

Figure 1 (JonesEtAl01.png) shows the fractionation of HNO_4 and HNO_3 in typical Antarctic snow packs. Please refer to the supporting information for details on the calculation. HNO_3 and HNO_4 are completely adsorbed to the snow surface for snow with a surface-area-to-air-volume ratio of 50 to 500 cm^{-1} up to 250 K, even though the partitioning coefficient of HNO_4 is much smaller than that of HNO_3.

This calculation shows that for both species the majority of the molecules is associated to the snow. Results are in agreement and support the discussion on page 12782 of the manuscript and of Ulrich, 2012.

At first sight, one might not expect a strong shift of the partitioning of both trace gases towards the gas phase with rising temperature. Next, I calculate the gas-phase concentration of HNO_3 and HNO_4 based on the equilibrium partitioning.

Literature:

- Ulrich, T., Ammann, M., Leutwyler, S., & Bartels-Rausch, T. (2012). The adsorption of peroxynitric acid on ice between 230 K and 253 K. Atmospheric Chemistry and Physics, 12(4), 1833-1845. doi:10.5194/acp-12-1833-2012

Mixing ratio of HNO_3 and HNO_4 above snow

The gas-phase mixing ratio of HNO_3 and HNO_4 are calculated at T 220-255 K based on K_{LinC} and a given surface concentration. The surface concentration is considered to be constant in this temperature range and set to the calculated surface concentration at a) the coldest temperature and b) the warmes temperature of the study. The surface concentration is calculated for both temperatures based on the measured gas phase concentration:

Figure 2 (JonesEtAl02.png) shows the mixing ratio of both nitrogen oxides in equilibrium with snow as calculated based on the K_{LinC} (lines). The measured mixing ratio (crosses) are also shown. Please refer to the supporting information for details on the calculation.

For this rough estimate, the surface concentration is constant with temperature and set to the surface concentration of 1.4E12 molec cm^{-2} for HNO_3 and of 1.5E9 molec cm^{-2} for HNO_4 derived based on the $K_{\mathrm{LinC}} \approx$ 33000 cm (HNO_3) and 90 cm (HNO_4), T = -42.5 °C, 1.4 ppt HNO_3 or 0.6 ppt HNO_4 (solid line). The dashed line shows calculations with a surface concentration of 1.0E12 molec cm^{-2} for HNO_3 and of 0.7E9 molec cm^{-2} for HNO_4 derived based on the $K_{\mathrm{LinC}} \approx$ 7000 cm (HNO_3) and 8 cm (HNO_4), T = -23.05 °C, 5.7 ppt HNO_3 or 3.2 ppt HNO_4.

Generally, the calculated equilibrium distribution matches the measurements well indicating that the gas phase concentrations can indeed result from the partitioning equilibrium. In particular the measured and predicted HNO_3 mixing ratio agree very well

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and the temperature trend is perfectly captured.

Mass Balance - Is there enough HNO_3 and HNO_4 adsorbed to fuel observed mixing ratio?

Depth of the snow pack that exchanges gases with the atmosphere

Adsorption significantly slows the diffusive migration through porous snow. Here, I'd like to estimate the depth of the surface snow from which HNO_3 and HNO_4 can escape to the atmosphere in reasonable time scales:

In porous materials, such as surface snow, diffusive transport through the open space (i.e., gas phase) is generally described by an effective diffusivity in the two-phase sample. The effective diffusivity (D_{eff}) is described by the gas-phase diffusion coefficient (D_{air}), the free volume in the porous material (porosity, ϕ), and the microscopic shape of the pores (tortuosity, τ). For trace gases that interact with the surface of the porous material by surface adsorption, the gas – solid partitioning coefficient (K_{LinC}), the ice-to air volume ratio (r_{sp}), and the specific surface area (SSA) are additionally included in the parameterization of D_{eff}. The effective diffusivity of any gas can thus be calculated based on known gas-phase diffusivity, microstructure of the porous medium and sorption characteristics:

$$D_{\text{eff}} = D_{\text{air}} \times \frac{\phi}{\tau} \times \frac{1}{1 + r_{\text{sp}} \times K_{LinC} \times SSA}$$

$$D_{\text{inert}} = D_{\text{air}} \times \frac{\phi}{\tau}$$

with D_{inert} = 0.06 cm^2 s^{-1} for Antarctic surface snow and r_{sp} given by:

$$r_{sp} = \rho_{\text{snow}} * (1 - \frac{\rho_{\text{snow}}}{\rho_{\text{ice}}})$$

with ρ being the density of snow or ice. The diffusive length is given by:

$$l = \sqrt{t \times D_{eff}}$$

with t, the mean diffusive time. I have chosen 3 h for calculations, because:

- Table 1 shows mean mixing ratio for each 5 °C, thus equilibrium should be reached within the time that temperatures need to change by 5 °C.
- Figure 6 of the manuscript indicates a strong correlation of temperature and HNO_3 flux from the snow during warming indicating a fast response of HNO_3 to temperature changes. It takes about 3h for the temperature to raise by 5 °C.

Please refer to the supporting information for details on the calculation.

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Literature:

- Bartels-Rausch, T., Wren, S. N., Schreiber, S., Riche, F., et al. (2013). Diffusion of volatile organics through porous snow: Impact of surface adsorption and grain boundaries. Atmospheric Chemistry and Physics, 13(14), 6727-6739. doi:10.5194/acpd-13-6131-2013

- Domine, F., Albert, M., Huthwelker, T., Jacobi, H. W., Kokhanovsky, A. A., Lehning, M., et al. (2008). Snow physics as relevant to snow photochemistry. Atmospheric Chemistry and Physics, 8(2), 171-208. doi:10.5194/acp-8-171-2008

```
Diffusive length of HNO3 during 3 h at 220 K: 0.1 mm
Diffusive length of HNO3 during 3 h at 255 K: 0.3 mm
Diffusive length of HNO4 during 3 h at 220 K: 1 mm
Diffusive length of HNO4 during 3 h at 255 K: 11 mm
```

Figure 3 (JonesEtAl03.png) shows that only the HNO_3 adsorbed at less than the upper mm of a snow pack can reach the overlying air. For HNO_4 this length is a few mm. Please refer to the supporting information for details on the calculation.

Release from that upper snow layer during warming event

Here I calculate the total release of HNO_3 and HNO_4 from 1 m^2 of snow pack to the overlying air:

- The depth from which the acidic trace gases are released is given by the mean diffusive length at -20 °C.

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- The total surface area for that snow pack volume is calculated based on the specific surface area and the density of the snow.
- The difference in surface coverage of the acidic gases at -40 °C to -20 °C multiplied by the total surface area of the snow in the snow pack volume that exchanges with the overlying air gives the total release of acidic trace gas molecules.
- The surface coverage at -40 °C and -20 °C is calculated bases on the measured gas phase mixing ratio and the K_{LinC}.

Please refer to the supporting information for details on the calculation.

Increase of gas phase concentration during warming event

Jones state a mean mixing time in the boundary layer of 500s for 5 m.

- During the time of diffusive transport through the porous snow pack (3h) the air is mixed in a layer of ≈ 100 m.
- The increase in mixing ratio is then calculated for an air volume of 1m x 1m x ≈ 100m.

Please refer to the supporting information for details on the calculation.

```
Release of HNO3 by desorption during warming from -42 to -23 deg.C: 1e+16 molecules
Increase of HNO3 in gas phase during warming from -42 to -23 deg.C: 1e+16 molecules
Release of HNO4 by desorption during warming from -42 to -23 deg.C: 1e+15 molecules
Increase of HNO4 in gas phase during warming from -42 to -23 deg.C: 8e+15 molecules
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This back-of-the-envelope calculation indicates that the release from the upper layer of the snow pack by desorption is in excellent agreement with the increase in gas phase

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concentration for HNO_3 and HNO_4. Ergo, the surface concentration of HNO_3 and HNO_4 is large enough to explain observed mixing ratio.

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Can a solid solution explain gas phase mixing ratios?

Trace gas concentrations in the Arctic gas phase have been well described based on the partitioning between solid-solution and air for formaldehyde. Taken that HNO_3 is even more soluble in solid ice, diffusion and solubility in ice might also explain the observed gas-phase mixing ratios.

Here, I calculate the equilibrium gas phase concentrations based on the solubility in ice:

$$P_{HNO3} = A_0 \times e^{-\Delta H_{HNO3}/(RT)} \times X_{HNO3}^{n}$$

with:

- P_HNO3: partial pressure of HNO_3 [Pa]
- X_HNO3: equilibrium mole fraction of HNO_3 in ice [-]
- A_0: constant, 5.47E26 Pa
- DeltaH_HNO3: enthalpy of sublimation from ice, 67.5 kJ/mol
- n, ice vapour pressure depression factor, 2.3

Thibert (1998) gives:

$$X^0_{HNO_3} = 2.37E - 12 \times exp(3532.2/T) \times P^{(1/2.3)}_{HNO_3}$$

Literature:

- Bartels-Rausch, T., Jacobi, H. W., Kahan, T. F., Thomas, J. L., Thomson, E. S., Abbatt, J. P. D., et al. (2014). A review of air–ice chemical and physical interactions (AICI): liquids, quasi-liquids, and solids in snow. Acp, 14(3), 1587-1633.

- Thibert, E. & Domine, F. (1998). Thermodynamics and kinetics of the solid solution of HNO3 in ice. The Journal of Physical Chemistry B, 102(22), 4432-4439. doi:10.1021/jp980569a

- Barret, M., Domine, F., & Houdier, S. (2011). Thermodynamics of the Formaldehyde?Water and Formaldehyde–Ice Systems for Atmospheric Applications. The Journal of Physical Chemistry A, 115(3), 307-317. doi:10.1021/jp108907u

Figure 4 (JonesEtAl04.png) shows the mixing ratio of HNO_3 in equilibrium with snow as calculated based on the equilibrium solubility (lines). The measured mixing ratio (crosses) are also shown. Please refer to the supporting information for details on the calculation.

For this rough estimate, the concentration in ice is constant and set to the concentration derived based on the equilibrium mole fraction (X=1.1E-8 mol/mol), T = -42.5 °C, and the gas phase mixing ratio (at this T) of 1.4 ppt (solid line). Calculations are also done with X=0.6E-8 mol/mol, T= -23.05 °C„ and 5.7 ppt (dashed line).

The mixing ratio are well reproduced by the equilibrium calculations. Just at very warm temperatures a larger release of HNO_3 from its solid solution in ice would be expected, leading to higher mixing ratio in the gas phase (up to 45 ppt) than those observed (up to 5 ppt). At equilibrium diffusion from a solid solution in ice might thus explain the observed mixing ratio. The question remains if diffusion is fast enough to operate at the short time scales:

Mass Balance - Is there enough HNO_3 as solid solution in snow?

Release from upper layer of the snow pack during warming event

Here, I calculate how much HNO_3 would be released in 3 h from a area of 1 m^2 of a snow pack to the overlying air:

- The diffusive depth in solid ice within 3 hours is calculated based on the diffusivity given by Thibert: D_{solid} = 1.37 x 10ˆ(-2610/T)
- The volume of ice from which HNO_3 can diffuse into the overlaying air is given by: 1m x 1 m x solid-to-air-ratio (r_{sp}) x diffusive depth in ice.

Please refer to the supporting information for details on the calculation.

```
Diffusive depth of HNO3 during 3 h at 250 K in ice crystal: 7 micro-m
Release of HNO3 by diffusion during warming from -42 to -23 deg.C: 2e+14 molecules
Increase of HNO3 in gas phase during warming from -42 to -23 deg.C: 1e+16 molecules
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The release through diffusion from a solid solution in 3 h is about 100 times lower than the observed increase, indicating that only a negligible fraction of HNO_3 in the gas phase can be released via solid state diffusion from a solid solution.

General Conclusion

The reversible snow/firn/ice **surface – air partitioning** describes the measured gas phase mixing ratio at a fixed surface coverage very well (Figure 2):

- HNO_3: Very good agreement of absolute mixing ratio and of trend with temperature. Based on K_{LinC} of Ullerstam, 2005.
- HNO_4: Good agrement of absolute mixing ratio. Trend with temperature based on K_{LinC} of Ulrich slightly steeper than observed mixing ratio.

The difference in surface coverage at -40 °C and -20 °C agrees with the increase in gas phase mixing ratio. Thus, the reservoir of adsorbed HNO_3 and HNO_4 in the upper snow pack ($\approx$ mm) is large enough to fuel the observed emissions.

The reversible **solid-solution – air partitioning** predicts the measured gas phase mixing ratios of HNO_3 well (Figure 4). Trend with temperature based on equilibrium solubility is steeper than observed one. The reservoir of HNO_3 in the outer part of the snow crystals, from where HNO_3 can diffuse to the air within 3 h, is too small to explain the observed increase in mixing ratio.

In summary, this rough calculations indicate that HNO_3 and HNO_4 are adsorbed to the surface of snow in Antarctic snow packs and change in partitioning during temperature changes can explain measured gas phase mixing ratio. Diffusion through solid ice seems to be too slow to explain the observed gas phase mixing ratio. In reality, both processes will occur simultaneously, this calculation shows the dominating character of adsorption/desorption. For a detailed analysis, one should:

- Physical parameters of snow were only estimated. Parameter variations are needed to estimate the systematic error. However, because the genrally large surface are available in snow (compared to cirrus clouds) and the relatively strong partitioning of both trace gases to snow, only minor changes in the partitioning with variation of the physical snow parameters can be expected.
- Change of snow surface area with temperature was not considered (metamorphism). However, this is old and compact snow thus metamorphism is slow.
- Release of HNO_3 or HNO_4 from solid or liquid aerosol particles that might be present in coastal snow packs was not considered.

I'd like to thank H.-W. Jacobi for discussion of the manuscript.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/14/C4673/2014/acpd-14-C4673-2014-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 12771, 2014.

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Figure 1: Fractionation of HNO_3 and HNO_4 in Antarctic interstitial air

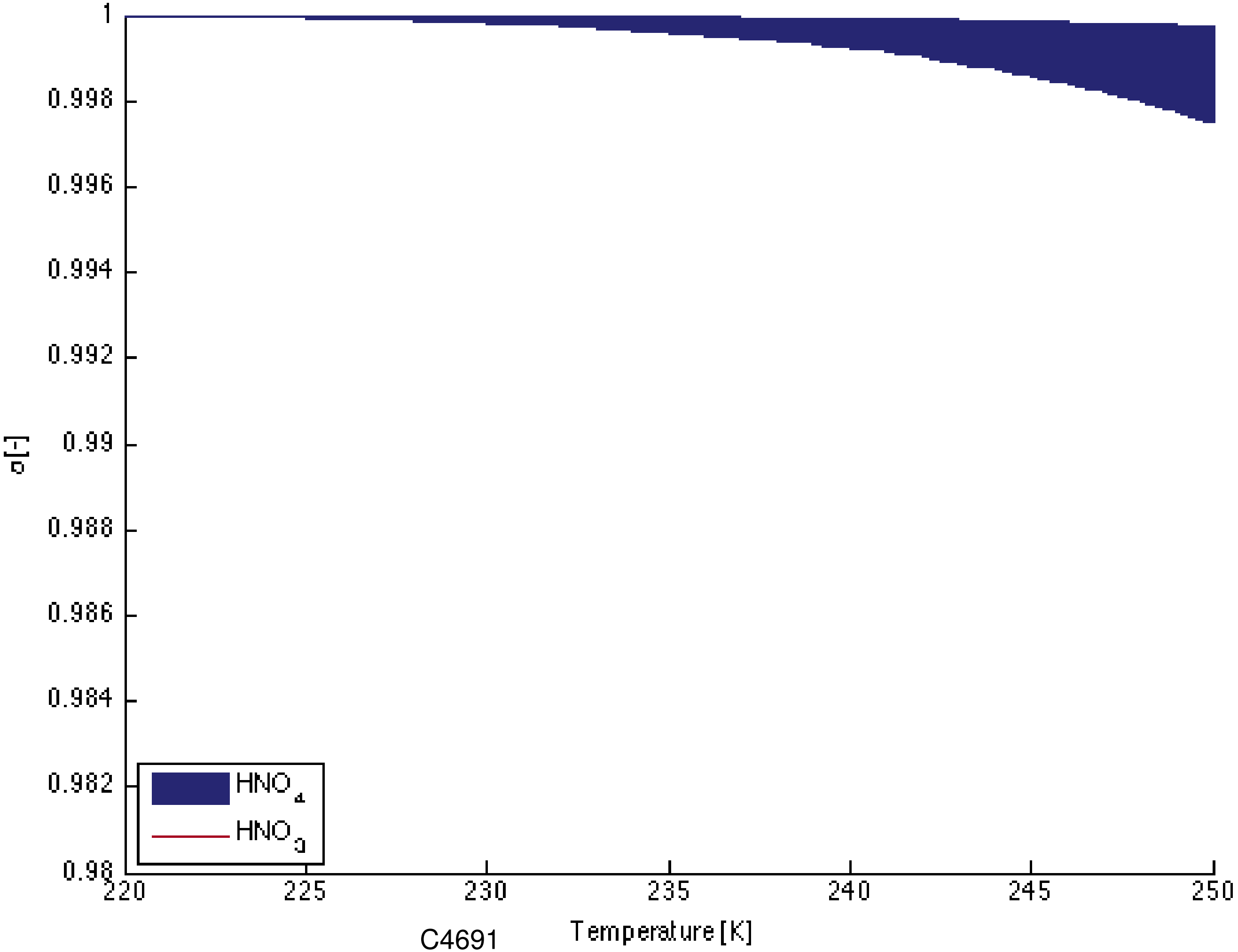

Figure 2: Mixing ratio of HNO_3 and HNO_4 in Antarctic interstitial air - adsorption

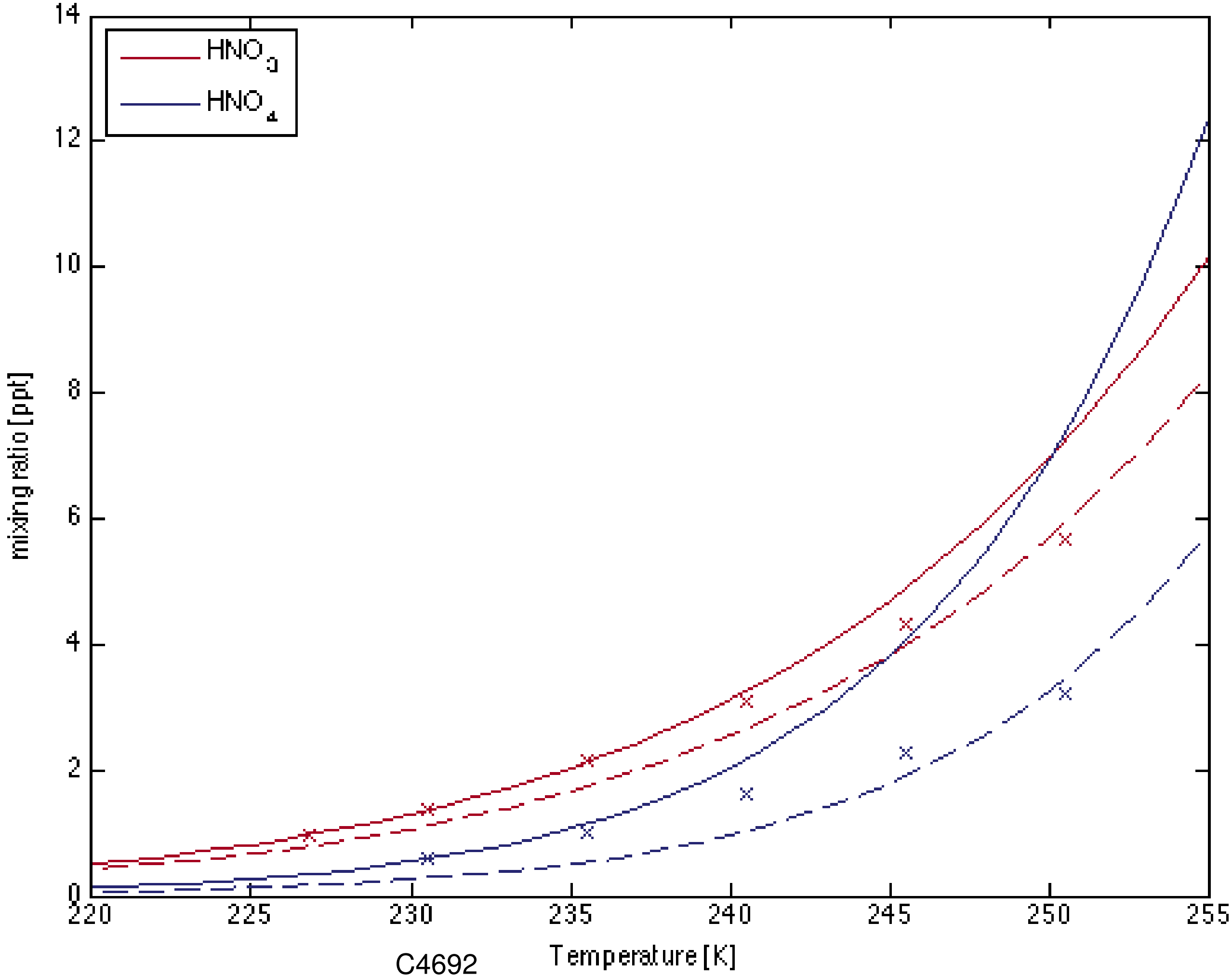

Figure 3: Diffusive length through snow pack within 3h

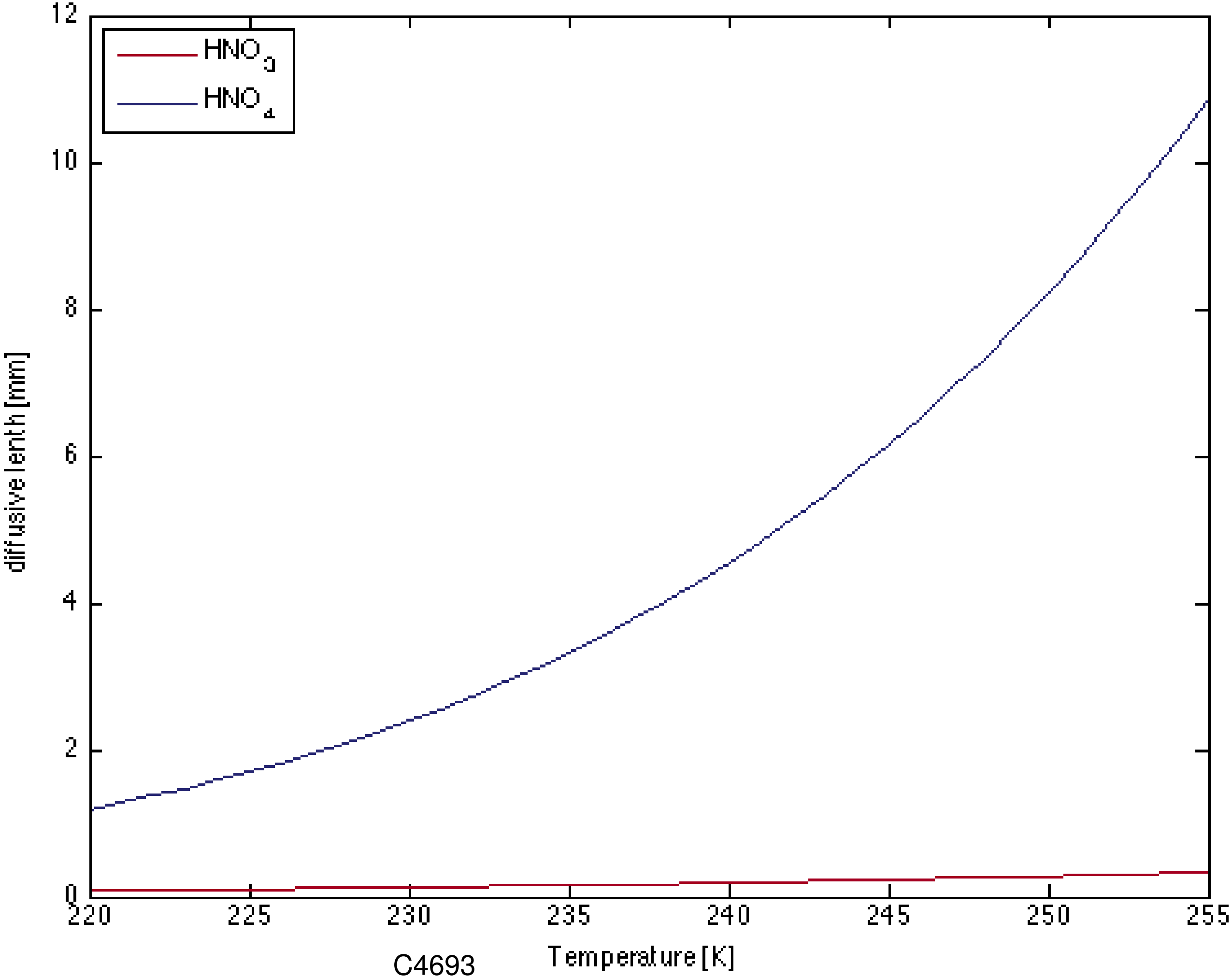

Figure 4: Mixing ratio of HNO_3 in Antarctic interstitial air - solid solution