Nitric acid in cirrus clouds

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[1] Uptake of nitric acid (HNO_3) in Arctic cirrus ice crystals was observed on 11 February 2003 by in-situ instruments onboard the M55 Geophysica aircraft. The cirrus cloud with a mean ice water content of 5.4 mg m^{-3} covered northern Scandinavia for several hours and extended up to the thermal tropopause at 12.3 km. Within the cirrus region, on average 9% of the total HNO_3 measured as reactive nitrogen (NO_y) is present in ice particles, increasing to 19% at temperatures below 205 K. In contrast to previous studies, we discuss the HNO_3 uptake in ice in terms of HNO_3/H_2O molar ratios in ice crystals. The HNO_3 content of the ice increases with increasing gas phase HNO_3 concentrations and decreasing temperatures. Enhanced uptake of HNO_3 in ice and heterogeneous chemistry on cold cirrus clouds may disturb the upper tropospheric ozone budget. **Citation:** Voigt, C., H. Schlager, H. Ziereis, B. Kärcher, B. P. Luo, C. Schiller, M. Krämer, P. J. Popp, H. Irie, and Y. Kondo (2006), Nitric acid in cirrus clouds, *Geophys. Res. Lett.*, *33*, L05803, doi:10.1029/2005GL025159.

1. Introduction

[2] Cold temperatures of the Arctic upper troposphere/lower stratosphere (UTLS) make this region a favorable indicator for climate change. Arctic cirrus with optical depths >0.1 cover up to 20% of the Earth surface in polar regions (>60°N) [*Rossow and Schiffer*, 1999], hence radiative forcing by Arctic cirrus clouds is an important parameter for the discussion of climate change. Besides their radiative effects, Arctic cirrus may disturb the UTLS ozone budget through heterogeneous reactions, such as chlorine activation [*Borrmann et al.*, 1996] or HNO_3 uptake on ice followed by ice sedimentation and evaporation [e.g., *Meier and Hendricks*, 2002].

[3] Observations of the uptake of reactive nitrogen (NO_y, the sum of NO, NO_2, HNO_3, PAN, N_2O_5, $ClONO_2$,...) in cirrus clouds were first reported by *Weinheimer et al.* [1998]. Efficient HNO_3 uptake in cold cirrus clouds (air temperature $T < 220$ K) was detected in recent field campaigns in the Arctic [*Schlager et al.*, 1999; *Kondo et al.*, 2003] and the subtropics [*Popp et al.*, 2004]. *Ziereis et al.* [2004] measured moderate NO_y uptake in warm ($T > 220$ K) midlatitude cirrus clouds. Laboratory studies of HNO_3 uptake on prepared ice films in flow tubes have been performed under equilibrium conditions [e.g., *Abbatt*, 1997; *Hudson et al.*, 2002; *Ullerstam et al.*, 2005]. These equilibrium data have been fitted with a Langmuir type adsorption model [e.g., *Tabazadeh et al.*, 1999; *Ullerstam et al.*, 2005] or by a Frenkel-Halsey-Hill model [*Hudson et al.*, 2002].

[4] In the atmosphere, the ice surfaces are rarely in equilibrium, but are continuously growing and evaporating due to temperature fluctuations acting on various spatial and temporal scales. Thus it is an open question how equilibrium data measured in the laboratory on prepared ice surfaces can be related to non-equilibrium observations of growing/evaporating ice crystals taken in the field. *Kärcher and Basko* [2004] discuss the possibility of HNO_3 to be trapped during ice growth using a novel model of trace gas uptake. Recent laboratory measurements by *Ullerstam and Abbatt* [2005] on ice films growing in a flow tube indeed show an enhanced HNO_3 uptake compared to equilibrium. Because it is not known to which degree HNO_3 is present in the ice particle volume or at the surface, we take a fresh look on this issue. We discuss our data without making use of the ice surface area, which is a poorly known quantity introducing large uncertainties in most data sets. In contrast to most previous studies parameterizing the HNO_3 coverage on ice surfaces, we quantify the HNO_3 content in cirrus ice as molar ratios of HNO_3 and H_2O in ice.

[5] Arctic cirrus clouds were observed by a suite of instruments onboard the Geophysica aircraft during the European Polar stratospheric cloud and Leewave Experiment (EuPLEx/ENVISAT) campaign. Particulate and gas phase reactive nitrogen and water as well as optical particle properties were measured in situ in cirrus clouds above northern Scandinavia on 11 February 2003. We derive the temperature and HNO_3 partial pressure ($P_{HNO3,gas}$) dependencies of the HNO_3 content in cirrus particles. We compare our results to data from previous field campaigns and discuss the impact on the UTLS ozone budget.

2. Instrumentation

[6] The NO_y instrument [*Voigt et al.*, 2005] measures gas phase reactive nitrogen $NO_{y,gas}$ through a rear facing inlet and particulate $NO_{y,part}$ through a forward facing inlet, each with a separate detection channel. At the rear inlet, particles larger than the cut-off diameter of 0.2 μm, estimated here based on simple aerodynamical considerations, are inertially stripped from the sample air and predominantly gas phase

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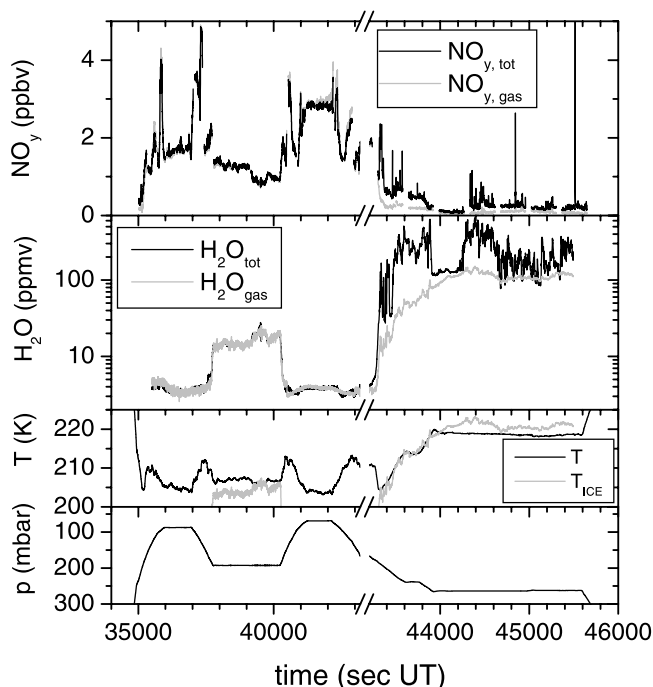
Figure 1. Measurements of total and gas phase reactive nitrogen, total and gas phase water, T, T_{ICE} and pressure along the flight path on 11 February 2003 over Scandinavia.

$NO_{y,gas}$ is measured. Total $NO_{y,tot}$ (the sum of enhanced particulate $NO_{y,part}$ and $NO_{y,gas}$) is measured through the forward facing inlet, heated to 35°C to evaporate the ice crystals. $NO_{y,part}$ is released from the crystals and the resulting gas phase NO_y is catalytically reduced to NO in a gold converter (300°C) with CO as reducing agent. Finally, the chemiluminescence of the reaction of NO with O_3 is detected. The transition time through the inlet and the converter is ~0.1 sec, hence by orders of magnitude larger than the estimated evaporation time of ice particles in the inlet.

[7] In the forward facing inlet, particles are enhanced due to anisokinetic sampling by a pressure and size dependent factor, $E(p, d)$. For particles with geometric diameters $d > 8$ μm, the deviation of E from its maximum $E_{max}(d)$ at a given pressure is less than 5%. Median ice particle diameters of 12 μm have been measured on 11 February 2003, hence we neglect the size dependence of E in this study. For large particles, $E_{max}(p)$ is proportional to the ratio of the aircraft velocity and the sample flow velocity inside the inlet [*Belyaev and Levin*, 1974]. We account for changes in flight velocity and altitude leading to $27.1 < E_{max}(p) < 37.7$ in the cirrus region. Particulate $NO_{y,part}$ is then derived as $(NO_{y,tot} - NO_{y,gas})/E_{max}(p)$. Outside the cirrus, the two NO_y channels agree within 0.1 ppbv. The detection limit for $NO_{y,part}$ is then derived by dividing this number by E leading to 3 pptv. We further assume that 100% of the particulate $NO_{y,part}$ is present in the form of HNO_3. The error of $NO_{y,part}$ depends on the accuracy of the NO_y measurements and the accuracy of E, combined it amounts to 19%. *Kondo et al.* [2003] determine an average gas phase HNO_3/NO_y ratio of 0.4 at Arctic tropospheric ozone concentrations, increasing to 1 in the stratosphere. Here we

assume a ratio of 0.5 in the upper troposphere with an error of ±0.3.

[8] In our study, we assume that HNO_3 is predominantly contained in ice and not in background aerosol. In the UTLS region, significant uptake of HNO_3 in binary background aerosol starts at $T < T_{NAT}$-2 K [*Irie et al.*, 2004]. On 11 February 2003, the Arctic cirrus cloud has been observed at $T \geq T_{NAT}$, hence we can neglect HNO_3 uptake in background aerosol in our study.

[9] Gas phase H_2O_{gas} and total H_2O_{tot} (H_2O_{gas} plus enhanced particle H_2O_{part}) are measured with two independent Lyman-α hygrometers. The gas phase instrument measures H_2O_{gas} with a rear facing inlet with an accuracy of 10%. In regions without particle observations, it was calibrated to the total water instrument FISH [*Schiller et al.*, 1999]. During the cirrus encounter, large particles are enhanced by a pressure dependent factor $6.9 < E_w(p) < 8.1$ in the forward facing FISH inlet. The accuracy of the FISH hygrometer is 8% in regions without particle observation. The detection limit for ice clouds depends on the ice saturation ratio and lies between 0.5 and 4 ppmv in the temperature range between 204 and 220 K. In the cirrus clouds, the ice water content (IWC) is derived as $(H_2O_{tot} - H_2O_{gas})/E_w(p)$.

[10] The temperature was measured with an accuracy of ±0.6 K with a PT100 thermistor. Comparisons with a Rosemount sensor onboard the Geophysica show that the Rosemount data are on average 0.2 K warmer than the PT100 data.

3. NO_y and H_2O Measurements in Arctic Cirrus Clouds

[11] During a flight on 11 February 2003 from Kiruna/ Sweden, cirrus clouds were detected with the NO_y and the FISH instrument for more than half an hour over the Scandinavian Alps at altitudes below 12.3 km at and below the thermal tropopause.
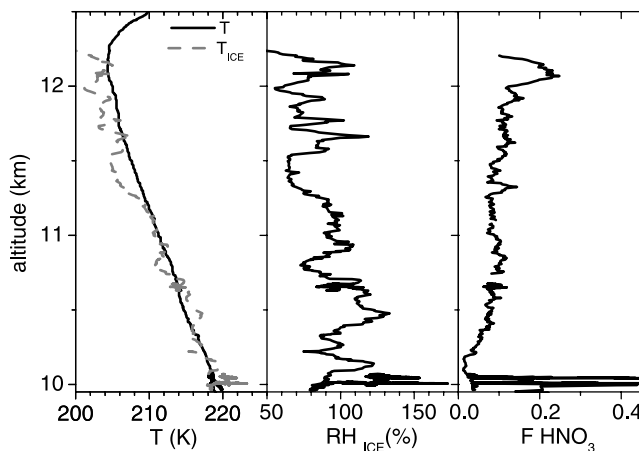
Figure 2. Vertical profile of T, T_{ICE}, RH_{ICE}, and the fraction F of $HNO_{3,tot}$ in ice particles ($HNO_{3,part}/HNO_{3,tot}$). Note that we use a HNO_3/NO_y ratio (R) of 0.5 for the gas phase ($R = 1$ for particles, see text). The cirrus cloud was observed at $58 < RH_{ICE} < 173$%. On average 9% of $HNO_{3,tot}$ is contained in ice, increasing to 19% at $T < 205$ K.
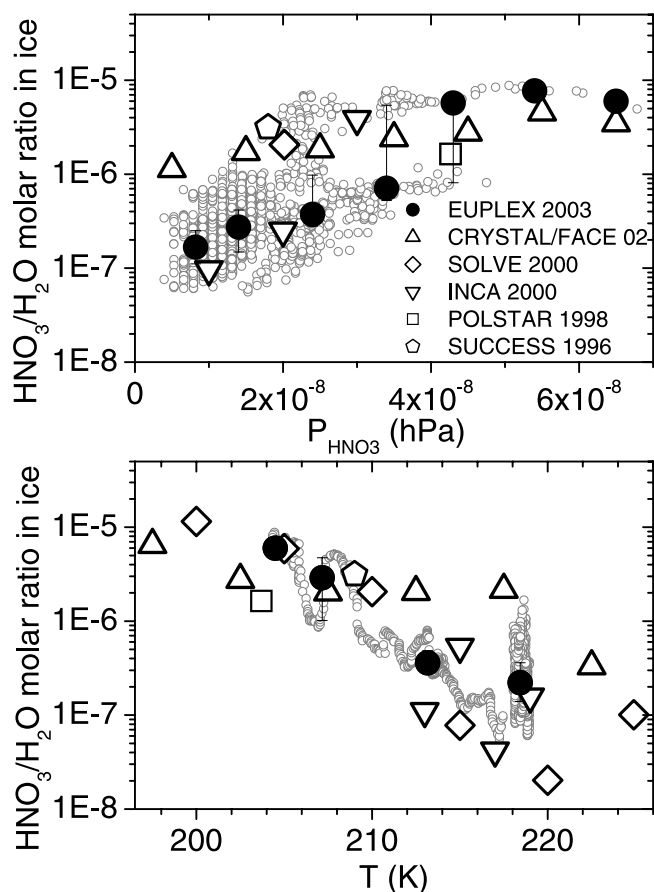
Figure 3. Dependence of the HNO_3/H_2O molar ratio in cirrus ice on the HNO_3 partial pressure and temperature. Hollow dots are 11 s running means of the EuPLEx data, filled dots are medians, binned by $P_{HNO3,gas}$ intervals of 1E-8 hPa and T intervals of 5 K. The errors bars of the molar ratios include 25% to 75% of the number of data points, the error of P_{HNO3} is determined by the uncertainty in the HNO_3/NO_y ratio of 0.5 ± 0.3. The mean T during the cirrus encounter is 216 K, the mean $P_{HNO3,gas}$ is 2E-8 hPa. The EuPLEx data are compared to previous observations in Arctic, mid-latitude and sub-tropical cirrus clouds as indicated in the legend. The HNO_3/H_2O molar ratio in ice increases with increasing P_{HNO3} and decreasing T.

[12] Ice particles were measured at temperatures between 204 and 220 K near the ice frost point ($T_{ICE} \pm 4K$, Figure 1). The ice cloud contains an average ice water content of 21.6 ppmv ($1.8 < IWC < 66$ ppmv) corresponding to 5.4 mg m^{-3} ($0.4 < IWC < 17$ mg m^{-3}). The ice particles were observed at inferred $P_{HNO3,gas}$ between 3×10^{-9} and 7×10^{-8} hPa, equivalent of 10 to 480 pptv. On average 6 pptv gas phase equivalent HNO_3 is present in the cloud particles, with maximum values up to 145 pptv.

[13] Figure 2 shows profiles of T, T_{ICE} and relative humidity over ice (RH_{ICE}) in the cirrus cloud detected between 43300 and 45500 sec UT on 11 February 2003. The cirrus clouds were observed at RH_{ICE} between 58 and 173%. Mesoscale meteorological simulations indicate enhanced gravity-wave activity over the Scandinavian coast-

line unresolved in the ECMWF analyses. It is therefore plausible, that the mostly subsaturated region above 10.8 km was caused by a local downdraft while updrafts frequently generated high supersaturations in the cirrus region close to 10 km altitude.

[14] To determine the importance of HNO_3 uptake in ice for global chemistry, we evaluate the fraction F of the total HNO_3 (gas phase plus particulate HNO_3) that is detected in ice ($HNO_{3,part}/HNO_{3,tot}$). We note that the total HNO_3 is influenced by sedimenting ice particles, therefore F gives a snapshot of the HNO_3 distribution in cirrus clouds taken during descent of the Geophysica. On average 9% of the total HNO_3 is observed in ice particles (Figure 2), increasing to 19% at temperatures below 205 K. Locally up to 45% of $HNO_{3,tot}$ is found in the Arctic cirrus crystals.

4. HNO_3 Uptake in Ice

[15] The uptake of HNO_3 on prepared ice films has been studied in a suite of laboratory experiments [e.g., *Abbatt*, 1997; *Hudson et al.*, 2002], recently also at lower, more atmospherically relevant HNO_3 partial pressures [*Ullerstam et al.*, 2005]. These measurements were performed by exposing ready-made ice surfaces in a flow reactor to HNO_3 vapor. The HNO_3 uptake on ice has been parameterized in terms of HNO_3 equilibrium coverage of the ice surface [*Tabazadeh et al.*, 1999; *Hudson et al.*, 2002]. Previous analyses of atmospheric measurements also assume that particulate HNO_3 is adsorbed at the ice particle surfaces. However, only a small fraction of UTLS cirrus are found in equilibrium. During EuPLEx, we observed cirrus particles in ice super- and subsaturated conditions ($56\% <$ $RH_{ICE} < 173\%$, see Figure 2), hence ice particles are continuously growing and evaporating. *Kärcher* [2005] suggests that HNO_3 initially adsorbed on the ice surface might be trapped in growing ice crystals in situations, where ice crystal growth rates exceed the rates at which molecules attached to the ice surface leave the ice. Further, buried HNO_3 molecules are not necessarily evenly distributed over the bulk ice volume (but could be concentrated near the surface). Hence at atmospheric non-equilibrium conditions, the distribution of the HNO_3 in and on ice particles is not known. Recent laboratory measurements carried out in ice supersaturated conditions [*Ullerstam and Abbatt*, 2005] show that HNO_3 uptake is enhanced in growing ice films and that trapping of HNO_3 in growing ice crystals is a viable mechanism in cirrus clouds.

[16] Therefore we choose here a different approach and quantify HNO_3 uptake as HNO_3/H_2O molar ratios in ice. For this purpose, we divide $HNO_{3,part}$ [ppbv] by IWC [ppbv]. With this basic approach, we do not judge which fraction of the HNO_3 is located in the ice volume and in a surface layer on the ice. Further, in contrast to most previous studies our results do not need information on the ice surface or crystal shape, which may introduce large uncertainties. Figure 3 shows HNO_3/H_2O molar ratios in ice versus $P_{HNO3,gas}$ and T. Hollow circles are 11 s running means of 1 s data intervals, black circles represent medians of the HNO_3/H_2O molar ratios in $P_{HNO3,gas}$ intervals of 1×10^{-8} hPa and T intervals of 5 K, respectively. The error bars include 25 to 75% of the number of data points. The small scatter in the low T and high $P_{HNO3,gas}$ data result from

limited measurement time. The error in $P_{HNO3,gas}$ is mainly determined by the uncertainty in the HNO_3/NO_y ratio of 0.5 ± 0.3. The HNO_3/H_2O molar ratio in cirrus particles increases with decreasing temperature and increasing gas phase HNO_3 concentrations. HNO_3 uptake in cirrus clouds is therefore particularly important below 210 K and at high $P_{HNO3,gas}$.

[17] Our measurements are compared to observations of HNO_3 uptake in Arctic cirrus clouds during SOLVE 2000 [*Kondo et al.*, 2003] and POLSTAR 1998 [*Schlager et al.*, 1999], to midlatitude cirrus measurements during SUCCESS 1996 [*Weinheimer et al.*, 1998] and INCA 2000 (a data subset for $T < 220$ K) [*Ziereis et al.*, 2004] and to subtropical, mostly convectively influenced anvil cirrus observations during CRYSTAL/FACE 2002 [*Popp et al.*, 2004]. Combined, those data show atmospheric cirrus observations at latitudes between 68°N and 53°S representative for a wide range of cirrus cloud compositions and ambient conditions and provide a basis for further modelling studies (B. Kärcher and C. Voigt, Formation of nitric acid/water ice particles in cirrus clouds, *Geophysical Research Letters*, 2006).

[18] In addition, we evaluated our data in terms of NOy coverage on the ice surface (not shown here). Our data are in general agreement with previous observations [e.g., *Kondo et al.*, 2003; *Ziereis et al.*, 2004; *Popp et al.*, 2004].

5. Implications for UTLS Chemistry

[19] Enhanced HNO_3 uptake in cirrus ice occurs locally on small scales, but most pronounced at low temperatures ($T < 210$ K). Despite the reduced availability of water at low temperatures and the tendency to form smaller ice particles [*Popp et al.*, 2004], the fraction F of $HNO_{3,tot}$ residing in ice increases significantly to 19% at $T < 205$ K in our case. An increase of F at low temperatures has also been reported by *Kondo et al.* [2003]. The higher fraction of $HNO_{3,tot}$ in ice is explained by the increasing HNO_3 content of ice at low temperatures (Figure 3).

[20] Further, also heterogeneous processing of HCl on ice increases at low temperatures [*Carslaw et al.*, 1994]. Interestingly, enhanced concentrations of activated chlorine (up to 50 pptv ClO) were observed during the flight near the cirrus region in the upper troposphere (F. Stroh, personal communication, 2005). Reduced $HNO_{3,gas}$ concentrations due to HNO_3 uptake in cirrus ice may slow down chlorine passivation and therefore prolong halogen activation and enhance ozone loss.

[21] Heterogeneous chemistry on cirrus ice may influence the ozone budget and the oxidation capacity of the upper troposphere, particularly at low temperatures. Because HNO_3 is a reservoir specie for NO_x, denoxification through HNO_3 uptake in ice may lead to a decrease in the NO_x and in the HO_x concentrations in the cirrus region, which may reduce the ozone production rate. *Meier and Hendricks* [2002] estimate an ozone loss up to 14% caused by midlatitude cirrus clouds. Low temperatures and high halogen concentrations in the winter Arctic UTLS may affect the ozone budget in the Arctic UTLS even more. Transport of ozone poor air from high latitudes might further contribute to the downward ozone trend in the midlatitude UTLS region.

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