

# Nitric acid partitioning in cirrus clouds: the role of aerosol particles and relative humidity

By M. KRÄMER<sup>1\*</sup>, C. SCHILLER<sup>1</sup>, H. ZIEREIS<sup>2</sup>, J. OVARLEZ<sup>3</sup> and H. BUNZ<sup>4</sup>,  
<sup>1</sup>FZ Jülich, ICG-I, Germany; <sup>2</sup>DLR Oberpfaffenhofen, IPA, Germany; <sup>3</sup>Lab. de Mét. Dyn. (LMPD), CNRS-IPSL, Palaiseau, France; <sup>4</sup>FZ Karlsruhe, IMK, JMK-AAF, Germany

(Manuscript received 25 February 2005; in final form 1 November 2005)

## ABSTRACT

Owing to the potential of cirrus clouds to vertically redistribute  $\text{HNO}_3$  in the upper troposphere, the uptake of  $\text{HNO}_3$  in ice particles is at the focus of recent research. Here, we investigate whether  $\text{HNO}_3$  residing in freezing aerosol particles could be a relevant source of  $\text{HNO}_3$  in ice clouds. To this end, model studies on the sensitivity of the uptake of  $\text{HNO}_3$  in aerosol particles to temperature, relative humidity with respect to ice ( $\text{RH}_{\text{ice}}$ ), particle composition and amount of available  $\text{HNO}_3$  were performed. Combining the model results with the history of  $\text{RH}_{\text{ice}}$  during cirrus formation and comparison with field measurements indicates that at temperatures  $<200$  K a considerable part of the  $\text{HNO}_3$  in ice may originate from freezing particles containing  $\text{HNO}_3$ .

## 1. Introduction

The role of cirrus clouds in the chemistry of upper tropospheric ozone is presently unclear and is an area of active research. One possible mechanism important for atmospheric chemistry and trace gas distribution is the denitrification of the tropopause region by sedimenting cirrus ice particles (Lawrence and Crutzen, 1998). However, up to now the question of the partitioning of nitric acid ( $\text{HNO}_3$ ) in cirrus clouds has not been satisfactorily answered.

Cirrus ice particles nucleate homogeneously at ice saturations of about 140–170% in the temperature range of about 190–230 K (e.g. Koop et al., 2000; Möhler et al., 2003). Heterogeneous ice nucleation takes place at lower supersaturations (about 110–160%, Kärcher and Lohmann, 2003; Mangold et al., 2005; Möhler et al., 2005). Only the fraction of the aerosol particle population suitable for ice formation is activated, whilst the remaining part of the aerosol population, the interstitial aerosol particles, adjust to a certain size depending on the ambient relative humidity with respect to ice ( $\text{RH}_{\text{ice}}$ ) and coexist with the ice crystals.  $\text{RH}_{\text{ice}}$  decreases after ice nucleation, but in many cases ranges inside the cirrus above the saturation value between 100% and 180% (Ovarlez et al., 2002; Spichtinger et al., 2003; Gao et al., 2004). When the temperature increases and the ice cloud evaporates,  $\text{RH}_{\text{ice}}$  drops below 100% and the aerosol particles equilibrate again to the new relative humidity.

During the formation phase of a cirrus cloud, the highly water-soluble  $\text{HNO}_3$  is partitioned along with  $\text{H}_2\text{O}$  among the aerosol particles ( $\text{HNO}_3^{\text{ptcl}}$ ) and gas phase ( $\text{HNO}_3^{\text{gas}}$ ), and, in the course of cloud lifetime, additionally among the ice particles ( $\text{HNO}_3^{\text{ice}}$ ). Parameters controlling  $\text{HNO}_3$  uptake by aerosol particles are particle composition,  $\text{RH}_{\text{ice}}$ , available  $\text{HNO}_3$  as well as temperature and pressure. Likewise, adsorption of  $\text{HNO}_3$  on ice particles is controlled by the available  $\text{HNO}_3$ , temperature, pressure as well as the ice surface area and morphology.

A series of field and model studies were performed recently on  $\text{HNO}_3$  uptake on ice (Weinheimer et al., 1998; Meilinger et al., 1999; Tabazadeh et al., 1999; Hudson et al., 2002; Hynes et al., 2002; Meier and Hendricks, 2002; Kärcher, 2003; Kondo et al., 2003; Krämer et al., 2003; Popp et al., 2004; Ziereis et al., 2004).  $\text{HNO}_3$  uptake in upper tropospheric particles has attracted less attention, though it is known that cold sulphuric acid particles take up  $\text{HNO}_3$  even at stratospheric  $\text{H}_2\text{O}$  concentrations (Peter, 1997). Under cirrus conditions, Meilinger et al. (1999) and Krämer et al. (2003) show for some field experiments by means of a thermodynamic equilibrium model that a substantial part of the  $\text{HNO}_3$  can be taken up by interstitial particles, especially at temperatures  $<200$  K. More recently, Irie et al. (2004) measured the uptake of  $\text{HNO}_3$  in upper tropospheric aerosol, while, also based on field measurements and using an equilibrium model, Romakkaniemi et al. (2004) show that the uptake of  $\text{HNO}_3$  in aerosol particles depends on particle chemistry and  $\text{RH}_{\text{ice}}$ .

Here, we perform model sensitivity studies on  $\text{HNO}_3$  uptake in upper tropospheric aerosol particles by using both a

---

\*Corresponding author.  
e-mail: mkraemer@fz-juelich.de

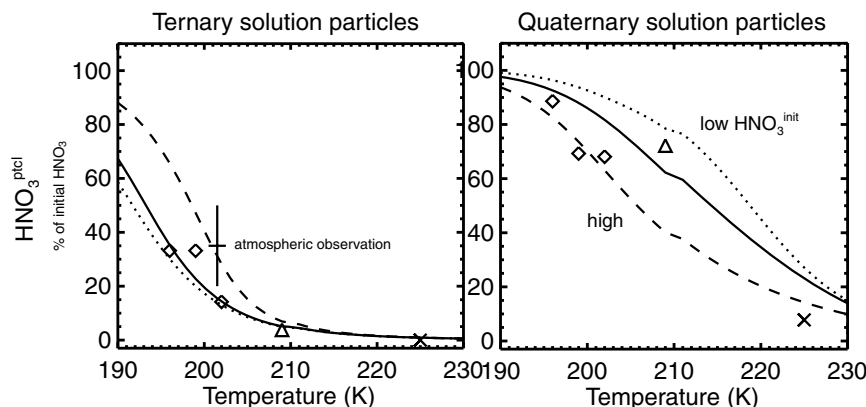


Fig. 1. Equilibrium nitric acid in aerosol particles versus temperature for different  $\text{HNO}_{3,\text{init}}$  and for two types of particles (left: ternary solutions  $\text{H}_2\text{O}-\text{H}_2\text{SO}_4-\text{HNO}_3$ ; right: quaternary solutions  $\text{NH}_3-\text{H}_2\text{O}-\text{H}_2\text{SO}_4-\text{HNO}_3$ ); model calculations are performed using the thermodynamic equilibrium model AIM; initialization of sensitivity studies (lines), mainly based on measurements during POLSTAR 1998 (for details see Krämer et al., 2003):  $^1\text{HNO}_{3,\text{init}} = 0.05-0.26-1.7$  ppbv,  $\text{H}_2\text{SO}_{4,\text{init}} = 0.55$  ppbv,  $\text{NH}_{3,\text{init}} = 0.7$  ppbv,  $p = 178$  hPa,  $\text{RH}_{\text{ice}} = 100\%$ ; model calculations for  $\diamond$ : POLSTAR and  $\triangle$ : SUCCESS field data,  $\times$ : model study by Meier and Hendricks (2002) (data for ternary solutions from Krämer et al., 2003);  $+$ : atmospheric observations (Irie et al., 2004); for details see text.

thermodynamic equilibrium model and a detailed kinetic model. We discuss the dependence of  $\text{HNO}_3$  uptake on temperature, particle composition (ternary  $\text{HNO}_3-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ /quaternary  $\text{NH}_3-\text{HNO}_3-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$  solutions), the initial amount of  $\text{HNO}_3$  and on the ambient relative humidity in thermodynamic equilibrium and, moreover, the relaxation times to reach equilibrium. By taking into account the history of  $\text{RH}_{\text{ice}}$  during cirrus formation, we further discuss the relevance of  $\text{HNO}_3$  uptake in aerosol particles for  $\text{HNO}_3$  partitioning in cirrus clouds and estimate whether  $\text{HNO}_3$  from freezing aerosol particles can be a relevant source of  $\text{HNO}_3$  in ice clouds.

## 2. Methods

Sensitivity studies on  $\text{HNO}_3$  uptake in aerosol particles were performed for upper tropospheric ranges of temperature,  $\text{HNO}_3$  and  $\text{RH}_{\text{ice}}$  during cirrus formation for two particle types, namely ternary ( $\text{HNO}_3-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ ) and quaternary ( $\text{NH}_3-\text{HNO}_3-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ ) solution particles. Although the particle composition in the upper troposphere is not well known, most likely particulate  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and possibly  $\text{NH}_3$  will be present at this altitude (for measurements of UT particle composition e.g. Chen et al., 2000; Irie et al., 2004, and references herein). The particulate  $\text{H}_2\text{SO}_4$  and  $\text{NH}_3$  determine, together with  $\text{H}_2\text{O}$ , the amount of  $\text{HNO}_3$  inside the ternary/quaternary solution droplets (Kärcher and Solomon, 1999; Lin and Tabazadeh, 2001). Organic and insoluble material present in particles are assumed not to influence the  $\text{HNO}_3$  uptake into the liquid. For the model calculations, we used the interactive thermodynamic equilibrium Aerosol Inorganic Model, AIM (Clegg et al., 1998, <http://www.hpc1.uea.ac.uk/~e770/aim.html>; 1K temperature step). The initialization of the models calculations is mainly based on field measurements (see caption of Fig. 1) and are de-

scribed in detail by Krämer et al. (2003). The results are presented in Section 3.1.

The relaxation times necessary to reach thermodynamic equilibrium are estimated by applying a detailed kinetic model for  $\text{HNO}_3$  uptake in ternary solution particles. The kinetic model (Bunz et al., 2003) is based on equations describing the growth kinetics of particles as a function of the saturation levels of condensing/evaporating trace gases. It calculates the growth of  $\text{H}_2\text{SO}_4$  particles with time due to uptake of  $\text{H}_2\text{O}$  and  $\text{HNO}_3$  (+ HCl and HBr). The vapour pressures of the traces gases as a function of particle composition and temperature were determined using the parameterization of Luo et al. (1995). Particle composition, vapour and partial pressures of the condensing trace gases are updated at each time step in the model calculations by taking into account the mass balance of the whole system, that is, the particles as well as gas phase. Like the vapour and partial pressures, the relaxation time to reach particle equilibrium composition and size depends strongly on temperature. Relaxation times for particle  $\text{HNO}_3$  reaching 50%, 90% and 99% of the equilibrium values are determined, for the same initial conditions as the equilibrium calculations, at  $\text{RH}_{\text{ice}} = 100, 130$  and  $160\%$  and  $T = 190$  and  $230\text{K}$ , respectively. The results are presented in Section 3.2.1.

With the findings of the sensitivity studies, we finally discuss the history of  $\text{HNO}_3$  partitioning between aerosol and ice particles during cirrus formation (see Section 3.2).

## 3. Results and discussion

### 3.1. Nitric acid uptake by upper tropospheric aerosol particles

#### 3.1.1. Dependence of particle $\text{HNO}_3$ on temperature and $\text{HNO}_{3,\text{init}}$ : Equilibrium values of nitric acid in upper tropospheric

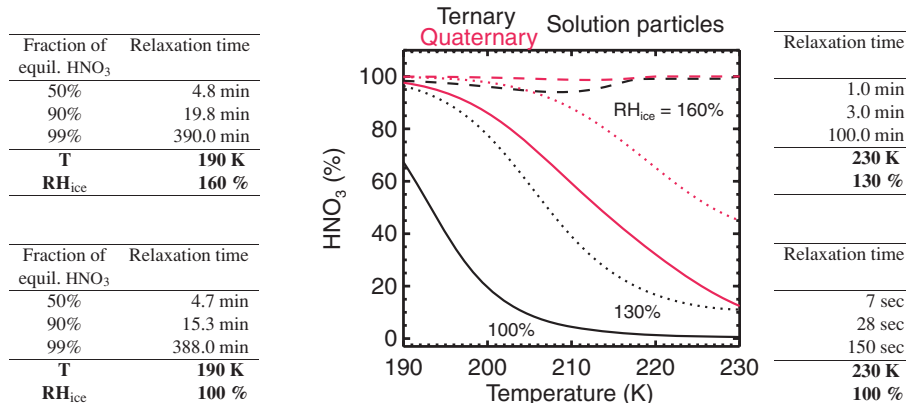


Fig. 2. Same as Fig. 1 but for  $RH_{ice} = 100\%$  (—),  $130\%$  (....) and  $160\%$  (---) at middle  $HNO_{3,init}$  (0.26 ppbv). The small tables show relaxation times of  $HNO_3$  for ternary solution particles calculated by means of a detailed kinetic model for particle  $HNO_3$  that reach 50%, 90% and 99% of the equilibrium value.

ternary and quaternary aerosol particles at  $RH_{ice} = 100\%$  are shown in Fig. 1 for varying initial  $HNO_3$  in the temperature range of upper tropospheric cirrus clouds.<sup>1</sup>

In the presence of ternary solution particles the  $HNO_3$  uptake is, as expected, strongly dependent on temperature (Fig. 1, left panel). At temperatures  $< 200$  K, up to 90% of the  $HNO_3$  was scavenged by the ternary solutions, depending on the initial amount of  $HNO_3$ .

The uptake of  $HNO_3$  is likewise dependent on temperature if the particles are quaternary solutions (Fig. 1, right panel), but more  $HNO_3$  resides in the particles over the whole temperature range. This is because the additional amount of ammonia causes a stronger uptake of  $HNO_3$  by neutralizing the sulfuric acid. For the sensitivity studies presented here, a large amount of  $NH_3$  (0.7 ppbv) is assumed. For smaller  $NH_3$  mixing ratios, the  $HNO_3$  residing in the particles will be lower.

Altogether, the temperature dependence of equilibrium  $HNO_3$  uptake in aerosol dominates the influence on the initial  $HNO_3$  amount for both types of particles. These results are consistent with simulations of equilibrium  $HNO_3$  uptake in quaternary aerosol at fixed  $H_2O$  mixing ratios (here: fixed  $RH_{ice} = 100\%$ ) performed by Lin and Tabazadeh (2001). For comparison with the sensitivity studies, equilibrium  $HNO_3$  uptake of the two particle types was determined for the conditions of several field studies and a model study (Fig. 1,  $\diamond$ ,  $\Delta$ ,  $\times$ ). Almost all the data are in the range of  $HNO_3$  uptake determined by the sensitivity studies. The very recent first direct measurements of particle  $HNO_3$  in the upper troposphere, reported by Irie et al. (2004) (Fig. 1, left panel, +), are in this range as well, suggesting that in this case the particles were ternary solutions.

<sup>1</sup>Brief comment to initialization:  $HNO_3$  is measured during Polstar and represents well the UT  $HNO_3$  range (0.05–1.7 ppbv);  $H_2SO_4$  is calculated in consistency with the aerosol volume measured during Polstar (0.55 ppbv);  $NH_3$  is an estimate of the UT upper limit (0.7 ppbv).

**3.1.2. Dependence of particle  $HNO_3$  on  $RH_{ice}$ :** Equilibrium uptake of nitric acid in upper tropospheric ternary and quaternary aerosol particles is shown in Fig. 2 for the middle value of initial  $HNO_3$  and the same temperature range as in Fig. 1, but for  $RH_{ice}$  varying between saturation and the typical freezing thresholds of heterogeneous (130%) and homogeneous (160%) ice nucleation (note that the timescales of supersaturation during cirrus formation in the atmosphere may be shorter than the time to reach equilibrium; see also Table 1 and Section 3.2.1).

From Fig. 2 it becomes obvious that for both ternary (black lines) and quaternary solution aerosol (red lines) the  $HNO_3$  uptake strongly depends on  $RH_{ice}$ . The higher  $RH_{ice}$ , the more  $HNO_3$  is taken up by the particles even at higher temperatures. At  $RH_{ice} = 160\%$ , all  $HNO_3$  would be taken up in the aerosol independently of temperature (note here that in the upper troposphere very high  $RH_{ice} > \approx 150\%$  only occur at temperatures of 190–210 K). These findings are in good agreement with the study by Romakkaniemi et al. (2004) at  $T = 206$  K (based on POLSTAR 1997 field measurements), who report that uptake of  $HNO_3$  starts at  $RH_{ice} \approx 90\%$  [80%] for ternary solution [Ietovicite:  $(NH_4)_3H(SO_4)_2$ ] particles and that at  $\approx 140\%$  almost all the  $HNO_3$  is taken up by both particle types.

## 3.2. Nitric acid partitioning at cirrus formation

**3.2.1.  $HNO_3$  uptake in particles in the timescales of cirrus formation:** Relaxation times of  $HNO_3$  into ternary solution particles are calculated using the detailed kinetic model (see Section 2) for the same initial conditions as the equilibrium calculations shown in Fig. 2 (the particle number size distribution is initialized to be unimodal and lognormal with  $r_p = 0.125 \mu m$ ,  $N = 110 cm^{-3}$  and  $\sigma = 1.7$ ; the particles uniformly grew during the model simulations; thus, no effects of  $HNO_3$  uptake in particles of different sizes occurred here).

The relaxation times to reach 50%, 90% and 99% of the equilibrium  $HNO_3$  (see Tables in Fig. 2) are about 5 min, 15 min and

Table 1. Estimate of HNO<sub>3</sub> in ice originating from particle freezing

	Cirrus type			T (K)	RH <sub>ice</sub> <sup>crit</sup> (%)	
	Synoptic ≈ 180 min	Gravity wave 5–10 min	Convective 0.5–1 min			
Timescales of cirrus formation	(from Kärcher & Lohman, 2002 + Kärcher, 2003)					(1)
HNO <sub>3</sub> in particles	<b>100</b>	<b>50–80</b>	<b>7–11</b>	<b>&lt;200</b>	<b>130–160</b>	(2)
@ RH <sub>ice</sub> <sup>crit</sup> (% of equilibrium)	100	70–80	30	>210	110–145	(3)
HNO <sub>3</sub> in particles	<b>90–100</b>	<b>45–75</b>	<b>5–12</b>	<b>&lt;200</b>	<b>130–160</b>	(4)
@ RH <sub>ice</sub> <sup>crit</sup> (% of initial)	0–20	0–15	0–12	>210	110–145	(5)
				T (K)	N <sub>ice</sub> (%)	
HNO <sub>3</sub> in ice from freezing particles	<b>2–10</b>	<b>1–6</b>	<b>0.1–0.6</b>	<b>&lt;200</b>	<b>2–5<sup>a</sup></b>	(6)
(% of initial)	0.1–0.4	0.1–0.3	0.15	>210	1–2 <sup>a</sup>	(7)
	Entire range					
HNO <sub>3</sub> in ice from freezing particles	<b>0.1–10</b>			<b>&lt;200</b>	estimate	(8)
(% of initial)	0.1–0.3			>210		(9)
HNO <sub>3</sub> in ice	<b>1–15<sup>b</sup></b>			<b>&lt;200</b>	observation	(10)
total (%) = frozen+adsorbed	15–100 <sup>b</sup>			>210		(11)

HNO<sub>3</sub><sup>init</sup> = 0.26 ppbv, p = 178hPa.

RH<sub>ice</sub><sup>crit</sup>: freezing humidity, HNO<sub>3</sub> in particles @ RH<sub>ice</sub><sup>crit</sup>: fraction of HNO<sub>3</sub> scavenged by particles up to freezing (determined using the HNO<sub>3</sub> relaxation times shown in Figure 2), N<sub>ice</sub>: fraction of particles forming ice, <sup>a</sup>: Mangold et al. (2005), <sup>b</sup>: taken from Popp et al. (2004) (CRYSTAL FACE 2002) and Krämer et al. (2003) (POLSTAR 1997 and 1998).

6.5 h at 190K, independently of RH<sub>ice</sub>. At 230 K the uptake is faster and correlates with RH<sub>ice</sub> since the amount of HNO<sub>3</sub> in the solution droplets raises with raising RH<sub>ice</sub>: only 7 s, 28 s and 2.5 min are needed to stepwise converge to equilibrium at RH<sub>ice</sub> = 100%, while at 130%, the typical freezing threshold at 230K, already 1 min, 3 min and 100 min are necessary (note that for RH<sub>ice</sub> = 160% the situation changes in the simulations: because of the high amount of available water the solution particles can grow to highly diluted solution drop sizes that take up HNO<sub>3</sub> very quickly; this is due to the suppression of ice formation in the model simulations).

Altogether, increasing with temperature, an increasing fraction of the equilibrium HNO<sub>3</sub> can be taken up by the aerosol in the timescale of cirrus formation. The time needed to raise the RH<sub>ice</sub> of an air parcel from about 80% to the freezing threshold (see below) depends on the air parcels updraft velocity or cooling rate, respectively. Following Kärcher and Lohmann (2002), the average updraft velocities (cooling rates) in synoptic waves, gravity waves or convective systems are 4, 54 and 550 cm s<sup>-1</sup> (≈0.03, 0.35 and 3.3 K min<sup>-1</sup>). The respective times for cirrus formation, shown in row (1) of Table 1, are 3 h, 5–10 min (Kärcher, 2003, cirrus formation at about 210–215K) and 30–60 s (extrapolation of Kärcher, 2003).

The thresholds of RH<sub>ice</sub> necessary to initiate particle freezing (RH<sub>ice</sub><sup>crit</sup>), that is cirrus formation, is a function of temperature and decreases from ≈130–160% at T < 200K to ≈110–145% for T > 210K (see Introduction).

Superposing the HNO<sub>3</sub> relaxation times on the timescales of cirrus formation and the freezing thresholds provides the following scenario (see Table 1, second and third row): at low temperatures the aerosol particles scavenge ≈100%, 50–80% and 7–11% of the equilibrium HNO<sub>3</sub> during the formation time of synoptically, gravity wave or convectively induced cirrus. At high temperatures, due to the shorter relaxation times, more HNO<sub>3</sub> is taken up by the aerosol particles during the formation time of gravity wave or convective ice clouds (≈70–80% and 30%; note that for these estimates the lowest limits of the freezing thresholds are considered because during the time of cirrus formation the supersaturation is not constant but increasing up to the freezing thresholds).

Expressing these amounts of particle HNO<sub>3</sub> as a fraction of initial HNO<sub>3</sub> (rows (4) and (5) of Table 1) it becomes obvious that at low temperatures about ≈45–100% of the initial HNO<sub>3</sub> can be contained in the particles at the moment of cirrus formation for slowly forming (synoptic and gravity wave) cirrus, while in fast-forming convective ice clouds only ≈5–12% HNO<sub>3</sub> can be scavenged during the time of cirrus formation. At higher temperatures, where the particle HNO<sub>3</sub> uptake is lower, also only little (≈0–20%) of the initial HNO<sub>3</sub> will be scavenged by the particles during the formation of all types of cirrus clouds.

**3.2.2. HNO<sub>3</sub> in freezing particles at cirrus formation:** When ice particles are forming, the HNO<sub>3</sub> contained in those particles that freeze is assumed to be retained in the particles while freezing. This assumption is supported by the findings of Stuart

and Jacobson (2003), studying volatile chemical retention during hydrometeor freezing. They show that, due to its high dissociation rate,  $\text{HNO}_3$  will likely be retained completely under all conditions in freezing supercooled drops in the drop size range 1–2000  $\mu\text{m}$  at temperatures down to  $-39^\circ\text{C}$ . Stuart and Jacobson (2003) investigated diluted drops larger than upper tropospheric liquid particles, but, on the one hand they show that retention increases with decreasing particle size and on the other hand the weight percentage of  $\text{HNO}_3$  in the particles considered in this study is only between 0.05–3 wt% (corresponding mole fraction  $\approx 0.006$ ). Such low  $\text{HNO}_3$  weight percentages in particles are also reported by Lin and Tabazadeh (2001) for a broad range of upper tropospheric conditions. Additional support for the retention of  $\text{HNO}_3$  during particle freezing can be derived from the study of Beyer et al. (2004): following their phase diagram for the  $\text{H}_2\text{SO}_4$ – $\text{HNO}_3$ – $\text{H}_2\text{O}$  ternary system, water ice and hydrates (NAT, SAT) may co-exist in a solution composed similar to upper tropospheric particles (60–75 wt%  $\text{H}_2\text{O}$ , 22–37 wt%  $\text{H}_2\text{SO}_4$ , 3 wt%  $\text{HNO}_3$ ), especially at temperatures  $< 200\text{ K}$ . As will be shown in Section 3.2.3,  $\text{HNO}_3$  measurements in cold cirrus clouds can be explained under the hypothesis of  $\text{HNO}_3$  retention during particle freezing.

The amount of  $\text{HNO}_3$  in the ice phase that may originate from particle freezing is determined by (i) the fraction of  $\text{HNO}_3$  in particles and (ii) the percentage of particles that freeze. Since both the fraction of  $\text{HNO}_3$  in particles (see previous section) and the fraction of particles that freeze (see Table 1,  $N_{\text{ice}}$  in rows (6) and (7)) increase with decreasing temperature, one can expect that the amount of  $\text{HNO}_3$  captured by ice particles via the freezing pathway will also show this behaviour.

An estimate of the amount of  $\text{HNO}_3$  in ice that may originate from freezing particles is shown in Table 1 (rows (6) and (7)) for two temperature ranges. At  $T < 200\text{ K}$  superposition of particle  $\text{HNO}_3$  at the moment of cirrus formation (rows (4) and (5)) on the number of particles that freeze yields about 1–10% of the initial  $\text{HNO}_3$  in the ice at the onset of cirrus for slowly forming (synoptic and gravity wave) cirrus. For fast-freezing convective cirrus and for all ice cloud types forming at  $T > 210\text{ K}$ , only 0.1–0.6% of the initial  $\text{HNO}_3$  may pass to the ice phase.<sup>2</sup>

**3.2.3. Comparison of  $\text{HNO}_3$  in ice from freezing particles with total ice phase  $\text{HNO}_3$ :** During the lifetime of a cirrus cloud,  $\text{HNO}_3$  will be adsorbed at the ice particle surfaces in addition to the  $\text{HNO}_3$  from freezing particles. Comparison of our estimate of  $\text{HNO}_3$  in ice from freezing particles with field measurements of

total (=frozen + adsorbed)  $\text{HNO}_3$  in ice will provide information on the possible importance of the two pathways as a function of temperature.

In Table 1 (rows (8) and (9)) the estimated entire range of  $\text{HNO}_3$  in ice that may originate from freezing particles is shown for the two temperature ranges, while in rows (10) and (11) the observed total ice phase  $\text{HNO}_3$  is shown. At lower temperatures the two ranges are similar (0.1–10%  $\text{HNO}_3$  in ice from freezing, 1–15% total  $\text{HNO}_3$  in ice), while at higher temperatures  $\text{HNO}_3$  in ice from freezing particles is very much lower than the total (0.1–0.3% compared to 15–100%).

Obviously, at low temperatures particle freezing at the formation of the ice cloud can be a substantial source of  $\text{HNO}_3$  in the ice phase, while at higher temperatures  $\text{HNO}_3$  adsorption on the ice surfaces after ice formation in the course of the clouds lifetime is the dominant pathway.

The following chain of reasoning may provide a possible explanation for this hypothesis. In cold cirrus clouds (a)  $\text{RH}_{\text{ice}}$  tends to stay high (130–180%, Spichtinger et al., 2003; Gao et al., 2004) over a time period between about 5–200 min (Jensen et al., 2005) (b) most of the remaining (=initial–ice phase)  $\text{HNO}_3$  will reside in the interstitial particles at high  $\text{RH}_{\text{ice}}$  (see Fig. 2 and Meilinger et al., 1999; Krämer et al., 2003). In this case, hardly any  $\text{HNO}_3$  will be available in the gas phase for adsorption on the ice surfaces and thus particle freezing at the formation of the ice cloud can be a major source of  $\text{HNO}_3$  in ice. In warmer cirrus, (c)  $\text{RH}_{\text{ice}}$  decreases rapidly after ice formation to about 100% (Spichtinger et al., 2003) and (d)  $\text{HNO}_3$  will escape from the interstitial particles at low  $\text{RH}_{\text{ice}}$  and high temperatures (see Fig. 2 and Meilinger et al., 1999; Krämer et al., 2003). Here, almost all  $\text{HNO}_3$  seems to be available in the gas phase for adsorption on the ice surfaces.

Additional support for the hypothesis can be derived from Fig. 3, where ice phase  $\text{HNO}_3$  measurements (expressed as ice surface coverages) are plotted versus  $\text{RH}_{\text{ice}}$ :  $\text{HNO}_3$  from particle freezing can be detected inside ice clouds as long as  $\text{RH}_{\text{ice}}$  is high, because (a)  $\text{RH}_{\text{ice}}$  is high at the onset of ice formation and (b) in the case of high  $\text{RH}_{\text{ice}}$  almost all  $\text{HNO}_3$  that is not frozen inside the ice is contained in the interstitial particles (see previous paragraph). Ice phase  $\text{HNO}_3$  measurements in the temperature range 212–245 K during the INCA field experiment (Fig. 3, black dots) show high  $\text{RH}_{\text{ice}}$  coupled only with low  $\text{HNO}_3$  coverages around 0.001, indicating low  $\text{HNO}_3$  from particle freezing. In contrast, measurements of  $\text{HNO}_3$  coverages at high  $\text{RH}_{\text{ice}}$  and low temperatures during CRYSTAL FACE (Fig. 3, grey area) yields much higher values (0.01–0.1), pointing to high  $\text{HNO}_3$  in the ice phase at ice formation.

## 4. Summary and conclusions

Model sensitivity studies on the amount and timescale of  $\text{HNO}_3$  uptake in upper tropospheric aerosol particles were performed as a function of  $\text{RH}_{\text{ice}}$ , temperature, the amount of available

<sup>2</sup>Note here that this estimate is for ternary solution particles, in the case of quaternary solutions the amount of  $\text{HNO}_3$  in ice originating from particle freezing may probably be higher. Also note that the estimate is made for the fixed value of  $\text{H}_2\text{SO}_4 = 0.55\text{ ppbv}$ . Lower values of  $\text{H}_2\text{SO}_4$ —as for example assumed by Lin and Tabazadeh (2001)—may lead to lower  $\text{HNO}_3$  in particles @  $\text{RH}_{\text{ice}}^{\text{crit}}$ . However, sensitivity tests—not shown here—indicate that the influence of the initial  $\text{H}_2\text{SO}_4$  on the percentage  $\text{HNO}_3$  in ice from particle freezing is small.

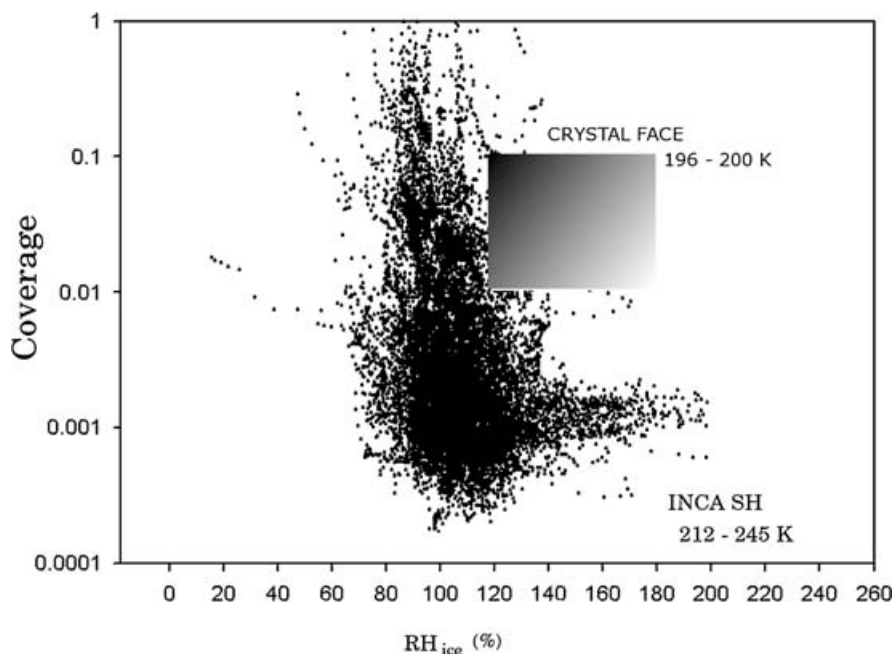


Fig. 3. Measurements of  $\text{HNO}_3$  coverage of ice particles versus  $\text{RH}_{\text{ice}}$ ; black dots: INCA 2000, southern hemisphere, temperature range 212–245 K; grey area: CRYSTAL FACE 2002, temperature range 195–200 K, data range from Popp et al. (2004) and Gao et al. (2004) ( $\text{HNO}_3$  coverage: fraction of monolayer, here defined as  $1 \times 10^{15} \text{ molec cm}^{-2}$ ).

gas-phase  $\text{HNO}_3$  and particle composition by means of a thermodynamic equilibrium as well as a detailed kinetic model. Based on the model calculations, the amount of  $\text{HNO}_3$  in freezing aerosol particles at cirrus formation is estimated.

The equilibrium model calculations show that, besides temperature and particle composition, the most sensitive parameter controlling  $\text{HNO}_3$  uptake in particles is the ambient relative humidity with respect to ice,  $\text{RH}_{\text{ice}}$ . For  $\text{RH}_{\text{ice}} \approx 100\%$ , the  $\text{HNO}_3$  uptake increases with decreasing temperature for both ternary and quaternary solution particles, but on a significantly higher level for the latter (ammoniated ternary solutions). For  $\text{RH}_{\text{ice}}$  close to 160%, almost all nitric acid resides in the particles independent of temperature or particle composition.  $\text{RH}_{\text{ice}}$  can increase up to 180% in the time period of ice cloud formation. Using the detailed kinetic model, the relaxation times for taking up a considerable amount of  $\text{HNO}_3$  in aerosol particles are found to be in this time frame.

We finally estimate that at the formation of cold cirrus ( $T < 200 \text{ K}$ ) about 0.2–10% of the initial gas-phase  $\text{HNO}_3$  may enter the ice phase by particle freezing. The percentage of  $\text{HNO}_3$  in ice observed during field experiments at low temperatures is found to be in the same range, implying the possibility that only little  $\text{HNO}_3$  adsorbs on the ice surfaces after ice formation at  $T < 200 \text{ K}$ . The reason for the low adsorption of  $\text{HNO}_3$  could be, that a substantial part of the  $\text{HNO}_3$  resides in the interstitial particles at low temperatures. This finding may give some indication of why surface adsorption models do not satisfactorily reproduce

the  $\text{HNO}_3$  uptake at low temperatures (e.g. Krämer et al., 2003; Popp et al., 2004).

If an ice cloud forms at higher temperatures ( $T > 210 \text{ K}$ ), only about 0.1–0.3% of the initial  $\text{HNO}_3$  may reach the ice particles via the freezing pathway. This is much lower than the observed amount of  $\text{HNO}_3$  in cirrus ice particles, ranging between 15% and 100% of the initial gas-phase  $\text{HNO}_3$ . Apparently, with increasing temperature adsorption on the ice surface becomes the dominant pathway for  $\text{HNO}_3$  in ice.

## 5. Acknowledgments

The authors are grateful to Rolf Müller, Johannes Hendricks and Stefanie Meilinger for many helpful discussions and comments which improved the manuscript and, most important, for their confidence in the final success of this study. They also would like to thank the anonymous referees for their helpful comments. The text has been revised by a native English speaker from the FZJ Language Service. This paper was created using the  $\text{\LaTeX}$  class file.

## References

- Beyer, K. D., Hanson, A. R. and Raddatz, N. 2004. Experimental determination of the  $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$  phase diagram in regions of stratospheric importance. *J. Phys. Chem.* **108**, 770–780.
- Bunz, H., Koyro, M. and Möhler, O. 2003. Impact of growth kinetics of electrolytic particles on their ice formation potential during AIDA expansion experiments. *Geophysical Research Abstracts* **5**, 09904.

- Chen, Y., DeMott, P. J., Kreidenweiss, S. M., Rogers, D. C. and Sherman, D. E. 2000. Ice formation by sulfate and sulfuric acid aerosol particles under upper-tropospheric conditions. *J. Atmos. Sci.* **57**, 3752–3766.
- Clegg, S. L., Brimblecombe, P. and Wexler, S. A. 1998. A thermodynamic model of the system  $\text{H}^+ - \text{NH}_4^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{H}_2\text{O}$  at tropospheric temperatures. *J. Phys. Chem. 102A*, 2137–2154, (<http://www.hpc1.uea.ac.uk/e770/aim.html>).
- Gao, R. S., Popp, P. J., Fahey, D. W., Marcy, T. P., Herman, R. L. and co-authors 2004. Evidence that nitric acid increases relative humidity in low-temperature cirrus clouds. *Science* **303**, 5657: 516–520.
- Hudson, P. K., Shilling, J. E., Tolbert, M. A. and Toon, O. B. 2002. Uptake of nitric acid on ice at tropospheric temperatures: Implications for cirrus clouds. *J. Phys. Chem. A* doi: 10.1021/jp020508j.
- Hynes, R. G., Fernandez, M. A. and Cox, R. A. 2002. The uptake of  $\text{HNO}_3$  on water ice and the co-adsorption of  $\text{HNO}_3$  and  $\text{HCl}$  in the temperature range 210–235 K. *J. Geophys. Res.* **107**, 4797, doi:10.1029/2001JD001557.
- Irie H., Kondo, Y., Koike, M., Takegawa, N., Tabazadeh, A., Reeves, J. M., Sachse, G. W., Vay, S. A., Anderson, B. E. and Mahoney, M. J. 2004. Liquid ternary aerosols of  $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  in the Arctic tropopause region. *Geophys. Res. Lett.* **31**, L01105, doi:10.1029/2003GL018678.
- Jensen, E., Pfister, L., Bui, T., Weinheimer, A., Weinstock, E., Smith, J., Pittman, J., Baumgardner, D., Lawson, P. and McGill, M. J. 2005. Formation of a tropopause cirrus layer observed over Florida during CRYSTAL-FACE. *J. Geophys. Res.* **110**, D03208, doi:10.1029/2004JD004671.
- Kärcher, B. and Solomon, S. 1999. On the composition and optical extinction of particles in the tropopause region. *J. Geophys. Res.* **104**, 27 441–27 459.
- Kärcher, B. and Lohmann, U. 2002. A parametrization of cirrus cloud formation: Homogeneous freezing of supercooled aerosols. *J. Geophys. Res.* **107**(D2), doi:10.1029/2001JD000470.
- Kärcher, B. and Lohmann, U. 2003. A parametrization of cirrus cloud formation: Heterogeneous freezing. *J. Geophys. Res.* **108**, 4402, doi:10.1029/2002JD003220.
- Kärcher, B. 2003. Simulating gas-aerosol-cirrus interactions: Process-oriented microphysical model and applications. *Atmos. Chem. Phys.* **3**, 1645–1664.
- Kondo, Y., Toon, O. B., Irie, H., Gambin, B., Koike, M., Takegawa, N., Tolbert, M. A., Hudson, P. K., Viggiano, A. A., Avallone, L. M., Hallar, A. G., Anderson, B. E., Sachse, G. W., Vay, S. A., Hunton, D. E., Ballenthin, J. O. and Miller, T. M. 2003. Uptake of reactive nitrogen on cirrus cloud particles in the upper troposphere and lowermost stratosphere. *Geophys. Res. Lett.* **30**, 4, 1154, doi:10.1029/2002GL016539.
- Koop, T., Luo, B., Tsias, A. and Peter, Th. 2000. Water activity as the determinant for homogeneous ice nucleation in aqueous solutions. *Nature* **406**, 611–614, doi:10.1038/35020537.
- Krämer, M., Beuermann, J., Schiller, C., Grimm, F., Arnold, F., Peter, Th., Meilinger, S., Meier, A., Hendricks, J., Petzold, A. and Schlager, H. 2003. Nitric acid partitioning in cirrus clouds: a synopsis based on field, laboratory and model studies. *Atmos. Chem. Phys. Discuss.* **3**, 413–443.
- Lawrence, M. and Crutzen, P. 1998. The impact of cloud particle gravitational settling on soluble trace gas distributions. *Tellus* **50B**, 263–289.
- Lin, J.-S. and Tabazadeh, A. 2001. A parametrization of an aerosol physical chemistry model for the  $\text{NH}_3/\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$  system at cold temperatures. *J. Geophys. Res.* **106**, 4815–4829.
- Luo, B., Carslaw, K. S., Peter Th. and Clegg, S. L. 1995. Vapour pressures of  $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{HCl}/\text{HBr}/\text{H}_2\text{O}$  solutions to low stratospheric temperatures. *J. Geophys. Res.* **22**, 247–250.
- Mangold, A., Wagner, R., Saathoff, H., Schurath, U., Gieseemann, C., Ebert, V., Krämer, M. and Möhler, O. 2005. Experimental investigation of ice nucleation by different types of aerosols in the aerosol chamber AIDA: implications to microphysics of cirrus clouds. *Meteorol. Zeit.* **14**(4), 1–13.
- Meier, A. and Hendricks, J. 2002. Model studies on the sensitivity of upper tropospheric chemistry to heterogeneous uptake of  $\text{hno}_3$  on cirrus ice particles. *J. Geophys. Res.* **107**, 4696, doi:10.1029/2001JD000735.
- Meilinger, S. K., Tsias, A., Dreiling, V., Kuhn, M., Feigl, Ch., Ziereis, H., Schlager, H., Curtius, J., Sierau, B., Arnold, F., Zöger, M., Schiller, C. and Peter, T. 1999.  $\text{HNO}_3$  partitioning in cirrus clouds. *Geophys. Res. Lett.* **26**, 2207–2210.
- Möhler, O., Stetzer, O., Schäfers, S., Linke, C., Schnaiter, M., Tiede, R., Saathoff, H., Krämer, M., Mangold, A., Budz, P., Zink, P., Schreiner, J., Mauersberger, K., Haag, W., Kärcher B. and Schurath, U. 2003. Experimental investigation of homogeneous freezing of sulphuric acid particles in the aerosol chamber AIDA. *Atmos. Chem. Phys.* **3**, 211–223.
- Möhler, O., Wagner, R., Büttner, S., Schnaiter, M., Saathoff, H., Stetzer, O., Krämer, M., Mangold, A., Ebert, V. and Schurath, U. 2005. Effect of sulphuric acid coating on heterogeneous ice nucleation by soot aerosol particles. *J. Geophys. Res.* **110**, D11210, doi:10.1029/2004JD005169.
- Ovarlez, J., Gayet, J.-F., Gierens, K., Ström, J., Ovarlez, H., Auriol, F., Busen, R. and Schuhmann, U. 2002. Water vapour measurements inside cirrus clouds in Northern and Southern hemispheres during INCA. *Geophys. Res. Lett.* **29**, 1813, doi:10.1029/2001GL014440.
- Peter, Th. 1997. Microphysics and heterogeneous chemistry of polar stratospheric clouds. *Annu. Rev. Phys. Chem.* **48**, 785–822.
- Popp, P. J., Gao, R. S., Marcy, T. P., Fahey, D. W., Hudson, P. K. and co-authors 2004. Nitric acid uptake on subtropical cirrus cloud particles. *J. Geophys. Res.* **109**, D06302, doi:10.1029/2003JD004255.
- Romakkaniemi, S., Kokkola, H. and Laaksonen, A. 2004. Growth of upper tropospheric aerosols due to uptake of  $\text{HNO}_3$ . *Atmos. Chem. Phys.* **4**, 549–556.
- Spichtinger, P., Gierens, K., Smit, H. G. J., Ovarlez, J. and Gayet, J.-F. 2003. On the distribution of relative humidity in cirrus clouds. *Atmos. Chem. Phys.* **4**(4), 639–647.
- Stuart, A. L. and Jacobson, M. Z. 2003. A timescale investigation of volatile chemical retention during hydrometeor freezing: Nonrime freezing and dry growth riming without spreading. *J. Geophys. Res.* **108**, doi:10.1029/2001JD001408.
- Tabazadeh, A., Toon, O. P. and Jensen, E. J. 1999. A surface chemistry model for nonreactive trace gas adsorption on ice: Implications for nitric acid scavenging by cirrus. *Geophys. Res. Letters* **26**, 2211–2214.
- Weinheimer, A. J., Campos, T. L., Walega, J. G., Grahek, F. E., Rodley, B. A., Twohy, C. H. and Gandrud, B. 1998. Uptake of  $\text{NO}_y$  on wave-cloud ice particles. *Geophys. Res. Lett.* **25**, 1725–1728.
- Ziereis, H., Minikin, A., Schlager, H., Gayet, J. F., Auriol, F., Stock, P., Baehr, J., Petzold, A., Schumann, U., Weinheimer, A., Ridle, B. and Ström, J. 2004. Uptake of reactive nitrogen on cirrus cloud particles during INCA. *Geophys. Res. Lett.* **31**, L05115, doi:10.1029/2003GL018794.