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The effect of organic coating on the heterogeneous ice nucleation efficiency of mineral dust aerosols

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Abstract

The effect of organic coating on the heterogeneous ice nucleation (IN) efficiency of dust particles was investigated at simulated cirrus cloud conditions in the AIDA cloud chamber of Forschungszentrum Karlsruhe. Arizona test dust (ATD) and the clay mineral illite were used as surrogates for atmospheric dust aerosols. The dry dust samples were dispersed into a 3.7 m³ aerosol vessel and either directly transferred into the 84 m³ cloud simulation chamber or coated before with the semi-volatile products from the reaction of α -pinene with ozone in order to mimic the coating of atmospheric dust particles with secondary organic aerosol (SOA) substances. The ice-active fraction was measured in AIDA expansion cooling experiments as a function of the relative humidity with respect to ice, RHi, in the temperature range from 205 to 210 K. Almost all uncoated dust particles with diameters between 0.1 and 1.0 μ m acted as efficient deposition mode ice nuclei at RHi between 105 and 120%. This high ice nucleation efficiency was markedly suppressed by coating with SOA. About 20% of the ATD particles coated with a SOA mass fraction of 17 wt% were ice-active at RHi between 115 and 130%, and only 10% of the illite particles coated with an SOA mass fraction of 41 wt% were ice-active at RHi between 160 and 170%. Only a minor fraction of pure SOA particles were ice-active at RHi between 150 and 190%. Strong IN activation of SOA particles was observed only at RHi above 200%, which is clearly above water saturation at the given temperature. The IN suppression and the shift of the heterogeneous IN onset to higher RHi seem to depend on the coating thickness or the fractional surface coverage of the mineral particles. The results indicate that the heterogeneous ice nucleation potential of atmospheric mineral particles may also be suppressed if they are coated with secondary organics.

Keywords: ice, nucleation, minerals, organics, coating, atmosphere

1. Introduction

Atmospheric mineral dust particles, mainly originating from deserts in Africa and Asia, are considered to be efficient heterogeneous ice nuclei (Roberts and Hallett 1968, Archuleta *et al* 2005, Field *et al* 2006, Knopf and Koop 2006, Möhler *et al* 2006). They have been found as residual particles of

evaporated ice crystals collected in ice clouds (Heintzenberg *et al* 1996, Twohy and Poellot 2005, Targino *et al* 2006), and could be related to the formation of ice in tropospheric clouds (DeMott *et al* 2003, Sassen *et al* 2003, Cziczo *et al* 2004). Single-particle mass spectrometry demonstrated the abundance of mineral dust particles in the atmosphere and also showed that a large fraction of particles contain organics, in



Figure 1. Schematic of the AIDA facility with aerosol preparation and characterization vessel APC, cloud simulation vessel AIDA, and main instrumentation for aerosol preparation as well as aerosol, ice particle and water vapour measurements.

particular in the upper troposphere (Murphy 2005, Murphy *et al* 2006). Semi-volatile products from the oxidation of biogenic volatile organic compounds contribute a large fraction to the aerosol organics, especially over tropical continental regions (Andreae and Crutzen 1997). Dominant secondary organic aerosol (SOA) forming processes are the reactions of monoterpenes with OH radicals, NO₃ radicals, and ozone, which results in SOA mass production with highly variable yields (Griffin *et al* 1999). The ozonolysis of monoterpenes is supposed to be one of the major atmospheric sources of SOA mass (Griffin *et al* 1999, Kanakidou *et al* 2005). These photochemical reaction products can either contribute to the nucleation of new atmospheric aerosol particles (Sotiropoulou *et al* 2006, Kourtchev *et al* 2008) or condense on other particles like mineral dust (Hinz *et al* 2005).

Studies in high altitude clouds showed that organic-rich particles preferentially remained unfrozen in cirrus clouds, which indicates that organics have the potential to influence aerosol-cloud interaction (Cziczo *et al* 2004). In this paper we investigate the effect of coating with SOA from the reaction of α -pinene with ozone on the heterogeneous ice nucleation efficiency of Arizona test dust (ATD) and illite particles as surrogates for atmospheric dust particles.

2. Experimental methods

2.1. The AIDA facility

The ice nucleation experiments were performed in the cloud simulation chamber of the AIDA facility (Möhler *et al* 2003, 2005, Benz *et al* 2005, Möhler *et al* 2006). Figure 1 schematically shows the main AIDA components and instruments used for the experiments discussed here. The cloud simulation chamber consists of a cylindrical vessel encased in a large, thermally insulated box and is connected to a vacuum and air supply system. The aerosol vessel (4 m diameter, 84 m³ volume) can be evacuated to a pressure below 0.1 hPa and filled with particle-free synthetic air to start the experiments with an aerosol background concentration of less than 0.1 cm⁻³. At constant temperature and pressure conditions, a high relative humidity between 90 and 95% is maintained inside the cloud

simulation chamber by a partial ice coverage of the inner chamber walls. The ice coverage is achieved by filling the chamber with humidified air at warmer temperature before cooling to the starting temperature of the cloud expansion experiments described in section 2.3. The excess water vapour forms a frost layer at the inner chamber walls which serves as a water reservoir during the low temperature experiments.

The AIDA facility is equipped with a comprehensive set of water, aerosol, and cloud instruments (see figure 1). For the present study we used a chilled mirror frost point hygrometer (MBW Calibration Ltd) for total water concentration measurements, a tunable diode laser absorption spectrometer (Ebert et al 2005) for fast and samplingfree open-path water vapour measurements inside the AIDA vessel, an in situ light scattering and depolarization setup for the sensitive detection of droplet and ice particle growth, an infrared extinction spectrometer (FTIR) for the characterization of droplet and ice clouds (Wagner et al 2006, 2007), two optical particle counters (Welas, Palas GmbH) for measuring the number concentrations of droplets and ice clouds (Benz et al 2005), as well as the condensation particle counter (CPC3010), the scanning mobility particle sizer (SMPS), and the aerodynamic particle spectrometer (APS) (all TSI Inc.) for aerosol measurements.

The aerosols were prepared and characterized in the aerosol preparation and characterization (APC) vessel of 3.7 m^3 volume (see section 2.2). The APC vessel is made of stainless steel and can also be evacuated to a pressure below 1 hPa and then filled with particle-free synthetic air prior to aerosol generation. After generating and characterizing the aerosol in the APC vessel, only a minor fraction of the aerosol was transferred to the AIDA vessel through a stainless steel tube. The ice nucleation experiments in the large AIDA vessel will be described in section 2.3.

2.2. Aerosol preparation and characterization

The effect of organic coating on the heterogeneous ice nucleation efficiency of mineral dust particles was investigated for Arizona test dust (ATD) and illite particles as surrogates for desert dust aerosol. The ATD sample is the same as the



Figure 2. Number size distribution of illite aerosol in the APC vessel before (left) and after (right) coating with SOA.

Table 1. Density ρ , dynamic shape factor χ , number concentration n_{ae} , and mass concentration m_{ae} of the aerosol prepared in the APC chamber. The mass fraction $f m_{SOA}$ was obtained from the calculated yield of secondary organic aerosol mass, y_{SOA} .

Exp key	Aerosol type	$ ho~({\rm g~cm^{-3}})$	χ	$n_{\rm ae} \ ({\rm cm}^{-3})$	$m_{\rm ae} \ ({\rm mg} \ {\rm m}^{-3})$	$y_{\rm SOA} \ ({\rm mg} \ {\rm m}^{-3})$	$fm_{\rm SOA}$ (wt%)
IN07_01	ATD	2.6	1.3	2.6×10^4	2.6		
IN07 <u>0</u> 4 IN07_19	ATD + SOA	2.4 2.6	1.2	2.0×10^4 1.8 × 10 ⁴	3.5	0.6	17
IN07_12	Illite $+$ SOA	2.0	1.1	1.0×10^{4} 2.0×10^{4}	2.9	1.2	41
IN07_16	SOA	1.25	1.0	5.1×10^{5}	1.9	2.0	105

one already used for previous AIDA experiments (Field et al 2006, Möhler et al 2006). The illite sample is a commercial clay mineral product from Arginotec. The sample is of natural origin with a mineralogical composition of about 77 wt% illite, 10 wt% kaolinite, 12 wt% calcite, and 1 wt% other trace minerals. The dry ATD and illite samples were dispersed with a rotating brush disperser (RBG-1000, Palas). The dust aerosol was further deagglomerated in a dispersion nozzle, and then passed through a cyclone impactor to remove particles larger than about 1 μ m in diameter. The resulting aerosol was then added to the APC chamber and uniformly distributed with the help of a mixing fan. Both the brush disperser and the dispersion nozzle were operated with dry and particle-free synthetic air to avoid contamination of the dust aerosol with particles of unknown origin. The dispersion pressure of the nozzle was 1.5 bar.

The initial number and mass concentrations, n_{ae} and m_{ae} , of the aerosol added to the APC chamber are listed in table 1. The number concentration was measured with a CPC3022 condensation particle counter (TSI Inc.), the mass concentration was calculated from a combined particle number size distribution (PSD) measured with SMPS and APS instruments. To compare the results of the two instruments, the mobility-equivalent particle diameter d_{me} of the SMPS and the aerodynamic diameter d_{ae} of the APS were converted into a volume-equivalent sphere diameter d_p according to

$$d_{\rm p} = \frac{1}{\chi} d_{\rm me} \tag{1}$$

$$d_{\rm p} = \sqrt{\frac{\chi \ \rho_0}{\rho}} \, d_{\rm ae} \tag{2}$$

where ρ_0 is the unit density of 1 g cm⁻³, ρ is the particle density and χ is the dynamic shape factor which accounts for the non-spherical particle shape. Sand particles composed of a mixture of different minerals typically have a density of 2.5 g cm⁻³ and a dynamic shape factor of 1.3–1.6 (Davies 1979, Linke *et al* 2006). For the dry and uncoated dust particles used in the present study, best agreement between the mobilityequivalent and the aerodynamic diameter was achieved with a density of 2.6 g cm⁻³ and a dynamic shape factor of 1.3 (see table 1).

Coating with secondary organic aerosol (SOA) mass was achieved by first adding ozone to the dust aerosol in the APC chamber, and then a certain amount of α -pinene. The initial volume mixing ratios ranged from 0.5 to 1.5 ppmv for ozone and from 0.3 to 1.0 ppmv for α -pinene. Ozone was always added in excess to ensure complete conversion of the α -pinene to the SOA products. The semi-volatile products of the chemical reaction between ozone and α pinene condensed on the mineral dust particle surface. This condensation occurred in the transition regime between kinetic and diffusional control of the molecular flux to the particle surface, where the condensation rate per particle surface area starts to decrease with the particle diameter. Therefore we can assume a tendency of decreasing SOA coat mass fraction for the larger dust particles.

Figure 2 shows PSDs for illite before (left panel) and after (right panel) coating with SOA. As mentioned above, the PSDs were measured with an SMPS (circles) and an APS (triangles) instrument. All PSDs in this paper are shown as a function of the volume-equivalent particle diameters calculated

Table 2. Parameters of lognormal fits to the aerosol size distribution measured in the AIDA chamber. The total aerosol mass concentration, m_{ae} , was calculated from the lognormal fits to the size distribution measured with the SMPS and APS, and the SOA mass concentration, m_{SOA} , was measured with the aerosol mass spectrometer Q-AMS.

		Aerosol mode 1			Aerosol mode 2			Aerosol mass	
Exp key	Aerosol type	$n_{\rm ae,1} ({\rm cm}^{-3})$	$d_{m,1}$ (μ m)	σ_1	$n_{\rm ae,2} \ ({\rm cm}^{-3})$	$d_{m,2}$ (μ m)	σ_2	$m_{\rm ae}~(\mu { m g~m^{-3}})$	$m_{\rm SOA}~(\mu {\rm g~m^{-3}})$
IN07_01	ATD	132	0.42	1.46	14	0.17	1.69	25.4	
IN07_04	ATD + SOA	90	0.53	1.28	19	0.18	1.32	22.1	>0.4
IN07_19	Illite	59	0.46	1.25	39	0.18	1.60	10.6	
IN07_22	Illite $+$ SOA	47	0.56	1.21	40	0.27	1.34	12.0	>1.8
IN07_16	SOA	188	0.19	1.29				1.1	1.3
IN07_17	SOA	121	0.18	1.31				0.64	

with equations (1) and (2). The respective particle density and dynamic shape factor are given in table 1.

The illite aerosol shows a bimodal PSD with a major mode of particles with diameters between 0.15 and 1.0 μ m and a minor fraction of smaller particles around 0.1 μ m. This bimodal PSD results from the nature of the dust sample and is not a measurement artefact. We were not able to further analyse the chemical or mineralogical nature of the both modes. The solid line represents a bimodal lognormal fit to the measured PSD. The lognormal parameters number concentration *n*, mode diameter *d*, and geometric standard deviation σ in the uncoated case were 21 676 cm⁻³, 0.38 μ m, and 1.41 for the major mode 1 and 1788 cm⁻³, 0.11 μ m, and 1.24 for mode 2. For the SOA-coated illite aerosol, the lognormal parameters were 12 200 cm⁻³, 0.46 μ m, and 1.43 for the major mode 1 and 367 cm⁻³, 0.12 μ m, and 1.14 for mode 2.

For the SOA-coated illite aerosol, a density of 2.1 g cm⁻³ and a dynamic shape factor of 1.1 were needed to merge the SMPS and APS size distributions. This already indicated that a significant amount of SOA coating was achieved. However, the actual SOA mass fraction fm_{SOA} of the aerosol can hardly be obtained from a PSD analysis because the PSD also changes in the APC chamber due to physical aerosol processes like particle coagulation or sedimentation of larger particles to the vessel floor. A better estimate of fm_{SOA} was obtained from the amount of α -pinene added to the APC chamber and the aerosol yield for the reaction with ozone, which is about 35% at a temperature of about 300 K (Cocker et al 2001, Saathoff et al 2008). A density of 1.25 g cm⁻³ was used for the SOA material. The SOA mass fraction was 17% for experiment IN07_04 with ATD as seed aerosol and 41% for experiment IN07_22 with illite as seed aerosol. For experiment IN07_16 without seed aerosol, the yield calculation correctly resulted in about 100% SOA mass fraction. This aerosol was used as reference for the ice nucleation behaviour of pure SOA particles.

Table 2 summarizes the PSD lognormal parameters measured for the aerosol in the AIDA vessel before the cloud expansion experiments. For the uncoated and coated ATD and illite aerosols, the best approximation to the measured PSDs was obtained with a bimodal lognormal fit, with the main mode of particles around diameters of 0.5 μ m and a minor mode around 0.2 μ m. The pure SOA aerosol consisted of only one particle mode with diameters around 0.2 μ m. It

can be assumed that the coated dust particles transferred to the AIDA vessel had almost the same SOA mass fraction as the respective aerosol prepared in the APC vessel. Some of the larger particles may have been lost by settling processes in the connection tube, which had a horizontal length of about 5.5 m and an inner diameter of 1.6 cm. The smaller size mode tends to decrease with time due to efficient coagulation of these particles with the particles of the larger size mode. This together with the settling losses of some larger particles explains the tendency of σ to decrease during the coating step. The aerosol mass concentration m_{ae} calculated from the lognormal fit to the measured size distribution is also given in table 2.

The SOA mass concentration of the AIDA aerosol was also measured with an Aerodyne quadrupole aerosol mass spectrometer, Q-AMS (Jayne et al 2000, Canagaratna *et al* 2007). This instrument quantitatively analyses the non-refractory components of submicron aerosol particles (organics, nitrate, sulfate, and ammonium). The detection relies on thermal vapourization at 600 °C and subsequent electron impact ionization. The Q-AMS is not sensitive to mineral dust, but to the SOA coating on the surface of the dust particles. The aerodynamic inlet lens transmits particles with 100% efficiency in the size range (vacuum-aerodynamic diameter) between 0.06 and 0.6 μ m, which corresponds to an upper cut-off volume-equivalent diameter of about 0.3 μ m when dust particles were coated with SOA. Therefore, we were not able to measure the full size distribution of the SOA coating. The Q-AMS measured only a lower limit of the total aerosol SOA mass of the coated dust particles. These lower limits are consistent with the SOA mass fraction obtained from the yield calculation (see table 1). Only for the pure SOA aerosol did the Q-AMS sample and analyse almost all aerosol particles. In this case, the Q-AMS SOA mass concentration agreed well with the total aerosol mass concentration.

2.3. Cloud expansion experiments

All cloud expansion experiments discussed here were started at a pressure of about 1000 hPa and a homogeneous temperature of about 210 K with temporal and spatial temperature variability of less than ± 0.3 K throughout the cloud chamber. The interior of the vessel is stirred with a mixing fan which is located in the bottom part of the vessel. Under stirred conditions, the temperature variability inside the vessel is less



Figure 3. Comparison of data time series from the AIDA cloud expansion experiments IN07_01 with uncoated ATD aerosol (black) and IN07_04 with SOA-coated ATD aerosol (blue). Panel 1 depicts the gas pressure, panel 2 the gas temperature T_{gas} (solid lines) and the wall temperature T_{wall} (dotted lines), panel 3 the relative humidity with respect to ice (solid lines) and with respect to liquid water (dashed lines), and panel 4 the aerosol number concentrations measured with the CPC3010 (aerosol, dashed lines) and ice particle number concentrations measured with the Welas optical particle counter (Ice Welas, open circles).

than ± 0.2 K. Gas and wall temperatures are measured with an accuracy of ± 0.3 K.

The course of an AIDA cloud expansion experiment is illustrated in figure 3. Two sets of data time series are compared to each other, one from experiment IN07_01 with uncoated ATD aerosol (black lines and symbols), and the other from experiment IN07_04 with SOA-coated ATD aerosol (blue lines and symbols). The time series are plotted on a time axis (in seconds) relative to starting pumping at t =0. The first panel shows the gas pressure inside the AIDA vessel decreasing from about 1000 to 850 hPa within about 400 s. The same pumping speeds were applied during both expansion experiments, resulting in almost identical cooling rates due to adiabatic expansion. As shown in panel 2, there was only a small offset to warmer initial gas temperature T_{gas} and wall temperature T_{wall} for the second experiment with coated aerosol. The relative change of T_{gas} was similar in both experiments. During AIDA expansion experiments T_{wall} stays almost constant. The increasing temperature gradient between the well-mixed volume and the walls of the vessel provides an increasing heat flux to the vessel volume and causes T_{gas} to deviate from the adiabatic cooling profile.

Panel 3 of figure 3 shows the measured relative humidity with respect to ice (RHi, solid lines) and to the liquid water phase (RHw, dashed lines). In both experiments, RHi is about 93% before the start of the pumping expansion. This initial humidity is controlled by a partial ice coverage of the vessel walls and the respective wall and gas temperatures. After the start of the pumping expansion, the initial rise in relative humidity is identical in both experiments, mainly as a result of the gas temperature drop. After about 60 s of pumping, the RHi data start to deviate from each other, which is a result of the different amount of ice nucleated by the different aerosols. Panel 4 shows that ice nucleation on uncoated ATD aerosol starts earlier, i.e. at lower RHi, and that a larger number of ice particles n_{ice} is formed (black circles) compared to the experiment with SOA-coated ATD (blue circles). The growing ice particles start to deplete the water vapour and to lower the relative humidity. The more ice particles are nucleated and deplete the water vapour, the lower is the resulting peak relative humidity reached in experiments with the same expansion rate. The relation between T_{gas} , RHi, and n_{ice} will be discussed in section 3. Panel 4 of figure 3 also shows that the number concentration of aerosol particles, n_{ae} , was almost the same in both experiments (see also table 2).

3. Results

In this section we discuss the ice nucleation results of the AIDA expansion experiments with the aerosols listed in table 2. The aerosols were prepared and characterized as described in section 2.2. Figures 4 and 5 compare the results of experiments with uncoated and SOA-coated ATD and illite aerosol, respectively. Figure 6 compares the results of two subsequent expansion runs with the same SOA aerosol, but different pumping speeds. The left panel of these figures shows for any experiment the evolution of temperature and RHi (dotted lines). The solid line indicates the saturation conditions of the liquid water phase, with saturation vapour pressures taken from (Murphy and Koop 2005), and the dashed lines indicate the threshold conditions for the homogeneous freezing of solution particles (Koop *et al* 2000) calculated for $\Delta a_{\rm w}$ of 0.30 and 0.32. As discussed in section 2.3, all expansion experiments were started at a temperature of about 210 K and an RHi of about 93%. During the course of the expansion run, the temperature decreases and RHi increases to its peak value which, at a given cooling rate, mainly depends on the rate of water depletion by the growing ice phase.

The right panels of figures 4–6 show the relation of the ice-active fraction f_{ice} of the aerosol particles and the increasing RHi, with f_{ice} determined as the ratio of the ice particle concentration n_{ice} to the aerosol particle concentration n_{ae} . These plots show only data recorded between starting pumping and the time when the peak RHi was reached. In all experiments, n_{ice} steadily increased as long as RHi continued to rise, but stayed almost constant as soon as RHi approached or reached its peak value. Such a relationship between the iceactive number fraction of dust particles and RHi was already



Figure 4. Plots of relative humidity with respect to ice, RHi, versus the gas temperature (left panel), and ice-active aerosol fraction, f_{ice} , versus RHi (right panel) for experiment IN07_01 with uncoated ATD aerosol (black lines and symbols) and experiment IN07_04 with SOA-coated ATD aerosol (blue lines and symbols). In the left panel the solid line indicates the saturation conditions of the liquid water phase and the dashed lines indicate the threshold conditions for the homogeneous freezing of solution particles (see the text for more details).



Figure 5. Plots of relative humidity with respect to ice, RHi, versus the gas temperature (left panel), and ice-active aerosol fraction, f_{ice} , versus RHi (right panel) for experiment IN07_19 with uncoated illite aerosol (black lines and symbols) and experiment IN07_22 with SOA-coated illite aerosol (blue lines and symbols). In the left panel the solid line indicates the saturation conditions of the liquid water phase and the dashed lines indicate the threshold conditions for the homogeneous freezing of solution particles (see the text for more details).



Figure 6. Plots of relative humidity with respect to ice, RHi, versus the gas temperature (left panel), and ice-active aerosol fraction, f_{ice} , versus RHi (right panel) for experiments IN07_16 (black symbols) and IN07_17 (blue symbols) with pure SOA particles. In the left panel the solid line indicates the saturation conditions of the liquid water phase and the dashed lines indicate the threshold conditions for the homogeneous freezing of solution particles (see the text for more details). The second expansion was performed with the SOA aerosol remaining in the chamber after filling the AIDA vessel with particle-free synthetic air at the end of the first expansion experiment. Due to the faster pumping a higher peak RHi was reached during the second expansion.

observed in previous AIDA experiments on the deposition ice nucleation to mineral dust particles and was interpreted as the result of a distribution of surface sites which are rapidly activated as soon as the respective RHi thresholds are reached (Möhler *et al* 2006). The deposition mode of ice nucleation occurs on the surface of the dry dust particles without any liquid water or solute phases being involved (Vali 1985).

During the expansion experiment with uncoated ATD (figure 4), the peak RHi is only 115% and almost all aerosol particles are activated as deposition mode ice nuclei

at RHi between 105 and 115%, in agreement with previous AIDA experiments on the deposition mode ice nucleation on ATD particles (Möhler *et al* 2006). The heterogeneous ice nucleation of the SOA-coated ATD particles is significantly lower (see the blue circles in the right panel of figure 4) with significant ice formation only for RHi larger than 115%. At the peak RHi of 130% only about 20% of the aerosol particles were activated.

The uncoated illite particles are also very efficient ice nuclei in the deposition mode (see figure 5). The RHi is limited to a peak value of 120%, and almost all illite particles nucleate ice in the RHi range between 105 and 120%. The ice nucleation of the SOA-coated illite particles is even more suppressed than that of the SOA-coated ATD particles. Only 10% of the SOA-coated illite particles nucleate ice between 160 and 170%, which is above the threshold for homogeneous freezing of solution particles at the same temperature (see the left panel of figure 5). The more pronounced suppression of ice nucleation is probably due to the larger SOA mass fraction of about 41% compared to about 17% for the ATD case.

Figure 6 shows that during the first SOA expansion experiment with a peak RHi of about 190%, only about 1% of the SOA particles nucleated ice at RHi between 150 and 190%. Further experiments with a much higher number concentration of pure SOA aerosol revealed a similar ice-active particle fraction at an RHi of about 160% (Wagner et al 2007). After the first expansion experiment IN07_16, the AIDA vessel was refilled with particle-free synthetic air to atmospheric pressure and a second expansion experiment, IN07_17, was started with the same SOA aerosol. The pumping speed was increased during this experiment to reach a higher peak RHi. Again, a minor fraction of the SOA particle nucleated ice below 190% RHi, but a distinct peak of ice nucleation was observed at RHi between 200 and 210%. From this we conclude that, at a temperature of about 205 K, the majority of SOA particles with diameters around 0.2 μ m need a significant water supersaturation for ice-activation.

4. Conclusions

This paper investigates the effect of coating with secondary organic aerosol (SOA) compounds on the heterogeneous ice nucleation efficiency of Arizona test dust (ATD) and illite aerosol particles with diameters between about 0.1 and 1.0 μ m. The mineral aerosol particles were coated at room temperature by condensation of semi-volatile products from the reaction of α -pinene with ozone. The ice nucleation behaviour was investigated in AIDA cloud expansion experiments at temperatures between 210 and 205 K.

The RHi threshold for the heterogeneous ice nucleation onset (1% ice-active particles) is about 105% for uncoated ATD and illite particles, about 115% for SOA-coated ATD particles (about 17 wt% SOA), about 165% for SOA-coated illite particles (about 41 wt% SOA), and about 170% for pure SOA particles. From this we conclude that an increasing amount of coating with secondary organic aerosol compounds suppresses the heterogeneous ice nucleation potential of mineral dust aerosols. This is probably the result of an increasing fractional surface coverage of the mineral particles with SOA mass. Mineral particles completely immersed in SOA mass seem to significantly induce heterogeneous ice nucleation only above the RHi threshold for homogeneous ice nucleation of solution particles, at least at a temperature close to 205 K. Strong ice-activation of pure SOA particles, i.e. more than 2% ice-active number fraction, was only observed at RHi above 200%. From this we conclude that, at a temperature of about 205 K, the majority of SOA particles with diameters around 0.2 μ m need a significant water supersaturation for ice-activation.

The present work demonstrates the marked changes of heterogeneous ice nucleation efficiency of dust particles due to coating with secondary organic aerosol compounds. Because a large abundance of organic matter was found in tropospheric aerosol particles (Murphy 2005, Murphy *et al* 2006), we can assume that the heterogeneous ice nucleation potential of atmospheric dust particles is lowered by organic coatings. Further studies should analyse the full ice-activation spectra or the surface density of active sites for heterogeneous ice nucleation as a function of various coating layers, and should also investigate if the degree of ice nucleation suppression only depends on the coating thickness or also on the nature of the dust cores and the coating layers.

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References

- Andreae M O and Crutzen P J 1997 Science 276 1052-8
- Archuleta C M, DeMott P J and Kreidenweis S M 2005 Atmos. Chem. Phys. 5 2617–34
- Benz S, Megahed K, Möhler O, Saathoff H, Wagner R and Schurath U 2005 J. Photochem. Photobiol. A **176** 208–217
- Canagaratna M R et al 2007 Mass Spectrom. Rev. 26 185–222 Cooler D R. Clagg S L. Flagger R C and Sainfold LH 2001 Atmos
- Cocker D R, Clegg S L, Flagan R C and Seinfeld J H 2001 Atmos. Environ. **35** 6049–72
- Cziczo D J, DeMott P J, Brooks S D, Prenni A J, Thomson D S, Baumgardner D, Wilson J C, Kreidenweis S M and Murphy D M 2004 Geophys. Res. Lett. 31 12
- Cziczo D J, Murphy D M, Hudson P K and Thomson D S 2004 J. Geophys. Res. 109 D04201
- Davies C N 1979 J. Aerosol Sci. 10 477-513
- DeMott P J, Sassen K, Poellot M R, Baumgardner D, Rogers D C, Brooks S D, Prenni A J and Kreidenweis S M 2003 Geophys. Res. Lett. 30 1732

- Ebert V, Teichert H, Giesemann C, Saathoff H and Schurath U 2005 Tech. Mess. 72 23–30
- Field P R, Möhler O, Connolly P, Krämer M, Cotton R, Heymsfield A J, Saathoff H and Schnaiter M 2006 Atmos. Chem. Phys. 6 2991–3006
- Griffin R J, Cocker D R, Flagan R C and Seinfeld J H 1999 J. Geophys. Res. 104 3555–67
- Griffin R J, Cocker D R, Seinfeld J H and Dabdub D 1999 *Geophys. Res. Lett.* **26** 2721–4
- Heintzenberg J, Okada K and Ström J 1996 *Atmos. Res.* **41** 81–8 Hinz K P, Trimborn A, Wingartner E, Henning S,
- Baltensperger U and Spengler B 2005 J. Aerosol Sci. **36** 123–45 Jayne J T, Leard D C, Zhang X F, Davidovits P, Smith K A,
- Kolb C E and Worsnop D R 2000 *Aerosol Sci. Technol.* **33** 49–70
- Kanakidou M et al 2005 Atmos. Chem. Phys. 5 1053–123
- Knopf D A and Koop T 2006 J. Geophys. Res. 111 D12201
- Koop T, Luo B P, Tsias A and Peter T 2000 Nature 406 611-4
- Kourtchev I et al 2008 Plant Biol. 10 138-49
- Linke C, Möhler O, Veres A, Mohacsi A, Bozoki Z, Szabo G and Schnaiter M 2006 Atmos. Chem. Phys. 6 3315–23
- Möhler O et al 2003 Atmos. Chem. Phys. 3 211-23
- Möhler O et al 2005 J. Geophys. Res. 110 D11210

- Möhler O et al 2006 Atmos. Chem. Phys. 6 3007-21
- Murphy D M 2005 Science **307** 1888–90
- Murphy D M, Cziczo D J, Froyd K D, Hudson P K, Matthew B M, Middlebrook A M, Peltier R E, Sullivan A, Thomson D S and Weber R J 2006 *J. Geophys. Res.* **111** D23S32
- Murphy D M and Koop T 2005 Q. J. R. Meteorol. Soc. 131 1539-65
- Roberts P and Hallett J 1968 Q. J. R. Meteorol. Soc. 94 25–34
- Saathoff H, Naumann K H, Möhler O, Jonsson A M, Hallquist M, Kiendler-Scharr A, Mentel T F, Tillmann R and Schurath U 2008 in preparation
- Sassen K, DeMott P J, Prospero J M and Poellot M R 2003 *Geophys. Res. Lett.* **30** 1633
- Sotiropoulou R E P, Tagaris E, Pilinis C, Anttila T and Kulmala M 2006 *Aerosol Sci. Technol.* **40** 557–72
- Targino A C, Krejci R, Noone K J and Glantz P 2006 Atmos. Chem. Phys. 6 1977–90
- Twohy C H and Poellot M R 2005 Atmos. Chem. Phys. 5 2289-97
- Vali G 1985 Bull. Am. Meteorol. Soc. 66 1426–7
- Wagner R, Benz S, Möhler O, Saathoff H, Schnaiter M and Leisner T 2007 J. Phys. Chem. A **111** 13003–22
- Wagner R, Benz S, Möhler O, Saathoff H and Schurath U 2006 Atmos. Chem. Phys. 6 4775–800