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# Irreversible loss of ice nucleation active sites in mineral dust particles caused by sulphuric acid condensation

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## Abstract

During the FROST-2 (FReezing Of duST) measurement campaign conducted at the Leipzig Aerosol Cloud Interaction Simulator (LACIS), we investigated changes in the ice nucleation properties of 300 nm Arizona test dust mineral particles following thermochemical processing by varying amounts and combinations of exposure to sulphuric acid vapour, ammonia gas, water vapour, and heat. The processed aerosol's heterogeneous ice nucleation properties were determined in both the water subsaturated and supersaturated humidity regimes at  $-30^{\circ}\text{C}$  and  $-25^{\circ}\text{C}$  using Colorado State University's continuous flow diffusion chamber. The amount of sulphuric acid coating material was estimated by an aerosol mass spectrometer and from CCN-derived hygroscopicity measurements. The condensation of sulphuric acid decreased the dust particles' ice nucleation ability in proportion to the amount of sulphuric acid added. Heating the coated particles in a thermodenuder at  $250^{\circ}\text{C}$  – intended to evaporate the sulphuric acid coating – reduced their freezing ability even further. We attribute this behaviour to accelerated acid digestion of ice active surface sites by heat. Exposing sulphuric acid coated dust to ammonia gas produced particles with similarly poor freezing potential; however a portion of their ice nucleation ability could be restored after heating in the thermodenuder. In no case did any combination of thermochemical treatments increase the ice nucleation ability of the coated mineral dust particles compared to unprocessed dust. These first measurements of the effect of identical chemical processing of dust particles on their ice nucleation ability in both water subsaturated and mixed-phase supersaturated cloud conditions revealed that ice nucleation was more sensitive to all coating treatments in the water subsaturated regime. The results clearly indicate irreversible impairment of ice nucleation activity in both regimes after condensation of concentrated sulphuric acid. This implies that the sulphuric acid coating caused permanent chemical and/or physical modification of the ice active surface sites; the possible dissolution of the coating during droplet activation did not restore all immersion/condensation-freezing ability.

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# 1 Introduction

Mineral dust particles are some of the most efficient heterogeneous ice nuclei measured in laboratory studies, able to nucleate ice at higher temperatures and lower ice vapour pressures than other non-biological particle compositions. They are frequently detected in ice crystal residues and thus thought to play an important role in ice cloud microphysics (Cantrell and Heymsfield, 2005; DeMott et al., 2003a, b; Stith et al., 2009). The ice nucleating ability of mineral dust depends on its mineralogy, with aluminosilicate clay phases typically displaying the highest freezing potential (Archuleta et al., 2005; Eastwood et al., 2008; Kanji et al., 2008; Welts et al., 2009; Zimmermann et al., 2008). In general, larger dust particles can nucleate ice at higher temperatures and lower ice vapour pressures due to their larger surface area (Archuleta et al., 2005; Kanji et al., 2008; Phillips et al., 2008; Welts et al., 2009). Two principle mechanisms of heterogeneous ice nucleation by insoluble nuclei such as mineral dust are deposition and immersion/condensation-freezing ice nucleation (Cantrell and Heymsfield, 2005; Vali, 1985). Deposition-mode ice nucleation involves the direct formation of ice on a particle's surface in contact with an ice supersaturated vapour, and therefore is expected to be the primary ice nucleation mode for bare mineral surfaces below water saturation. Immersion/condensation-freezing ice nucleation occurs when liquid droplets that contain an insoluble ice nucleus freeze. This process typically requires conditions above water saturation to occur, although particles with sufficient hygroscopicity may begin to freeze via this mechanism below water saturation at sufficiently low temperatures. Heterogeneous ice nucleation allows atmospheric mineral dust particles to freeze under warmer conditions and lower water relative humidities than those required to freeze aqueous salt particles, which form ice via homogeneous nucleation only at temperatures below  $-38^{\circ}\text{C}$  (Cantrell and Heymsfield, 2005; Martin, 2000). Thus, the presence or lack of mineral dust particles in an air parcel at any time may alter the conditions for ice formation under mixed-phase and cirrus cloud conditions. The microphysical effects of ice nuclei can produce a change in top of the atmosphere radiative forcing,

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stimulate precipitation through cloud glaciation, influence cloud structure and lifetime, and facilitate heterogeneous chemical reactions of trace gases (Abbatt, 2003; Baker, 1997; Cantrell and Heymsfield, 2005; Lohmann and Feichter, 2005).

Individual atmospheric mineral dust particles are commonly observed to have accumulated secondary soluble material during atmospheric transport (Russell et al., 2002; Shi et al., 2008; Sullivan et al., 2007; Sullivan and Prather, 2007). The addition of secondary material to dust particles that occurs during atmospheric processing – via coagulation, condensation, cloud processing, and heterogeneous reactions – can potentially modify and impair the ice nucleation ability of atmospheric dust particles. Such effects have been observed in laboratory studies of dust particles coated by sulphuric acid or secondary organic aerosol (SOA) material (Archuleta et al., 2005; Cziczko et al., 2009; Eastwood et al., 2009; Möhler et al., 2008; Niedermeier et al., 2010). The addition of secondary compounds can shift a dust particle's ice nucleation mechanism from deposition to immersion/condensation-freezing below water saturation at  $T < -38^{\circ}\text{C}$ , often leading to apparent or real reduction in the heterogeneous ice nucleation ability of the mineral dust. However, there are a few observations reported where such treatments have resulted in no change or even an increase in the dust's freezing ability (Archuleta et al., 2005; Eastwood et al., 2009; Salam et al., 2007).

Here we investigate some important open questions regarding the effect of coatings on heterogeneous ice nucleation including: (1) the ice nucleation response to the same chemical processing in the water subsaturated versus supersaturated regime, (2) the reversibility of changes in ice nucleation behaviour induced by the addition and removal of particle coatings, and (3) the effect of converting sulphuric acid coatings to ammonium sulphate salts. These experiments were performed as part of the FROST-2 (FReezing Of duST) study conducted at the Leipzig Aerosol Cloud Interactions Simulator (LACIS) facility. Results from the related FROST-1 experiments are described by Niedermeier et al. (2010). A novel aspect of the study presented here is the assessment of the same chemical treatments on ice nucleation both below and above water saturation in the heterogeneous ice nucleation regime warmer than  $-38^{\circ}\text{C}$ .

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## 2 Experimental methods

### 2.1 Mineral particle generation

Arizona test dust (ATD: ISO12103-1, A1 Ultrafine Test Dust, Powder Technology Inc., Burnsville, Minnesota, USA) mineral particles were used in all experiments. ATD is a manufactured mineral dust intended to represent typical chemical and physical properties of desert dust common to the south-western United States. ATD particles have low hygroscopicity ( $\kappa_{\text{app}}=0.003\text{--}0.025$ ) as determined by water uptake properties below and above water saturation (Herich et al., 2009; Koehler et al., 2009; Vlasenko et al., 2005). At cirrus temperatures below  $-38^\circ\text{C}$ , deposition ice nucleation of ATD occurs above an ice supersaturation threshold of 110–115% (Möhler et al., 2006), with larger submicron particles nucleating at modestly lower ice supersaturation than smaller particles (Koehler, 2007; Welti et al., 2009). These ice nucleation properties are similar to those observed for various pure aluminosilicate clays (Connolly et al., 2009; Kanji et al., 2008; Knopf and Koop, 2006; Möhler et al., 2006, 2008). The bulk chemical composition of the resuspended ATD powder was found to be  $\sim 80\%$  aluminosilicates by mass, 5% each of Fe, Ca, and Mg (Vlasenko et al., 2005); the latter two elements can be attributed to the presence of alkaline  $\text{CaCO}_3$  and  $\text{MgCa}(\text{CO}_3)_2$ . ATD aerosol was suspended dry by a fluidized bed generator (TSI3400A, TSI Inc., St. Paul, Minnesota, USA) and passed through an in-house corona discharge source. The corona discharger did not change the IN ability. Particles larger than 560 nm in aerodynamic diameter were removed by a Micro-Orifice Uniform-Deposition Impactor (MOUDI: Model 100R, MSP Corporation, Shoreview, Michigan, USA). The remaining aerosol was passed through a Kr-85 neutralizer.

### 2.2 Chemical processing of particles

The ATD particles were subjected to a variety of chemical and physical treatments:

1. Coating with sulphuric acid (variable coating oven temperature: 45, 70, 85 °C)

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2. Heating in a thermodenuder (typically 250 °C, but 45, 70, and 85 °C also used)
3. Transport over a liquid water bath
4. Exposure to ammonia gas

The most commonly used treatment sequence is outlined in Fig. 1, and is similar to that used by Niedermeier et al. (2010). The principle treatment involved passing the aerosol through a heated vapour diffusion tube containing a reservoir of liquid sulphuric acid; upon cooling, sulphuric acid vapours condensed onto the particle surface. The amount of secondary material added to the dust particles was controlled by the tube's temperature. The tube was surrounded by a water jacket with temperature control of  $\pm 0.1$  K. The thermodenuder consisted of a heated region with a residence time of 4–5 s followed by an unheated charcoal denuder and was intended to remove a portion of the sulphuric acid condensed on the particles. The water bath was used to explore the effect of hygroscopic water absorption immediately following the sulphuric acid particle coating. The aerosol's residence time over the water bath was about 70 s. In some experiments, ammonia gas (10 ppm, Air liquide GmbH, Leipzig, Germany) was added at a flow rate of 0.50 Lpm to the aerosol flow to test the effect of neutralizing the sulphuric acid coating by conversion to ammonium sulphate. During the campaign we suspected that the branch used for the water bath exposure had become contaminated by the first ammonia exposure experiments. This may have exposed the ATD particles to an unknown concentration of ammonia gas when the water bath alone was subsequently used.

The sequential order of the treatments and the processing time was also changed in some cases; a total of 24 different treatment conditions were explored. Particles with a mobility diameter of 300 nm were selected from the processed polydisperse aerosol by a differential mobility analyzer (DMA) (Vienna "Medium Type" Model; sheath flow: 10 Lpm, aerosol flow: 1.0–1.5 Lpm). A condensation particle counter (CPC, Model 3010, TSI Inc.) measured the total concentration of size-selected particles (CN) exiting

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the DMA. The monodisperse aerosol was then delivered to the various aerosol instruments. These included a hygroscopic growth tandem differential mobility analyzer (HTDMA) and cloud condensation nuclei counter (CCNc: Droplet Technologies Inc., Boulder, CO, USA) to determine the hygroscopicity of the treated particles and thus infer the coating volume fraction. An aerosol mass spectrometer (AMS) and aerosol time-of-flight mass spectrometer (ATOFMS) performed online measurements of bulk and single-particle chemical composition, respectively. Finally, four different ice nucleation instruments (LACIS, the Portable Ice Nucleus Counter (PINC), the Fast Ice Nucleus Chamber (FINCH), and the Colorado State University (CSU) Continuous Flow Diffusion Chamber (CFDC)) sampled the aerosol and processed it at various temperatures and relative humidities to simulate ice nucleation as it might occur during cloud formation in the atmosphere. Here we present results on ice nuclei (IN) activated in the CSU CFDC, and complementary information on aerosol chemistry and hygroscopicity obtained by the AMS and CCN measurements.

### 2.3 Ice nuclei measurements

The CFDC consists of two cylindrical ice-coated temperature controlled walls (Rogers et al., 2001). The aerosol is passed through the 1.2 cm annulus between the two walls, surrounded by particle-free sheath air. By controlling the temperature of and gradient between the walls, the temperature, and water and ice vapour saturation ratios of the aerosol lamina can be controlled. Particles that are able to nucleate ice under the selected conditions grow to supermicron sizes and are counted by an optical particle counter (OPC) at the exit of the chamber. An evaporation region where the aerosol experiences ice vapour saturation but water vapour subsaturation lies in-between the main ice chamber and the OPC. This section evaporates activated cloud droplets so that they do not interfere with the optical detection of ice crystals. Above  $\sim 108\%$   $RH_w$  (water relative humidity – the percentage ratio of water vapour pressure to saturated water vapour pressure over supercooled liquid water), depending on temperature, droplets do not fully evaporate before reaching the OPC and thus ice crystals

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and water droplets cannot be discriminated at these conditions. During an experiment the aerosol lamina temperature is held approximately constant while  $RH_i$  (ice relative humidity) and  $RH_w$  are scanned upwards (by increasing the temperature gradient) to determine the fraction of particles capable of nucleating ice as a function of  $RH_w$  and  $RH_i$  (Petters et al., 2009). Processing conditions were determined from the formulas given by Rogers (1988) using the saturation vapour pressure parameterization over supercooled water and ice from Buck (1981) ( $e_{w3}$  and  $e_{i1}$  from his Table 2). Typical uncertainty in  $RH_w$  is  $\pm 3\%$  (absolute) at  $-30^\circ\text{C}$ , while temperature uncertainty is  $\pm 1^\circ\text{C}$ .

For all experiments the aerosol's freezing efficiency was determined from the ratio of IN measured by the CFDC to total CN measured by the CPC,  $f_{IN} = \text{IN}/\text{CN}$ . In some experiments full scans from  $\sim 75\%$  to  $\geq 110\%$   $RH_w$  were conducted at a rate of  $\sim 1\%$   $RH_w$  per minute, while in others a fixed relative humidity was maintained to specifically address differences between the impact of particle treatments on ice nucleation below and above water saturation. The selected reference values used for those experiments were 98% and 105%  $RH_w$ . These values were selected because minerals that do not have associated soluble content are expected to act as deposition-mode IN at 98%  $RH_w$ , whereas 300 nm particles should activate as CCN and grow to relatively dilute cloud droplets by 105%  $RH_w$ , allowing immersion/condensation-freezing to be investigated without interference from solute effects (DeMott et al., 2009; Petters et al., 2009). A particle with  $D_{\text{dry}} = 300$  nm and a hygroscopicity parameter, defined by Petters and Kreidenweis (2007), of  $\kappa_{\text{app}} = 0.002$  (untreated ATD, determined from the CCN experiments described below) is predicted to have  $s_c = 100.39\%$   $RH_w$ , while coated particles activate at lower  $RH_w$ . Considering the uncertainty of  $\pm 3\%$  in the CFDC's calculated  $RH_w$ , all particles tested in these experiments are expected to activate as dilute cloud droplets for  $RH_w > 103.39\%$ . Since IN measurements at 105%  $RH_w$  will represent the combination of ice nucleation processes that occur as particles adjust to this final  $RH_w$ , we expect the predominance of condensation and immersion freezing ice nucleation in activated water drops and will refer to such results as representing the immersion/condensation-freezing regime. This  $RH_w$  value is also free of interference



from droplets that survive the evaporation region. Measurements of treated ATD were performed at ice chamber temperatures of  $-25^{\circ}\text{C}$  (18 experiments) and  $-30^{\circ}\text{C}$  (55 experiments).

Periodic sampling of filtered, particle-free air provides a measure of the instrument's background ice counts from frost. These were typically  $<2\text{L}^{-1}$  at 75%  $\text{RH}_w$  during these experiments. Total CN concentrations sampled by the CFDC were typically  $\sim 60\text{--}80\text{cm}^{-3}$  but varied between  $50\text{--}150\text{cm}^{-3}$ . For the minimum CN of  $50\text{cm}^{-3}$  and a conservative upper limit of  $5\text{L}^{-1}$  background count, the CFDC's typical limit of quantification for these experiments was  $f_{\text{IN}} = \text{IN}/\text{CN} > 10^{-4}$ . For  $f_{\text{IN}} < 10^{-4}$  we cannot distinguish these low concentrations of IN from the small background frost counts and therefore we do not ascribe any meaning to observed differences in  $f_{\text{IN}}$  within this low range with any confidence.

## 2.4 Estimation of sulphuric acid mass added to treated particles

The total sulphate mass was determined following standard AMS calibration procedures (Jimenez et al., 2003). The particle sulphate mass fraction was estimated by dividing the total sulphate mass by the total particle mass. The later was estimated from the total CN counts measured by the CPC. As the aerosol was monodisperse, it has been assumed that all the particles of the selected size had the same surface area and thus had the same amount of sulphuric acid condensed. The uncertainty of the AMS mass loadings was estimated by the standard deviation of the average of the measured time series plus the propagated errors of the required correction factors. The sulphate particle mass fraction was above the detection limit for all treatments that included the sulphuric acid coating.

The hygroscopicity of the chemically processed particles was determined by cloud condensation nuclei (CCN) activation experiments using the CCNc. The CCN/CN ratio of the size-selected aerosol was measured at increasing  $\text{RH}_w$  above water saturation to produce the CCN activation curve (e.g. Sullivan et al., 2009; Wex et al., 2009). The determined critical supersaturation ( $s_c = \text{RH}_w - 100$ ) – dry diameter data pair was

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converted to an apparent hygroscopicity,  $\kappa_{\text{app}}$  (Petters and Kreidenweis, 2007). A surface tension of pure water was assumed in all cases following Petters and Kreidenweis (2007). We assumed that any secondary material added to the dust particles during treatment, such as metal sulphate salts that may have been produced, was dissolved above water saturation. This assumption ignores the possible contribution from components with limited solubility that could reduce apparent hygroscopicity (Petters and Kreidenweis, 2008; Sullivan et al., 2009). The  $\kappa_{\text{app}}$  is related to the particle volume fraction of sulphuric acid through Eq. (1), following the volume mixing rule (Petters and Kreidenweis, 2007):

$$\kappa_{\text{app}} = \varepsilon_{\text{H}_2\text{SO}_4} \kappa_{\text{H}_2\text{SO}_4} + \varepsilon_{\text{ATD}} \kappa_{\text{ATD}} \quad (1)$$

where  $\varepsilon_{\text{H}_2\text{SO}_4}$  and  $\varepsilon_{\text{ATD}}$  are the volume fractions of each component, and  $\kappa_{\text{H}_2\text{SO}_4}$  and  $\kappa_{\text{ATD}}$  the apparent hygroscopicities of sulphuric acid and Arizona test dust, respectively. As  $\varepsilon_{\text{H}_2\text{SO}_4} + \varepsilon_{\text{ATD}} = 1$ , Eq. (1) can be rearranged to derive the volume fraction of sulphuric acid from the measured  $\kappa_{\text{app}}$ :

$$\varepsilon_{\text{H}_2\text{SO}_4} = \frac{\kappa_{\text{app}} - \kappa_{\text{ATD}}}{\kappa_{\text{H}_2\text{SO}_4} - \kappa_{\text{ATD}}} \quad (2)$$

$\kappa_{\text{ATD}}$  was found to be 0.002 during these experiments (Table 1), which is similar to the  $\kappa_{\text{app}} = 0.002\text{--}0.003$  reported by Herich et al. (2009). Koehler et al. (2009) reported a larger hygroscopicity for dry-generated ATD,  $\kappa_{\text{app}} = 0.025$ . This could be due to differences between sample lots, differences in sample handling, or the fact that Koehler et al. (2009) used the A2 Fine grade of ATD while the A1 Ultrafine grade was used in this study and by Herich et al. (2009). For sulphuric acid  $\kappa_{\text{H}_2\text{SO}_4} = 0.68\text{--}0.74$  for dry diameters 30–80 nm ( $\kappa = 0.9$  was mistakenly given in Petters and Kreidenweis, 2007 and the correct value is reported in Shantz et al., 2008); here we assume  $\kappa_{\text{H}_2\text{SO}_4} \sim 0.7$ . We did not attempt to predict the chemical form of the sulphuric acid coating. Reactions with mineral components in ATD that form sulphate salts may have occurred which have a different solubility and apparent hygroscopicity than sulphuric acid. We also assumed

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the same  $\kappa_{\text{app}}$  for the coating when ammonia gas was used, though some fraction of the available sulphuric acid was converted to ammonium sulphate salts.  $(\text{NH}_4)_2\text{SO}_4$  has  $\kappa=0.61$  (Petters and Kreidenweis, 2007), slightly smaller than  $\kappa_{\text{H}_2\text{SO}_4}=0.7$ . The error in the fitted  $s_c$  was determined from the variability in the repeated instrument calibrations with ammonium sulphate aerosol, and converted to  $\kappa_{\text{app}}$  to produce an upper and lower estimate range of  $\varepsilon_{\text{H}_2\text{SO}_4}$  (Eq. 2).

### 3 Results

Figure 2 displays the fraction of particles that froze at  $-30^\circ\text{C}$  during  $\text{RH}_w$  scans from 75% to  $>110\%$ . The untreated ATD's freezing efficiency increased monotonically with increasing  $\text{RH}_w$ . Below water saturation  $f_{\text{IN}}$  is expected to increase with  $\text{RH}_w$  as higher water and ice relative humidities allow critical ice embryo formation and growth to occur at a larger fraction of ice-active surface sites which possess varying ice embryo energy barriers (Vali, 1985). At some point above water saturation, for which the particles are immersed in cloud droplets, ice nucleation at the active sites should no longer respond to changes in the gas-phase relative humidity. However, changes in IN fraction do occur until  $\sim 105\%$ . Several factors may be responsible for the increase in fractional ice activation with increasing  $\text{RH}_w$  above water saturation. Higher  $\text{RH}_w$  set points lead to slightly earlier CCN activation of droplets, and larger droplets that survive longer within the CFDC evaporation region. Using the microphysical model of CFDC processes from Rogers (1988) we calculate that droplets formed following CCN activation of 300 nm (spherical equivalent) particles and growing at  $-30^\circ\text{C}$  with an assumed water mass accommodation coefficient of 1 are expected to achieve a maximum diameter of  $1.7\ \mu\text{m}$  at a 102%  $\text{RH}_w$  set point,  $2.7\ \mu\text{m}$  for 105%  $\text{RH}_w$ , and  $4.0\ \mu\text{m}$  for 109%  $\text{RH}_w$  during residence time in the CFDC growth region. Corresponding residence times of cloud droplets in the chamber at sizes above  $1\ \mu\text{m}$  are calculated to be 3.5, 5.1, and 5.4 s at 102, 105, and 109%  $\text{RH}_w$ . The role of stochastic effects on freezing of mineral dusts with highly heterogeneous surface properties remains unresolved (Connolly et

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al., 2009; Marcolli et al., 2007; Niedermeier et al., 2010; Phillips et al., 2008), and the 50% increase in residence times of particles immersed in drops for supersaturations between 102 and 109% RH<sub>w</sub> seems unlikely as a major source of stronger activation at high RH<sub>w</sub>. The up to 4 times water volume increase (for 102 vs. 105% RH<sub>w</sub>), could affect microscale processes involving reactions and dissolution of surface contaminants responsible for freezing point depressions prior to heterogeneous freezing. Dissolution rates and reactions appear of more likely importance since equilibrium melting point depressions are less than 0.1 °C in all cases for the solution compositions predicted on the basis of coatings applied in this study. A consequence of droplet survival into the CFDC evaporation region is an additional cooling (during RH reduction to ice saturation conditions) calculated to be up to 2.5 °C for a set point of 105% RH<sub>w</sub>, and with sufficient time available for some percentage of those droplets nucleating ice to grow to detectable ice crystal sizes. This could be envisioned as an increased one-sided (cold) temperature uncertainty for higher RH activation conditions. It must be noted that all of these calculations were made for drops forming in the average conditions of the aerosol lamina in the CFDC. Any unexpected broadening of the aerosol particle distribution from the centre of the focused aerosol lamina would necessarily lead to a wider range of apparent activation conditions within the water supersaturated regime. While factors leading to the RH<sub>w</sub> activation signature require further study, our assumption in the present paper is that the plateau in  $f_{IN}$  at and above 105% RH<sub>w</sub> characterizes the maximum value due to a combination of ice nucleation mechanisms, but with predominance of condensation/immersion freezing. Similar trends of  $f_{IN}$  continuing to increase above water saturation have been observed in a variety of pure mineral dust particles (Welti et al., 2009) and biomass combustion particles (DeMott et al., 2009; Petters et al., 2009).

In Fig. 2 droplets are observed to break through the evaporation region and be erroneously counted as IN at RH<sub>w</sub>>108%. While the breakthrough point did vary between 107–112% between different days and experiments, the sudden increases in IN that indicate droplet breakthrough are, in our instrument, never observed below 107%

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RH<sub>w</sub> for dust, ambient particles, or ammonium sulphate test aerosol. Therefore the IN measurements performed at RH<sub>w</sub> ≤ 105% should not have experienced interference from droplets. The suitability of this criterion was confirmed during the project by sampling ammonium sulphate aerosol, which does not freeze above -38 °C; droplets broke through the evaporation region at >113% RH<sub>w</sub> at -30 °C.

Also shown in Fig. 2 are results for uncoated ATD that had been heated at 250 °C in the thermodenuder. This treatment slightly reduced the ice nucleation efficiency in the deposition nucleation regime, while freezing in the immersion/condensation-freezing regime was largely unaffected. Additional thermodenuder experiments not shown in Fig. 2 in which uncoated ATD was heated to 45, 70, 85, or 250 °C displayed similar behaviour within the experimental uncertainties.

Coating the ATD particles with sulphuric acid (Fig. 2) greatly reduced the IN fraction below water-saturation compared to the untreated particles, while  $f_{IN}$  was reduced to a lesser degree above water saturation. Heating the coated ATD caused a further reduction in  $f_{IN}$  for both ice nucleation regimes. Within the measurement uncertainty no further increase in  $f_{IN}$  was observed in Fig. 2 at 105% RH<sub>w</sub> for the untreated and heated ATD, compared to the low  $f_{IN}$  for coated and coated + heated ATD. This plateau indicates that this region is sensitive to changes in the immersion/condensation-freezing regime's behaviour.

### 3.1 Relationship between freezing ability and amount of soluble material added

The IN fractions for the -30 °C immersion freezing regime data from SA coating and SA coating + water bath experiments are plotted in Fig. 3a as a function of the particle volume fraction of sulphuric acid, as estimated from the CCN measurements (Eq. 2), and in Fig. 3b as a function of the mass of sulphuric acid per particle from the AMS measurements. Using either estimate of the amount of soluble material added to the dust particles produces a trend of decreasing  $f_{IN}$  with increasing sulphuric acid mass/volume per particle. In Fig. 3a  $f_{IN}$  is not as low as expected following this trend for the 85 °C coating. This may indicate that increasing the amount of sulphuric acid condensed has

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a limited effect on ice nucleation above a certain threshold. A similar but weaker effect can be seen for the same treatment in Fig. 3b. When the coated particles were also passed over the water bath a larger decrease in  $f_{IN}$  was achieved for a similar amount of sulphuric acid deposited on the particles, causing these points to lie off the trend for 45 and 70 °C coatings without the water bath. We do not include data from other treatment combinations such as the use of heat following the coating as these lie well off the trends in Fig. 3 and likely represent different physicochemical processes, as discussed below; heat decreased  $f_{IN}$  while also reducing the amount of sulphate.

### 3.2 Freezing efficiency of sulphuric acid coated mineral dust

The freezing efficiencies of ATD after various treatments in both the deposition and immersion/condensation-freezing regimes are compared in Fig. 4 for -30 °C and Fig. 5 for -25 °C. The treatments include (1) heating in the thermodenuder (TD), (2) sulphuric acid (SA) coating, (3) SA + TD, (4) SA + passage over the water bath (WB), (5) SA + WB + TD, (6) SA + WB + NH<sub>3</sub> gas exposure, (7) SA + WB + NH<sub>3</sub> + TD, (8) SA + NH<sub>3</sub>, (9) NH<sub>3</sub> exposure only. The average estimated sulphate mass per particle from the AMS is also shown for each treatment combination. Ice nucleation in the deposition regime was significantly more sensitive to all treatments compared to immersion/condensation-freezing;  $f_{IN}$  in the deposition regime was reduced by about one order of magnitude more after coating compared to the reduction in the immersion regime after coating. Measurements of  $f_{IN}$  at both -30 and -25 °C responded similarly to all but one of the various physicochemical processing combinations described below.

The sulphuric acid (SA) coating experiments are the reference treatment to which further treatment combinations are compared below, and thus we first describe the effects of this treatment. Coating with sulphuric acid at 70 or 85 °C caused large decreases in  $f_{IN}$  of at least one order of magnitude both below and above water saturation. Particles coated with sulphuric acid at 45 °C displayed a large decrease in  $f_{IN}$  below water saturation, but their immersion regime freezing efficiency was only slightly

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smaller and within experimental uncertainties compared to untreated or heated-only ATD. These were the only experiments in which the addition of sulphuric acid did not cause immersion/condensation-freezing  $f_{IN}$  to decrease below  $10^{-2}$  at the selected temperatures. The amount of sulphuric acid condensed on the particles at  $45^{\circ}\text{C}$  was  $\sim 42\%$  of that added by the  $70^{\circ}\text{C}$  coatings (AMS measurements, Table 1) and corresponds to an approximately 1.0 nm uniform particle coating assuming a 300 nm spherical physical diameter dust core. The thickness of one monolayer equivalent of pure sulphuric acid is estimated to be 0.55 nm, based on its molar volume, corresponding to 287 ag/particle of sulphate. The sulphate mass from the  $70^{\circ}\text{C}$  coating temperature corresponds to a 2.4 nm thickness, and the  $85^{\circ}\text{C}$  coating corresponds to a 4.1 nm thick uniform coating. Therefore for all coating temperatures we estimate that enough sulphate mass was condensed to potentially produce at least one complete monolayer coverage. No measurements of the coated particle morphologies were available and the estimates of monolayer coverage are not intended to suggest that the sulphuric acid coated the ATD particles uniformly, even when enough sulphate mass to produce a complete monolayer was present.

While heating uncoated ATD at  $250^{\circ}\text{C}$  in the TD caused just a small decrease in  $f_{IN}$  within the uncertainty limits, the addition of sulphuric acid at  $70$  or  $85^{\circ}\text{C}$  plus heating in the thermodenuder reduced deposition regime ice nucleation efficiency below the CFDC's quantification limit ( $f_{IN} < 10^{-4}$ ). Immersion/condensation-freezing was less sensitive to the thermochemical processing causing  $f_{IN}$  to be  $> 10^{-4}$  after SA coating, and thus allowing differences in the IN fraction to be discerned under the various treatment conditions. Coating with sulphuric acid at  $45^{\circ}\text{C}$  followed by heating caused a one order of magnitude reduction in  $f_{IN}$  at  $105\% \text{RH}_w$  compared to the reference treatment. The higher SA coating temperatures of  $70$  and  $85^{\circ}\text{C}$  decreased  $f_{IN}$  further at  $105\% \text{RH}_w$  after the thermodenuder.

In experiments where the coated particles were also passed over a water bath they encountered a humid environment before the aerosol was dried and analysed in the CFDC. Ammonia gas may have also been present in the water bath exposure

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branch. The additional humidification step caused a larger decrease in  $f_{\text{IN}}$  for the immersion/condensation-freezing regime compared to the SA coated reference treatment. The effect of the water bath was difficult to discern below water saturation, since  $f_{\text{IN}}$  was very small and sometimes below the quantification limit for both SA and SA + WB experiments. A restoration of immersion/condensation-freezing ability was observed when the SA + WB particles were subsequently heated in the thermodenuder. Comparing the AMS-derived sulphate mass measurements of SA + TD particles to SA-only particles (Table 1) demonstrates that the thermodenuder did remove a significant fraction of sulphuric acid mass ( $\sim 50\%$ ) from the coated particles, but that a smaller fraction of the coating ( $\sim 20\%$ ) was removed by heating when the particles were humidified before the thermodenuder.

In general, ice nucleation in the deposition and immersion/condensation-freezing regimes responded to thermochemical processing in the same manner at  $-25^\circ\text{C}$  as for  $-30^\circ\text{C}$ .  $f_{\text{IN}}$  were overall smaller at  $-25^\circ\text{C}$ , as expected given the exponential dependence of  $f_{\text{IN}}$  on temperature (Vali, 1985) that has been observed in mineral particle systems (e.g. Archuleta et al., 2005; Welti et al., 2009). ATD coated at 45 and  $70^\circ\text{C}$  and then heated had a  $f_{\text{IN}}$  at 98% RH<sub>w</sub> and  $-25^\circ\text{C}$  similar to uncoated ATD. This is the only qualitative difference compared to the measurements at  $-30^\circ\text{C}$ , where coated then heated particles (without water bath) always had a much reduced  $f_{\text{IN}}$  at 98% RH<sub>w</sub>; the overall low  $f_{\text{IN}}$  values ( $<10^{-3}$ ) measured for uncoated and coated dust at  $-25^\circ\text{C}$  make it difficult to distinguish between the two under these conditions. Above water saturation coated then heated ATD had a reduced  $f_{\text{IN}}$  at 105% RH<sub>w</sub> compared to untreated or coated-only particles at both  $-25$  and  $-30^\circ\text{C}$ .

### 3.3 Effect of exposing sulphuric acid coated dust to ammonia gas

Within our ability to discriminate between the effects of different treatments, exposure to ammonia gas after coating with sulphuric acid did not appear to alter the large decrease in the dust's ice nucleation ability below and above water saturation, nor the degree to which this was restored after heating in the thermodenuder for the



immersion/condensation-freezing regime (Figs. 4 and 5). In most ammonia exposure experiments, the water bath was used after the SA coating and before exposure to ammonia gas. The mass of sulphate per particle did not decrease after heating in the thermodenuder for the 70 °C SA + WB + NH<sub>3</sub> experiments, but was decreased with the thicker 85 °C SA coating. SA + WB experiments without ammonia had slightly reduced sulphate mass (~20%) following the thermodenuder. Not including the water bath did not alter the poor deposition nucleation or immersion/condensation-freezing ability of dust following treatment with SA + NH<sub>3</sub>. The deposition regime experiments at both -25 and -30 °C revealed that SA + WB + NH<sub>3</sub> treated dust did recover 10–20% of its water subsaturated ice nucleation ability when heated in the TD. These were the only observations of such a recovery in  $f_{IN}$  from the various deposition regime experiments. It is difficult to discriminate between coated dust that was or was not also exposed to ammonia in the deposition regime data because  $f_{IN}$  was so small in all cases. A set of experiments in which the concentration of ammonia gas was reduced by up to a factor of five did not produce a change in  $f_{IN}$ . Uncoated ATD particles exposed only to ammonia gas displayed similar immersion-regime freezing ability as untreated dust (Fig. 4b).

### 3.4 Summary of observed ice nucleation behaviour

From the observed ice nucleation response to the wide variety of treatment conditions explored in the experiments described above, we derive the following conclusions with high confidence – based on the number of replicate experiments performed and the observed uncertainty in the IN fractions – in the water subsaturated deposition regime (98% RH<sub>w</sub>), and water supersaturated immersion/condensation-freezing regime (105% RH<sub>w</sub>):

1. Heating uncoated dust did not alter ice nucleation in either regime.
2. Sulphuric acid coated dust particles always had reduced  $f_{IN}$  compared to uncoated dust, except for the 45 °C coating in the immersion/condensation-freezing

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regime.

3. The coating reduced  $f_{\text{IN}}$  by about one order of magnitude more in the deposition vs. immersion/condensation-freezing regime, compared to uncoated dust.
4. Heating coated dust reduced  $f_{\text{IN}}$  further in the immersion/condensation-freezing regime.  $f_{\text{IN}}$  was already below the limit of quantification in the deposition regime after coating.
5. The water bath further reduced  $f_{\text{IN}}$  of coated particles, in the immersion/condensation-freezing regime.
6. Exposing SA + WB treated particles to ammonia gas did not alter the already low  $f_{\text{IN}}$  observed without ammonia exposure. The water bath branch may have already exposed the particles to an unknown concentration of ammonia gas.
7. Heating SA + WB treated dust increased  $f_{\text{IN}}$  compared to unheated SA + WB treated dust, in the immersion/condensation-freezing regime.
8. Heating SA + WB +  $\text{NH}_3$  treated particles increased  $f_{\text{IN}}$  compared to the same treatment without heat, in both regimes.
9. No treatment combination increased  $f_{\text{IN}}$  above that of untreated dust.

The treatment condition, IN fraction ( $f_{\text{IN}}$ ) at 98% (deposition regime) and 105%  $\text{RH}_w$  (immersion/condensation-freezing regime), and the standard deviation from the 1-s  $f_{\text{IN}}$  measurements are listed in Table 1 for the  $-30$  and  $-25$  °C experiments. Also included are the critical supersaturation ( $s_c$ ), hygroscopicity parameter ( $\kappa_{\text{app}}$ ), estimate of the sulphate volume fraction from the CCN measurements, and the estimated sulphate mass per particle from the AMS measurements, when available.

## 4 Discussion

We interpret our experimental observations of thermochemical treatments on the ice nucleation properties of mineral dust particles under the framework that heterogeneous ice nucleation begins with the formation of a critical ice embryo at a specific ice-active surface site. According to the singular hypothesis there is a heterogeneous distribution of surface site ice nucleation energy barriers within and between individual particles, even those of the same physical size (Marcolli et al., 2007; Martin, 2000; Phillips et al., 2008; Vali, 1994, 2008). Any particle exposed to its critical temperature and  $RH_i$  instantaneously freezes, with no further ice nucleation after that point. This nucleation event is determined by the active site with the lowest nucleation barrier (i.e. highest critical temperature) on each particle. Chemical or physical modification of these ice active surface sites can alter the critical temperature and  $RH_i$  at which they nucleate ice, which is experimentally observed in this work by changes in the measured  $f_{IN}$ .

In all but one experiment the addition of sulphuric acid to Arizona test dust particles reduced their ability to nucleate ice compared to uncoated dust, both below and above water saturation, at  $-30$  and  $-25^\circ\text{C}$ . Further, the treated dust particles' ice nucleation ability decreased as the mass of sulphuric acid added increased. We interpret this effect as a concealing or physicochemical modification of increasing fractions of the ice active sites by the condensation of sulphuric acid. Since some freezing ability remained after the lower temperature coatings, this implies that either the particle was not completely coated at the lower coating temperatures, or that the coating was not thick enough to conceal and/or chemically alter all active sites in each particle. The  $45^\circ\text{C}$  coating condensed an amount of sulphuric acid greater than that estimated to form complete monolayer coverage around the particle. This treatment was observed to decrease  $f_{IN}$  below-water saturation, while  $f_{IN}$  above water-saturation was only slightly smaller than uncoated dust and within the uncertainty limits. Garland et al. (2008) observed oleic acid to condense on to silica mineral particles in the form of islands, as opposed to forming a uniform coating. The islands grew in height as more

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oleic acid was condensed, while gaps between the islands with bare silica surface remained. Cziczo et al. (2009) also obtained indirect evidence from single-particle mass spectrometry for incompletely coated ATD particles after exposure to hot sulphuric acid vapour. If similar structures formed when sulphuric acid was condensed on to the ATD particles in our experiments, a portion of the mineral surface would have remained uncoated with unaltered ice active sites.

The addition of soluble hygroscopic sulphuric acid would have caused the coated particles to absorb water under the high  $RH_w \geq 98\%$  conditions in the CFDC. The presence of concentrated salt solutions on the particle below water saturation may have shifted the ice nucleation mechanism to an immersion/condensation-freezing-like process, as opposed to deposition ice nucleation which occurs on a bare particle surface. At 98%  $RH_w$  the coating would have been more concentrated than after droplet activation at 105%  $RH_w$ . This could allow solute effects to cause a freezing point depression that potentially suppresses ice nucleation that proceeds by a condensation-freezing process below water-saturation. Dissolution of a portion of the sulphuric acid coating that reveals concealed active sites when the particle is activated into a droplet above water saturation may explain the lower sensitivity of  $f_{IN}$  to the coatings at 105%  $RH_w$  versus 98%  $RH_w$ . The fact that  $f_{IN}$  at 105%  $RH_w$  was still reduced by the coatings clearly indicates that dissolution during droplet activation does not completely reverse the detrimental effects caused by the sulphuric acid coating. Therefore some fraction of the ice active sites was irreversibly lost when the sulphuric acid was condensed on the mineral particles.

Coated particles then exposed to heat in the thermodenuder had further reduced ice nucleation ability, even though ~50–60% of the sulphate mass was removed by heating. We propose that the combination of concentrated acid plus heat accelerated chemical reactions between sulphuric acid and the mineral surface, causing a further irreversible loss of ice active sites which were not recovered by the reduction of sulphate mass. As temperatures between 45 and 85 °C were used to condense the sulphuric acid coating, similar thermal effects may have been unintentionally induced by the hot

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coating oven itself. Thus the relative contributions of sulphuric acid and heat to the observed decrease in ice nucleation ability cannot be clearly separated, although heating uncoated particles did not decrease  $f_{IN}$  significantly. Whether the lack of a decrease in  $f_{IN}$  at 105% RH<sub>w</sub> for the 45 °C SA coating was caused by the smaller amount of sulphuric acid condensed, by the lower oven temperature used, or by a combination of the two cannot be determined.

Exposing the coated particles to elevated RH by passing them over a water bath produced a larger decrease in  $f_{IN}$  even though the amount of sulphate/particle was unchanged. Absorption of water by the sulphuric acid coating that causes the island structures proposed above to swell and more evenly coat the entire particle surface could explain this behaviour. This would allow the acid to conceal and/or react with a larger fraction of the active sites. Although the coated particles also encountered elevated RH<sub>w</sub> in the CFDC, exposure to water vapour immediately after the sulphuric acid was applied appears to have had additional and important effects. The exposure to water shortly after coating and for a longer time period than experienced in the CFDC is the most feasible explanation for the additional effects of the water bath. We suspect that the water bath branch tubing became contaminated by ammonia during subsequent ammonia exposure treatments. Thus particles passing through the water bath branch may have been exposed to an unknown concentration of ammonia gas in addition to water vapour. Unfortunately the uncertainties in the AMS ammonium mass estimates are too large to distinguish between the mass of ammonium per particle for the WB versus NH<sub>3</sub> treatments. Therefore the WB and NH<sub>3</sub> treatments may have been equivalent.

When the coated and then humidified particles were heated, some ice nucleation ability was restored at 105% RH<sub>w</sub>, compared to the unheated SA + WB treatment. However, the mass of sulphate per particle was only reduced by ~20% for the 70 °C SA coating. Conversely, coated particles that were heated without passing over the water bath had reduced  $f_{IN}$  while losing ~50% of their sulphate mass. The dilution of the acidic coating by water absorption in the water bath could have reduced the irreversible

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chemical alterations of active sites that the acid encountered. Some active sites could then have been revealed when the small portion of sulphate mass was removed. Alternatively, the absorption of water vapour by the sulphuric acid coated dust may have accelerated chemical reactions between the acid and various minerals present in ATD, and/or facilitated previously inaccessible reaction pathways requiring water (Lasaga, 1995). The production of low volatility products from the combination of dilute sulphuric acid plus heat would explain the small fraction of sulphate mass removed. If these products were insoluble and produced new ice active sites, or if additional active sites were uncovered when the initial surface was digested by these chemical reactions, that could account for the observed partial recovering of ice nucleation ability at 105% RH<sub>w</sub>. We were unable to identify the products from these proposed chemical reactions. ATD is approximately composed by mass of 5% CaCO<sub>3</sub>, 5% MgCa(CO<sub>3</sub>)<sub>2</sub>, and 5% Fe compounds, with the remainder as aluminosilicate clays (Vlasenko et al., 2005). Possible reaction products include CaSO<sub>4</sub>, MgSO<sub>4</sub>, FeSO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, their hydrates, and products from the reaction of sulphuric acid with aluminosilicates. Archuleta et al. (2005) found that pure Fe<sub>2</sub>O<sub>3</sub> particles became more efficient IN when coated by sulphuric acid at 200 °C. CaSO<sub>4</sub> and MgSO<sub>4</sub> are insoluble, while the two iron sulphate salts will dissolve at typical water contents of haze particles. The anhydrous forms of all four compounds have decomposition or melting temperatures of 400 °C or higher. The thermodenuder was typically operated at 250 °C. A recovery in  $f_{IN}$  at 98% RH<sub>w</sub> was not observed for these experiments. It is possible that a partial recovery occurred but  $f_{IN}$  below water saturation remained below our limit of quantification of 10<sup>-4</sup>.

Exposing coated particles to ammonia gas was intended to convert most or all of the sulphuric acid to ammonium sulphate salts. The SA + WB + NH<sub>3</sub> treated particles exhibited similarly poor ice nucleation ability as particles from SA + WB treatments, both above and below water saturation. Heating the SA + WB + NH<sub>3</sub> particles produced a recovery of  $f_{IN}$  at 105% RH<sub>w</sub> and <5% loss of sulphate mass, while the heated SA + WB treated particles had a similar recovery of  $f_{IN}$  and lost ~20% of their sulphate. Converting the sulphuric acid coating to ammonium sulphate appears to have had no

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effect on the resulting ice nucleation ability; in both cases  $f_{IN}$  was greatly reduced. The contamination of the water bath branch by ammonia could explain this similarity if enough ammonia was present in both cases to neutralize all available sulphuric acid, causing the WB and  $NH_3$  treatments to be equivalent. Alternatively dust coated by sulphuric acid or ammonium sulphate may have similarly poor ice nucleation ability at the temperatures explored here. Particles exposed to ammonia following the sulphuric acid coating but without exposure to humid air in the water bath (SA +  $NH_3$ ) had similarly low  $f_{IN}$ . At 98%  $RH_w$  a small recovery in  $f_{IN}$  was observed at both  $-30$  and  $-25$  °C when the ammoniated particles were heated (SA + WB +  $NH_3$  + TD). This was the only observation of a partial restoration of ice nucleation ability in the deposition-regime.

Neutralization of sulphuric acid by the uptake of ammonia gas may have impeded the additional irreversible loss of surface sites when the coated particles were heated. This could explain the similar recovery of  $f_{IN}$  when the SA + WB and SA + WB +  $NH_3$  particles were heated if enough ammonia was introduced by the contaminated water bath branch. The reasons for this different behaviour above versus below water saturation are not known. Large solid ammonium sulphate particles have been observed to heterogeneously nucleate ice at temperatures lower than about  $-40$  °C (Abbatt et al., 2006). Therefore mineral dust coated with ammonium sulphate might have different ice nucleation properties compared to sulphuric acid coated particles; we did not observe any differences at  $-30$  or  $-25$  °C, above or below water saturation. This is similar to the observations of Eastwood et al. (2009) at  $-28$  °C, for mineral particles coated by deliquesced ammonium sulphate, or sulphuric acid. Cziczo et al. (2009) found similarly poor ice nucleation ability for sulphuric acid coated ATD and coated ATD exposed to ammonia gas, at  $-35$  °C.

### Comparison to previous studies and atmospheric implications

Previous investigations, although difficult to compare to quantitatively due to differences in experimental methods, have reported a similar decrease in heterogeneous ice nucleation ability by coating various mineral particles types with sulphuric acid (Archuleta

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et al., 2005; Cziczo et al., 2009; Eastwood et al., 2008; Niedermeier et al., 2010). The observations reported here and in previous studies clearly indicate a reduction in ice nucleation ability when sulphuric acid is condensed onto mineral dust particles – with the caveat that the contribution to this reduction caused by the heat used in the coating process is not known. Nevertheless, since individual atmospheric mineral dust particles are frequently observed to be mixed with such soluble aerosol components (Buseck and Posfai, 1999; Russell et al., 2002; Shi et al., 2008; Sullivan et al., 2007; Sullivan and Prather, 2007), the ice nucleation properties of these mixed particles may represent the best description of a large number fraction of atmospheric aerosol mixing states that can potentially nucleate cirrus or mixed-phase clouds. While sulphuric acid coated mineral dust particles were observed here to be worse IN compared to untreated dust, these mixed particles are still better IN than sulphuric acid solution droplets, which can only nucleate ice homogeneously at temperatures  $\leq -38^\circ\text{C}$  (Hung et al., 2003; Zuberi et al., 2002).

We propose that concentrated sulphuric acid deposited onto the mineral particle's surface irreversibly alters ice active sites via chemical reactions with various mineral components. This suggests that the manner in which sulphuric acid becomes mixed with the dust will have an important impact on the processed particle's resulting ice nucleation ability. Based on these results, dilute sulphuric acid that is produced during cloud processing in non-evaporating cloud droplets would be expected to have a lesser impact on the dust's freezing ability than concentrated sulphuric acid that is produced through heterogeneous uptake of  $\text{SO}_2(\text{g})$  and subsequent oxidation to  $\text{H}_2\text{SO}_4$  in non-activated particles. Similarly, while converting the sulphuric acid coating to ammonium sulphate through exposure to ammonia gas resulted in poor ice nucleation ability in our study, we were unable to test the effect of directly condensing/mixing ammonium sulphate with the mineral particles. We would expect that ammonium sulphate would have a lesser effect on immersion-mode freezing compared to concentrated sulphuric acid, due to their large differences in acidity and corrosive power. Ammonium sulphate could feasibly be irreversibly dissolved off the particle surface



during immersion/condensation-freezing to uncover the active sites, whereas sulphuric acid appears to induce irreversible chemical damage to the particle surface, based on the observations presented here. The potentially important effects that the pathway through which sulphuric acid, ammonium sulphate, and similar secondary components become mixed with mineral dust and other ice nuclei have on the chemically aged particle's resulting ice nucleation properties warrant further investigation.

## 5 Conclusions

The resulting ice nucleation properties of dust particles after a variety of thermochemical treatments focused on sulphuric acid condensation were investigated experimentally. Addition of soluble acidic material to ATD always reduced the fraction of particles that nucleated ice compared to uncoated dust, except for ice nucleation in the immersion/condensation-freezing regime for the smallest sulphuric acid coating. A trend of decreasing IN fraction with increasing soluble material condensed on the particles was observed. Ice nucleation in the deposition regime below water saturation was significantly more impaired by the chemical processing than was the immersion/condensation-freezing regime above water saturation for the same conditions. The additional loss of IN ability from passing the coated particles over a water bath was attributed to the dissolution and swelling of the coating. The formation of an aqueous solution was hypothesised to more completely coat the particle's active sites, while either reducing the ability of the acid to chemically alter these sites through dilution, or facilitating chemical reactions that produce or reveal new active sites and low volatility products after the addition of heat. Particles may have also been exposed to ammonia gas by the water bath. The role that water vapour plays in these processes and the resulting ice nucleation properties is atmospherically relevant, not well understood, and warrants further investigation.

The highly acidic and corrosive sulphuric acid appears to irreversibly chemically and/or physically modify the mineral particle's surface and ice-active surface sites

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5 which are responsible for the untreated dust's high freezing efficiency. The reduction of freezing ability under immersion/condensation-freezing conditions – where the coated particle was activated into a droplet before or during freezing – indicates that the dissolution of the coating in the droplet did not completely restore the particle's ice nucleation ability. The effects of processing on ice nucleation in the deposition regime are more convoluted, as the coatings may have shifted the ice formation mechanism below water saturation from a deposition mechanism to a condensation-freezing mechanism where solute effects can play an important role.

10 The observed enhanced loss of ice nucleation ability after coated particles were heated is attributed to an acceleration of the chemical alteration of surface sites. However, as heat was used to condense sulphuric acid onto the particle's surface in the coating oven, we cannot discriminate between the effect of the sulphuric acid coating alone, or in combination with heat, on the observed loss of ice nucleation ability. Further experiments that expose dust particles to acidic vapours for longer periods of time without the use of heat are required to separate these effects. Such experiments would address an obvious concern that the use of heat in great excess of atmospheric values introduces additional effects that do not represent atmospheric conditions, versus confirming the alternate hypothesis that heat simply accelerates processes that would already occur under longer atmospheric timescales.

20 These results add to the growing body of work indicating that in many cases the addition of soluble secondary material can significantly reduce the ice nucleation ability of mineral dust particles, both below and above water saturation (Archuleta et al., 2005; Cziczo et al., 2009; Eastwood et al., 2009; Möhler et al., 2008; Niedermeier et al., 2010). They have revealed that while both modes are irreversibly impaired by the condensation of concentrated acid, the deposition regime is significantly more sensitive to such chemical processing. This suggests that atmospheric ice production below water saturation can potentially be prohibited when atmospheric ice nuclei become mixed with secondary pollutants.

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**Table 1.** IN fractions measured at  $-30^{\circ}\text{C}$  and  $-25^{\circ}\text{C}$  for Arizona test dust particles subjected to different treatment combinations<sup>a</sup>, particle hygroscopicity and volume fraction of sulphuric acid estimated from CCN measurements<sup>b</sup>, and sulphate mass per particle estimated from AMS measurements.

Exp	SA ( $^{\circ}\text{C}$ )	TD ( $^{\circ}\text{C}$ )	WB	NH <sub>3</sub>	IN (RH <sub>w</sub> =98%)	St Dev	IN (RH <sub>w</sub> =105%)	St Dev	s <sub>c</sub> (%)	κ <sub>app</sub>	H <sub>2</sub> SO <sub>4</sub> (by volume) <sup>b</sup>	Sulphate (ag/particle)
Temperature = $-30^{\circ}\text{C}$												
1.1					3.77E-02	1.39E-02	5.03E-02	8.69E-03	0.380	0.0021	2.01E-04	BDL <sup>c</sup>
14a					6.54E-03	2.93E-03			0.385	0.0020	4.30E-05	
14i					6.17E-03	2.19E-03						BDL
16a							3.89E-02	8.23E-03				BDL
16i							3.98E-02	5.33E-03				BDL
2.1		250			6.20E-03	2.19E-03	3.52E-02	5.47E-03	0.390	0.0019	-8.60E-05	BDL
13.1		250			3.24E-03	1.54E-03	3.63E-02	5.36E-03	0.388	0.0020	-4.30E-05	BDL
14b		250			2.97E-03	1.91E-03						BDL
16b		250					2.43E-02	6.03E-03				BDL
20		45			3.59E-03	1.69E-03	2.83E-02	6.03E-03	0.388	0.0020	-2.87E-05	BDL
21		70			4.07E-03	2.64E-03	3.20E-02	6.56E-03	0.391	0.0019	-8.60E-05	BDL
36c		85					2.99E-02	4.53E-03				
29j			X	X			2.86E-02	6.52E-03				BDL
3.1	45				1.97E-04	3.64E-04	2.48E-02	4.99E-03	0.177	0.0165	2.08E-02	670
14d	45				4.42E-05	1.78E-04						485
16d	45						2.69E-02	4.79E-03				425
19	45	45			0		3.71E-03	2.64E-03	0.206	0.0116	1.38E-02	373
22	70	70			2.75E-04	9.81E-04	2.69E-04	6.49E-04	0.151	0.0218	2.84E-02	878
4.1	45	250			2.58E-04	5.44E-04	1.60E-03	1.07E-03	0.226	0.0089	9.87E-03	371
14c	45	250			8.01E-05	2.89E-04						
16c	45	250					2.28E-03	1.38E-03				318
6.1	70				0		2.38E-03	1.32E-03	0.134	0.0281	3.74E-02	1318
14e	70				3.10E-05	1.53E-04						1298
16e	70						7.81E-04	7.22E-04				1153
14f	70	250			3.46E-05	1.79E-04						701
16f	70	250					8.97E-05	2.65E-04				631
10.1	70		X		0		6.26E-04	6.63E-04	0.120	0.0351	4.74E-02	1505
14g	70		X		3.20E-05	1.75E-04						1153
17	70		X		1.13E-04	3.34E-04	4.12E-04	6.91E-04	0.127	0.0308	4.13E-02	1204
16h	70		X				2.51E-04	4.12E-04				1335
34a	70		X				3.34E-04	4.42E-04				1432
36b	70		X				8.46E-05	1.75E-04				
11.1	70	250	X		1.22E-04	4.25E-04	5.00E-03	2.56E-03	0.130	0.0297	3.97E-02	1243
14g	70	250	X		3.54E-05	2.02E-04						1153
16g	70	250	X				2.15E-03	1.41E-03				1130
18	70	250	X		3.93E-05	2.22E-04	3.77E-03	1.75E-03	0.137	0.0269	3.57E-02	959
23 <sup>d</sup>	70	250	X		0		0		0.164	0.0187	2.39E-02	807



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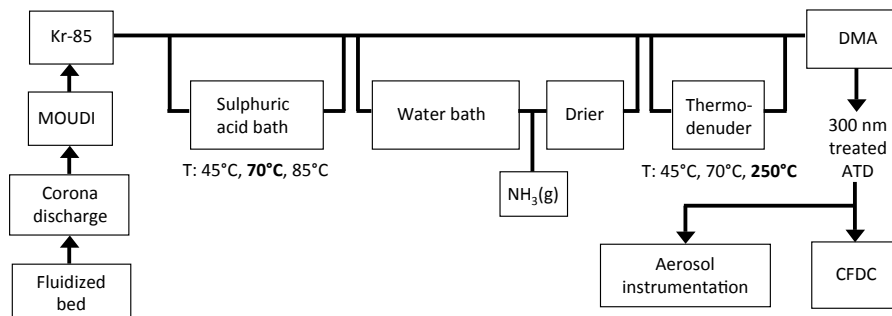
Table 1. Continued.

Exp	SA (°C)	TD (°C)	WB	NH <sub>3</sub>	IN (RH <sub>w</sub> =98%)	St Dev	IN (RH <sub>w</sub> =105%)	St Dev	s <sub>c</sub> (%)	K <sub>app</sub>	H <sub>2</sub> SO <sub>4</sub> (by volume) <sup>b</sup>	Sulphate (ag/particle)
Temperature = -30 °C												
30.1	85				4.82E-05	1.53E-04	1.27E-03	9.79E-04	0.064	0.1230	1.73E-01	2106
31.1	85	250			8.79E-05	2.32E-04	9.89E-05	2.48E-04	0.138	0.0268	3.55E-02	889
24.1	70		X	X	4.10E-05	2.05E-04	2.90E-04	6.83E-04	0.119	0.0356	4.81E-02	1145
28.1	70		X	X	6.40E-05	2.48E-04	4.10E-04	6.10E-04	0.131	0.0292	3.90E-02	761
34d	70		X	X			1.57E-04	2.13E-04				1142
25.1	70	250	X	X	6.14E-04	1.10E-03	2.26E-03	2.17E-03	0.129	0.0298	3.98E-02	954
34c	70	250	X	X			1.02E-03	7.30E-04				1001
34e	85		X				3.39E-05	1.06E-04				2573
34f	85	250	X				3.21E-04	4.91E-04				1732
34g	85	250	X	X			5.20E-04	5.22E-04				1702
34h	85		X	X			4.55E-05	1.11E-04				2369
32.1 <sup>e</sup>	70				4.99E-05	1.27E-04	6.42E-03	2.01E-03	0.136	0.0272	0.0361	1100
33.1 <sup>e</sup>	70	250			0		1.04E-04	2.14E-04	0.168	0.018	0.02292	
36a.1	70			X	0		1.63E-04	2.19E-04				1484
Temperature = -25 °C												
1.2					2.31E-04	4.65E-04	2.00E-02	3.93E-03	0.380	0.0021	2.01E-04	BDL
12.2					7.15E-04	6.53E-04	1.85E-03	8.25E-04	0.382	0.0021	1.29E-04	BDL
2.2		250					1.37E-02	2.67E-03	0.390	0.0019	-8.60E-05	BDL
13.2		250			4.02E-04	5.12E-04	1.16E-02	2.71E-03	0.388	0.0020	-4.30E-05	BDL
3.2	45						1.33E-02	3.20E-03	0.177	0.0165	2.08E-02	671
4.2	45	250			1.49E-04	3.48E-04	1.28E-03	8.19E-04	0.226	0.0089	9.87E-03	371
6.2	70						2.21E-03	1.22E-03	0.134	0.0281	3.74E-02	1318
7.2	70	250			3.58E-04	6.55E-04	8.60E-04	8.14E-04	0.172	0.0174	2.21E-02	729
10.2	70		X		2.17E-04	4.56E-04	3.64E-04	6.47E-04	0.120	0.0351	4.74E-02	1505
11.2	70	250	X				3.15E-03	2.26E-03	0.130	0.0297	3.97E-02	1243
24.2	70		X	X	1.25E-04	2.49E-04	6.36E-05	2.80E-04	0.119	0.0356	4.81E-02	1145
28.2	70		X	X	3.35E-05	1.25E-04	1.83E-05	9.23E-05	0.131	0.0292	3.90E-02	761
25.2	70	250	X	X	3.30E-04	6.73E-04	5.04E-04	9.50E-04	0.129	0.0298	3.98E-02	954
30.2	85				1.53E-05	7.97E-05	1.40E-04	2.50E-04	0.064	0.1230	1.73E-01	2106
31.2	85	250			4.65E-05	1.46E-04	6.38E-05	1.72E-04	0.138	0.0268	3.55E-02	889
32.2 <sup>e</sup>	70				1.43E-05	7.16E-05	2.78E-05	9.62E-05	0.136	0.0272	3.61E-02	1100
33.2 <sup>e</sup>	70	250			2.94E-05	1.10E-04	5.46E-05	1.44E-04	0.168	0.0180	2.29E-02	
36a.2	70			X	6.95E-06	3.97E-05	2.78E-05	8.06E-05				1484

<sup>a</sup> Treatment order was sulphuric acid coating (SA), water bath (WB), ammonia (NH<sub>3</sub>), thermodenuder (TD); if that component was used, unless otherwise indicated below. <sup>b</sup> See Eq. (2), <sup>c</sup> Below detection limit, <sup>d</sup> Order: SA+ TD + WB, <sup>e</sup> Longer SA coating time.

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**Fig. 1.** Schematic of dust aerosol generation, treatment, and analysis system. Arizona test dust was generated dry from the fluidized bed, and then subjected to a variety of thermochemical treatment options. The most commonly used sequence of treatment options is shown here. Temperatures listed in bold were the default settings used in the sulphuric acid coating oven and thermodenuder. A differential mobility analyser (DMA) selected 300 nm mobility diameter particles after treatment for analysis by the CFDC and other instruments including the AMS and CCNc.

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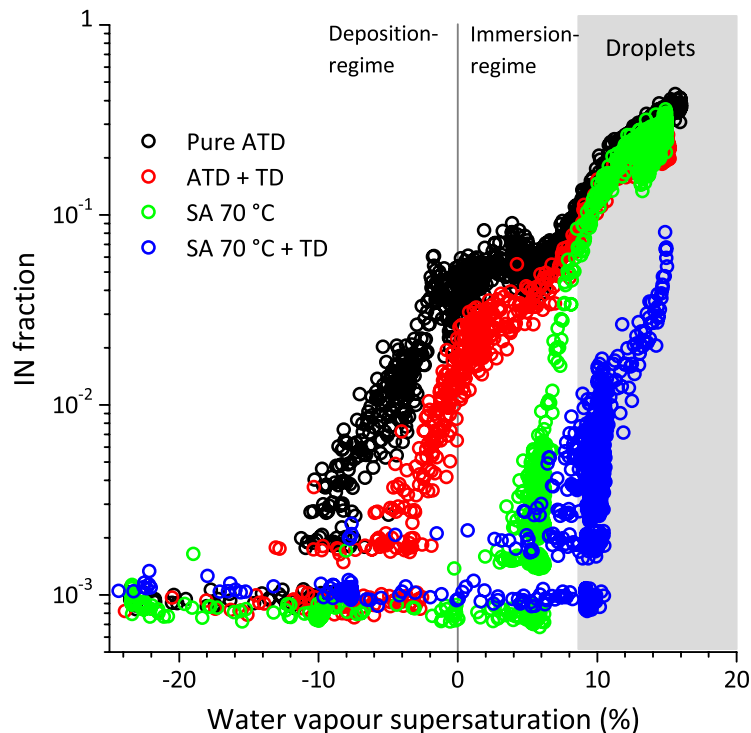
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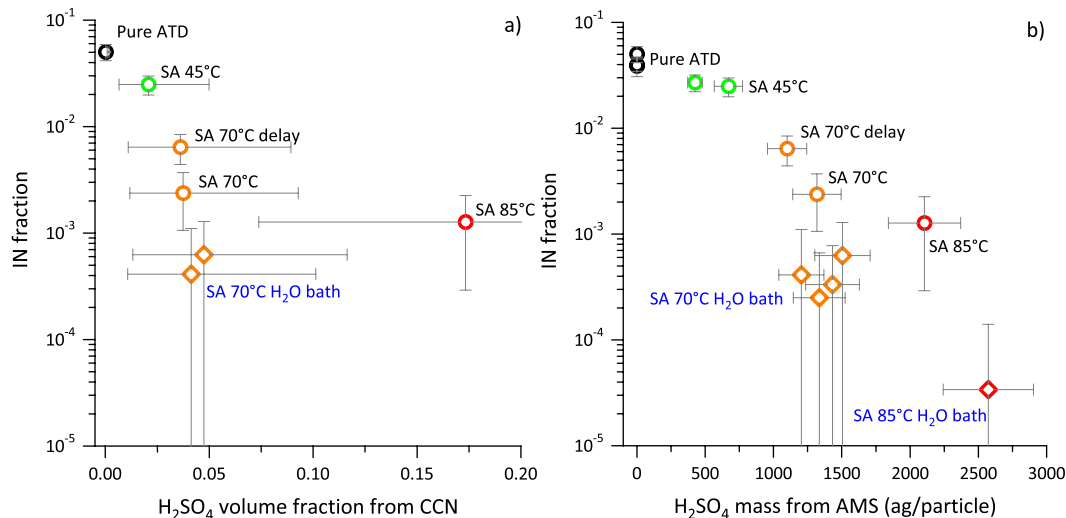
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**Fig. 2.** Fraction of 300 nm ATD particles that nucleated ice at  $-30^{\circ}\text{C}$  as the relative humidity with respect to water was increased. Data points collected at 1 Hz during slow  $\text{RH}_w$  scans. Results for untreated ATD are displayed along with those for ATD heated in the thermodenuder (TD) at  $250^{\circ}\text{C}$ , ATD coated with sulphuric acid (SA) at  $70^{\circ}\text{C}$ , and coated ATD subsequently heated in the TD before analysis in the CFDC. Above  $\sim 108\%$   $\text{RH}_w$  droplets broke through the evaporation region and cannot be distinguished from ice crystals (grey box).

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**Fig. 3.** Fraction of 300 nm ATD particles that nucleated ice at  $-30^{\circ}\text{C}$  and  $\text{RH}_w=105\%$  (condensation/immersion-regime) after different treatment combinations, plotted versus (a) the particle's sulphuric acid volume fraction estimated from the CCN hygroscopicity measurements, or (b) the mass of sulphate per particle estimated from the AMS measurements. Delay refers to experiments performed with an additional volume in the flow path to increase the treatment time.

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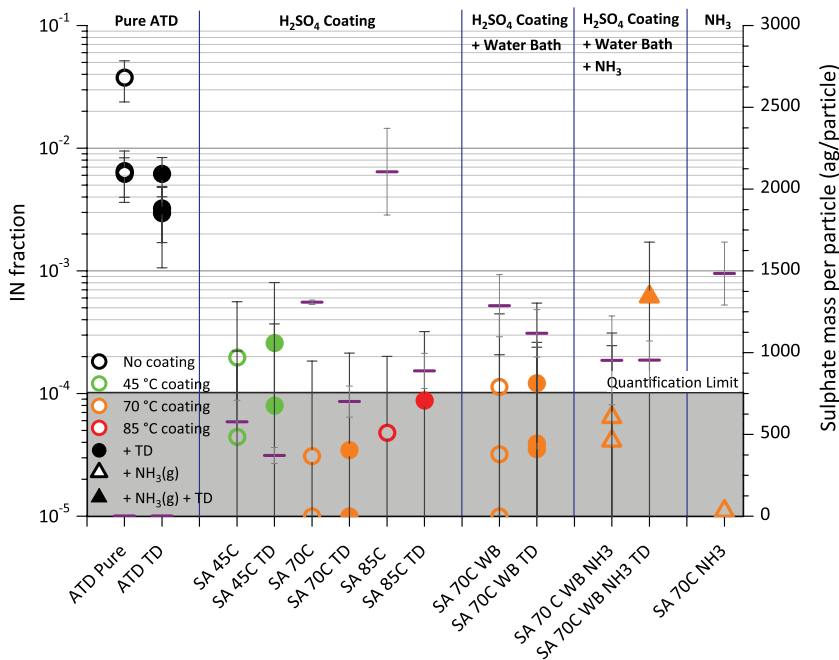
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a)  $T = -30\text{ }^{\circ}\text{C}$ ,  $\text{RH}_w = 98\%$



**Fig. 4a.** Fraction of 300 nm ATD particles that nucleated ice after various chemical treatment combinations at  $-30\text{ }^{\circ}\text{C}$  under (a) deposition regime ( $\text{RH}_w=98\%$ ) or (b) immersion regime ( $\text{RH}_w=105\%$ ) ice nucleation conditions. Error bars are the standard deviation of the 1 s IN/CN ( $=f_{\text{IN}}$ ) ratio. The shaded region of  $f_{\text{IN}} < 10^{-4}$  represents the CFDC's limit of quantification for these experiments due to background frost counts; no meaning should be ascribed to differences in observed  $f_{\text{IN}}$  within this region. The average sulphate mass per particle estimated from the AMS is plotted (horizontal line) for each treatment. The error bar corresponds to the standard deviation between experiments or from a single experiment. Thermodenuder (TD) temperature was  $250\text{ }^{\circ}\text{C}$  in all cases. SA=sulphuric acid, WB=water bath.

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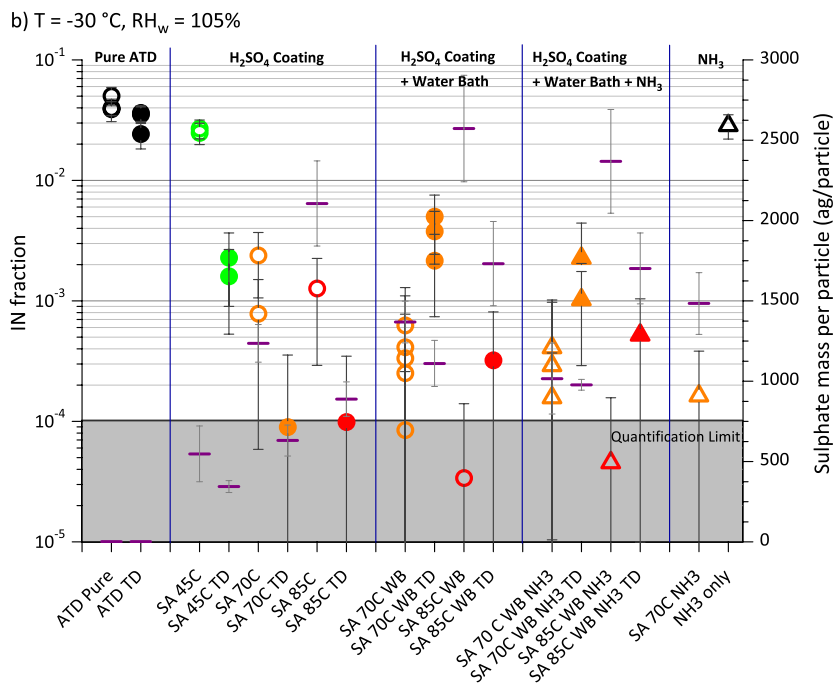


Fig. 4b.

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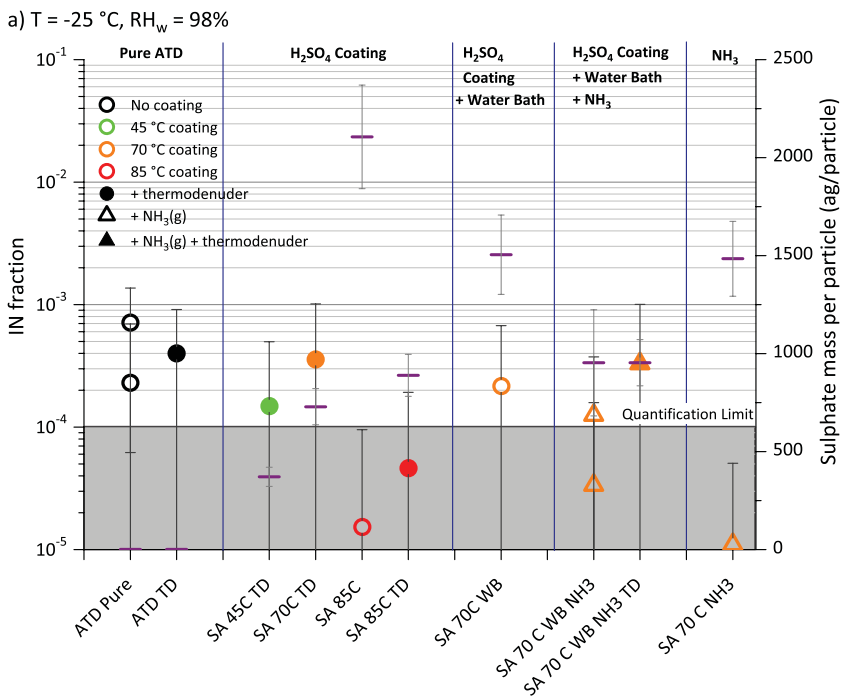
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**Fig. 5a.** Fraction of 300 nm ATD particles that nucleated ice at  $-25\text{ }^{\circ}\text{C}$ , as in Fig. 4.

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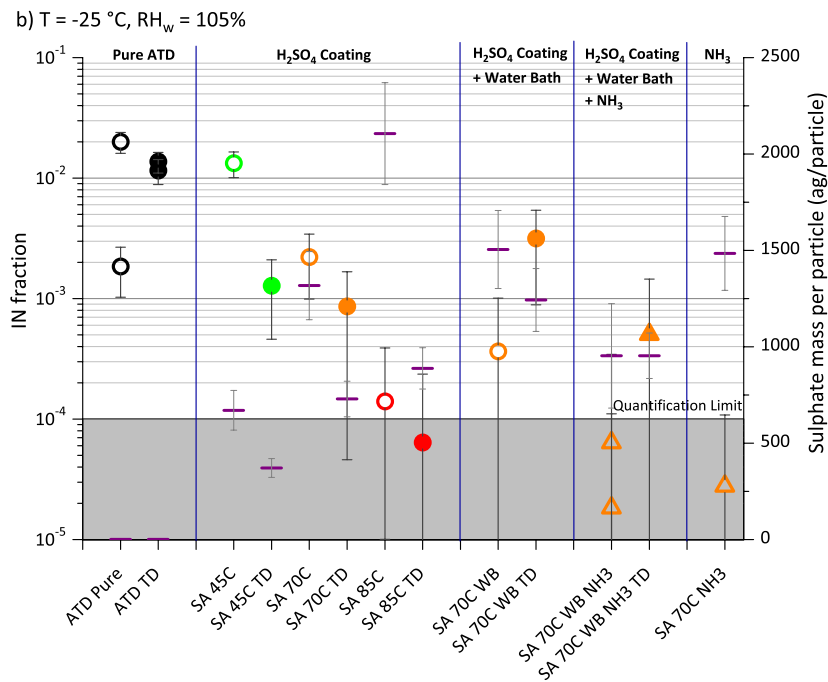


Fig. 5b.

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