The Role of Cloud Processing for the Ice Nucleating Ability of Organic Aerosol and Coal Fly Ash Particles

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Abstract  Ice nucleating particles are a minor fraction of tropospheric aerosol, yet they play a key role for cloud microphysical processes. One poorly understood process is the impact of atmospheric aging of aerosol particles on ice nucleation. Here we study the impact of cloud processing on the ice nucleation abilities of two physicochemically different aerosol particles by taking two model systems for atmospheric organic aerosol (OA), as well as coal fly ash (CFA) particles representing an inorganic aerosol type. The ice nucleation activity of the unprocessed particles is compared to aerosol particles that are first exposed to conditions mimicking trajectories through cirrus clouds (CC) and mixed-phase clouds (MPC) prior to testing their ice nucleation activity at temperatures below 243 K. We observed that unprocessed OA do not exhibit heterogeneous ice nucleation, requiring homogeneous freezing conditions of solution droplets to form ice. However, after CC processing raffinose particles showed heterogeneous ice nucleation activity at 218 K and a water saturation ratio of 0.68–0.82, reaching activated fractions of up to 0.3. This enhancement compared to unprocessed raffinose particles results from an increase in particle viscosity upon CC processing. We also present new results of unprocessed CFA particles exhibiting strong heterogeneous ice nucleation activity at temperatures below 235 K in the deposition and/or pore condensation and freezing mode. In contrast to the OA, the CFA show a decrease in ice nucleation activity after both MPC and CC processing. Furthermore, cloud processing and generating CFA particles from aqueous suspensions do not have the same effect on their ice nucleation ability.

1. Introduction

Aerosol particles are central to tropospheric cloud formation processes, some of which lead to the formation of cloud ice. The accurate determination of the role of aerosol particles acting as ice nucleating particles (INPs, Vali et al., 2015) is crucial for a reliable simulation of ice clouds in climate models, which strongly impact the Earth's energy budget (Boucher et al., 2013; Lohmann, 2015), and initiate most of the Earth's precipitation (Mülmenstädt et al., 2015). Despite extensive previous work, our understanding of aerosol-cloud interactions and of INP properties in particular is not constrained enough (Kreidenweis et al., 2019). The ability of an aerosol particle to act as an INP depends on its physicochemical properties, including surface chemical functionality, such as the presence of OH groups, and particle morphology, e.g., the presence of cracks or pores on the surface of the particles. Some of these properties provide energetically favorable conditions for the ice nucleation process (Glatz & Sarupria, 2018). In fact, various laboratory experiments have investigated the ice nucleation activity of different aerosol particles and found that it is closely linked to their physicochemical properties, as reviewed by e.g. Hoose and Möhler (2012), Knopf et al. (2018), and Kanji et al. (2017). These physicochemical properties can be altered during atmospheric aging. For instance, during in-cloud processes and exposure to different temperatures and humidities in the troposphere, the particle size and particle phase can be modified (Adler et al., 2013; Ladino et al., 2014), in turn affecting the INP potential (Mahrt et al., 2020; Umo et al., 2019; Wagner et al., 2012). Even though aerosol particles are on average cycled through multiple clouds during their atmospheric lifetime (Pruppacher & Jaenicke, 1995), it is poorly understood how such cloud processing would impact their INP potential. Previous studies on mineral dust (Knopf & Koop, 2006; Wagner et al., 2016), ambient dust (Kulkarni, 2018), soot (Mahrt et al., 2020), and organic aerosols (OAs, Wagner et al., 2012, 2014) have reported an enhanced ice nucleation activity of such cloud processed aerosol particles compared to unprocessed particles. Specifically, these
studies reported ice formation onsets at lower relative humidity and/or higher temperature compared to the first freezing-cycle (unprocessed particles).

One aging mechanism proposed for OA is the process of freeze-drying where particle vitrification and an increase in particle size due to the formation of highly porous aerosols occurs (Adler et al., 2013). Such larger particles are likely better INPs, as ice nucleation activity scales with particle size (Archuleta et al., 2005; Kanji & Abbatt, 2010; Lüönd et al., 2010; Welti et al., 2009). Even in the absence of an increase in particle size, changing the phase state of cloud processed OA can lead to altered ice nucleation activities (Berkemeier et al., 2014; Knopf et al., 2018; B. Wang et al., 2012; Zobrist et al., 2008). For instance Ladino et al. (2014) observed enhanced ice nucleation potential of OA derived from oxidation of α-pinene after exposing the particles to a pre-cooling cycle at T < 235 K, the homogeneous ice nucleation temperature (HINT). The authors attributed the enhanced ice nucleation activity to an increase in particle viscosity resulting from pre-cooling. The absolute viscosity of OA can span several orders of magnitude (Koop et al., 2011), ranging from liquid (Cappa et al., 2008), to semisolids (Song et al., 2016) to glassy particles (Berkemeier et al., 2014; Zobrist et al., 2011). Previous studies have reported OA particles to often be in a glassy state (Zobrist et al., 2008; Mikhailov et al., 2009; Virtanen et al., 2010; B. Wang et al., 2012, 2016), and glassy particles have been observed to act as heterogeneous INPs in the deposition mode (Ignatius et al., 2016; Murray et al., 2010; Wilson et al., 2012). Consistent with the findings of Ladino et al. (2014), an enhancement of ice nucleation activity with increasing viscosity has also been reported by Wagner et al. (2012), who observed formation of highly viscous OA upon expansion and cooling cycles. When re-probing the ice nucleation activity of the cloud processed glassy OA particles in a second cloud-cycle, they catalyzed ice formation at a lower ice supersaturation compared to the unprocessed particles. Besides the higher particle viscosity, the enhanced ice nucleation activity of cloud processed particles could result from a preactivation effect (Knopf & Koop, 2006; Marcolli, 2017; Pruppacher & Klett, 1997; Umo et al., 2019; Wagner et al., 2014).

During preactivation, a microscopic ice phase is retained within pores present on the particle, which can then grow into a macroscopic ice crystal in a subsequent cloud-cycle (without the need of an ice nucleation process). Preactivation can take place at bulk ice subsaturated conditions (S < 1), due to the lower equilibrium vapor pressure of ice in confinements (Marcolli, 2017), as long as T < 273 K. In the absence of preactivation, increasing the porosity of particles (change in physical properties), can still result in an enhancement of ice nucleation activity (Mahrt et al., 2020), by creating or increasing pore volume resulting in an increased ability to nucleate ice via pore condensation and freezing (PCF, Christenson, 2013; R. O. David et al., 2019; Marcolli, 2014). PCF has been implicated in the work of Umo et al. (2019), who measured the ice nucleation potential of coal fly ash (CFA) particles in a temperature-cycling experiment, and found an increased ice-active fraction of CFA particles previously exposed to lower temperatures. This enhancement effect was related to preactivation due to initial ice formation in pores by PCF. Lastly, Losey et al. (2018) investigated aging processes on CFA with acid-treatments and found an altered particle surface due to the formation of gypsum, which decreased the immersion freezing activity (change in chemical properties). Similarly, Grawe et al. (2018) report a change in the ice nucleation activity in the immersion freezing mode for wet-suspended compared to dry-generated CFA particles, suggesting that the particles are susceptible to cloud processing.

OA particles are a main contributor to the total submicron aerosol mass and are ubiquitous in the troposphere (e.g. Jimenez et al., 2009). Biomass burning, cooking and coal combustion constitute major sources of tropospheric OA (Daellenbach et al., 2017; Zhu et al., 2018). To demonstrate that diverse aerosol types react differently to cloud processing in terms of their ice nucleation behavior, here we study two physicochemically diverse aerosol proxies. Two model OA (levoglucosan and raffinose) and an inorganic aerosol sample (CFA) were investigated to assess the ability of different cloud processing scenarios on the ice nucleation ability. The OA chosen differ in their phase states under specific temperature and humidity conditions. The CFA sample is derived from burning pulverized coal in power plants. CFA can contain mineral impurities such as clay, feldspar and quartz and can show INP activities similar to mineral dusts (e.g., Grawe et al., 2018; Umo et al., 2015). By using an experimental setup with two horizontal ice nucleation chambers (HINCs, Lacher et al., 2017; Mahrt et al., 2018, 2020), novel INP results at temperatures below 243 K with size-selected aerosols are presented in this study. The cloud processing scenarios covered include cycling through cirrus or mixed-phase cloud conditions, as described next.
2. Material and Methods

2.1. Cloud Processing Scenarios

The cloud processing scenarios investigated here are illustrated in Figure 1, encompassing a cirrus cloud (CC) processing and a mixed-phase cloud (MPC) processing scenario. Each scenario can broadly be divided into four parts, as shown by the points (P1–P4) along each trajectory in Figure 1.

In the MPC processing scenario (green trajectory), emitted aerosol particles form supercooled liquid cloud droplets at $T > 235$ K and a relative humidity above water saturation (P2). If this MPC dissipates or gets detrained, the droplets evaporate and the supercooled liquid-processed aerosol particles are released back into the atmosphere (P3). In a subsequent cloud formation cycle, the processed aerosol particles can be exposed to cirrus or MPC conditions where they can act as INPs (P4). For the CC processing scenario (red trajectory) the aerosol particles follow similar trajectory. However, unlike the MPC scenario, the aerosol particles are already exposed to $T < 235$ K and homogeneous freezing conditions in the first cloud-cycle (P2), leading to ice crystal formation on the aerosol particles during the CC processing step. The ice crystals can sublime due to dehydration of the cloud, exposing them to ice subsaturated conditions, but sustaining $T < 235$ K (P3), thus releasing processed aerosol particles. In a subsequent CC formation cycle the CC processed aerosol particles are exposed to $S_i > 1$ at $T < 235$ K (P4), where they may act as INPs with potentially altered ice nucleation activity. Our goal is to investigate if the processed particles from either trajectory have a different INP activity compared to the unprocessed particles. The exact temperature and relative humidity conditions for each processing scenario and step within our experiments are outlined below.

2.2. Cloud Processing Experimental Setup

2.2.1. Overview

The experimental setup used to mimic the cloud processing scenarios is shown in Figure 2, and can be divided into four parts (dashed boxes), which correspond to P1–P4 along the trajectories in Figure 1. We achieved realistic atmospheric cloud processing conditions by carefully selecting the $T$ and $S_i/S_w$ for each step, as indicated at the bottom in Figure 2, where the red and green values represent the CC and MPC processing scenario, respectively.
First, the OA and CFA were generated and dried with a set of a silica and a molecular sieve diffusion driers in that order (see Section 2.2.2). The OA particles were then size-selected using a differential mobility analyzer (DMA, Model 3080, TSI, Inc.). A flow splitter (Model 3708, TSI Inc.) was used to direct the flow of size-selected particles to a condensation particle counter (CPC, Model 3776, TSI Inc.; 1.0 Lmin⁻¹) and to HINC_CP where the cloud processing of the aerosol particles was performed (dashed orange box). The flow with hydrometeors (droplets or crystals) exiting HINC_CP was then guided into the cloud aerosol transitioner Zurich (CATZ, Mahrt et al., 2020). CATZ is a temperature controlled, double walled jacketed flow tube, where the cloud particles are exposed to subsaturated conditions, causing the cloud droplets or ice crystals to evaporate and sublimate respectively. The particle transition time in CATZ is approximately 10 s at the flow rates used. Downstream of CATZ, the flow was split between a CPC (Model 3072, TSI Inc.; 1.0 Lmin⁻¹) and HINC_IN (P4; 0.215 Lmin⁻¹), where the ice nucleation activity of the cloud processed aerosol particles was tested. It was ensured that the OA phase state between two different experimental sections (e.g., between the HINCs and CATZ) did not change since the particles could be exposed to slightly varying T and RH conditions for ∼140 ms. The excess flow of ∼1.45 Lmin⁻¹ downstream of CATZ was dumped using a vacuum pump. High aerosol particle number concentrations (see Section 2.2.2) are needed upstream of HINC_CP as the particles become diluted by a factor of approximately 10 in each HINC_CP and HINC_IN, in order for the optical particle counter (OPC, Model GT-526S, MetOne Instruments, Grants Pass, Oregon, USA) downstream of HINC_IN to reliably detect a signal. For comparison the ice nucleation ability of the unprocessed aerosol particles was also investigated bypassing P2 and P3 as indicated by the dotted line in Figure 2, where the ice nucleation activity was determined by means of RH-scans in HINC_IN (see Section 2.2.3). In addition, for the OA types tested, particle size distribution measurements were performed at test points TP1-TP2 (see Figure 2) using a scanning mobility particle sizer (SMPS) consisting of a DMA (Model 3080, with a 3081 column and a polonium radiation source, TSI Inc.) and a CPC (Model 3776, TSI Inc.), in order to investigate potential changes in particle size upon cloud processing.

2.2.2. Aerosol Types Investigated and Particle Generation

The OA proxies studied here encompass raffinose and levoglucosan, which have widely been used as laboratory model systems representing OA (Lienhard et al., 2015; Wagner et al., 2012; Wilson et al., 2012).
Levoglucosan (1,6-Anhydro-β-D-glucose, CAS No.: 498-07-7) is formed by pyrolysis of carbohydrates, such as starch and cellulose, and is frequently used as a tracer for biomass burning aerosol (Lakshmanan & Hoelscher, 1970; B. Wang et al., 2012; Simonett et al., 1999; Aiken et al., 2010). Raffinose is a trisaccharide composed of galactose, glucose and fructose with five hydrates (D-(+)-Raffinose pentahydrate, CAS No.: 17629-30-0). Both OA proxies were obtained from Sigma Aldrich (purity ≥98%) as crystalline solids and used without further purification. Solutions of the organic compounds were prepared following Zobrist et al. (2006). In brief, all OA particles were produced from dilute aqueous solutions (0.1 M) using Milli-Q water (18.2 MΩ). The OA particles were generated using an atomizer (Model 3076, TSI Inc.) and dried by diffusion driers including a silica gel and molecular sieve drier to RH < 5%. The humidity was frequently checked by a humidity sensor (Vasalia, HUMIPAC) to ensure that the dried OA particles are not humidified. To obtain a particle diameter with sufficiently high particle number concentrations for our cloud processing experiments, solutions with different molarities were tested by measuring the size distributions of the atomized solution with an SMPS. For an electrical mobility diameter of $d_m = 200 \text{ nm}$, the SMPS size distribution of all OA proxies revealed a number concentration of $\sim 1,000 - 4,000 \text{ cm}^{-3}$ when using 0.1 M solutions, which is ideal for our experimental setup based on previous experience in our laboratory (Mahrt et al., 2020).

In our experiments, CFA particles were either dry- or wet-generated using a sample identical to the CFA1 sample described and characterized in detail by Grawe et al. (2018). Dry aerosol particles were produced from a mixture of CFA powder and bronze beads using a fluidized bed aerosol generator (Model 3400A, TSI Inc.). A suspension of CFA was produced to obtain wet-generated aerosol particles, following the procedure of Grawe et al. (2018). Therefore, 0.1 g of the ash powder was mixed with 100 ml Milli-Q water and sonicated for ~10 min. The suspension was then stirred with a magnetic stirrer for ~24 h, before the ice nucleation activity was tested. For all our CFA experiments the particles were not size selected, because the number concentration of $d_m = 200 \text{ nm}$ particles was insufficient ($<50 \text{ cm}^{-3}$) for our setup. For the experiments where CFA was dry-suspended a cyclone (URG corporation, Model: 2000-30-EHB; cut-off aerodynamic diameter of $d_a < 1.5 \mu m$) and a particle impactor were inserted upstream of HINC, in order to limit the number of super-micron particles that enter the ice nucleation setup.

### 2.2.3. Ice Nucleation of Cloud Processed Aerosols in HINC

The ice nucleation activity of cloud processed particles was measured in HINC_IN, by means of RH-scans at a fixed temperature. A detailed description of HINC is given elsewhere (Lacher et al., 2017; Mahrt et al., 2018). Here, we probed a temperature range of 243–218 K covering a $S_w$ range of $\sim 0.60-1.05$ depending on the sample temperature (see Figure 2). Downstream of HINC_IN, the OPC detects the ice crystals formed as a function of sampling $T$ and $S_w$ conditions. The fraction of aerosol particles that nucleates ice within HINC_IN, called the activated fraction (AF), is defined as:

$$ AF = \frac{n_{\text{ice,OPC}>1 \mu m}}{n_{\text{tot,CPC}}} $$

(1)

where $n_{\text{tot,CPC}}$ is the total aerosol number concentration entering HINC_IN as counted by the CPC operated in parallel, and $n_{\text{ice,OPC}>1 \mu m}$ defines the number concentration of ice particles detected by the OPC with diameters larger than the threshold size of 1 μm for the OA experiments. The OPC counts particles in six different, user-definable size bins. The uncertainty range in AF is ±14%, resulting from 10% counting uncertainty in each the OPC and the CPC. We constrain our analysis here to the 1 and 2 μm OPC bins. As the OA particles are size selected to $d_m = 200 \text{ nm}$, the inactivated aerosol particles were not detected by the 1 μm size bin. Therefore, the OA AF curves were calculated using data of the 1 μm OPC bin, including multiple-charged particles, i.e. particles that are larger than the electrical mobility diameter selected at the DMA. The electrical mobility diameter of doubly charged OA particles is approximately 328 nm and the percentage of doubly charged particles amounts to 13.3% as determined from measuring the size distribution of size selected particles downstream of the DMA (TP1 in Figure 2). This is in good agreement with the expected percentage of doubly charged particles of 12% calculated by following Wiedensohler (1988). For the CFA experiments, on the contrary, polydisperse aerosol was used, requiring evaluation of the AF using the 2 μm bin OPC data, because some inactivated aerosol particles were detected in the 1 μm bin. In addition, we applied an aerosol correction to the AF curves of the CFA. The aerosol correction is achieved by calculating the
mean $AF$ value in the range $S_w \approx 0.60–0.85$, where we can exclude ice nucleation, and subtracting this value from the entire $AF$ curve. All $AF$ curves presented below are background corrected, by probing filtered, aerosol-free air at the beginning and end of each RH-scan, as detailed in Lacher et al. (2017).

3. Results and Discussion

3.1. Overview of the Results

An overview of the CC processed ice nucleation results (circles) with their corresponding unprocessed measurements (squares) is shown in Figure 3. Results are shown for the onset of ice formation (defined as $AF = 10^{-2}$), as a function of temperature and the ice saturation ratio ($S_i$). At 243 K (MPC temperatures), the ice nucleation of neither the unprocessed nor the CC processed OA (levoglucosan and raffinose) and CFA particles is observed at conditions below the water droplet survival (WDS) line (dashed blue line in Figure 3). WDS indicates the maximum humidity beyond which an ice crystal and water droplet cannot be distinguished in the 1 µm OPC channel, that is, the water droplet survival (WDS) line. WDS was calculated, assuming an initial aerosol diameter of 200 nm and a residence time of 10 s. Uncertainties in $S_i$ are indicated as vertical bars, indicating the variation in $S_i$ across the aerosol lamina, resulting from variations in wall temperatures of 1.2 K (horizontal error bars). Data correspond to the 1 and 2 µm OPC channel for OA and CFA, respectively (see text for details). CFA, coal fly ash; OPC, optical particle counter; OA, organic aerosol.
At cirrus temperatures ($T < 233$ K), we find the ice nucleation onset for unprocessed OA particles to lie within or above the homogeneous freezing threshold of solution droplets, independent of sample type, implying that the unprocessed OA particles do not exhibit any heterogeneous ice nucleation activity for all temperatures below 233 K tested here. Our results are in agreement with those of Wilson et al. (2012), in which unprocessed levoglucosan particles did not show any heterogeneous ice nucleation for $T > 195$ K. In contrast to the unprocessed OA particles, the dry-generated unprocessed CFA particles show ice nucleation onsets at $S_i < S_{i,\text{hom}}$, at all cirrus temperatures, revealing that unprocessed CFA particles are very active INPs at these temperatures.

The CC processed ice nucleation measurements of the OA particles at $T < 233$ K, in general, reveal no major difference compared to the unprocessed OA particles. Interestingly, however, at 218 K, the lowest temperature tested here, the ice nucleation onsets for raffinose occur at much lower supersaturation ($S_i \approx 1.18 \pm 0.05$) compared to the unprocessed particles ($S_i \approx 1.52 \pm 0.05$). For the 1% AF threshold considered in Figure 3, these results reveal a potential for the raffinose particles to act as heterogeneous INPs after being CC processed. Instead, in the case of the CFA particles, the CC processing led to ice nucleation onsets at 0.13–0.22 higher $S_i$ compared to the unprocessed CFA particles (see Figure 3). This implies that

Figure 4. Activated fraction (AF) curves of unprocessed and CC processed 200 nm diameter raffinose particles for the temperature range 243–218 K as a function of the saturation ratio with respect to water ($S_w$). The value in brackets for each data point refers to the number of conducted experiments for each aerosol proxy in the corresponding cloud processing scenario. The AF is calculated according to Equation 1 using the data of the 1 µm OPC bin. Blue-dashed line panel (a): water droplet survival (WDS) condition explained in Figure 3 with the corresponding uncertainty range in blue-shaded regions. Black-dashed lines: homogeneous freezing conditions for solution droplets according to Koop et al. (2000). Gray-shaded regions: calculated $S_w$ variation across the aerosol-lamina that particles are exposed to in HINC for the given homogeneous freezing conditions. Error bars are shown for every fifth data point only for clarity, and represent uncertainties in $S_w$ in HINC_IN, for an aerosol to sheath flow ratio of 1:10. The starting $S_i$ of the RH-scan for each $T$ was always set to $\sim 1$, which differs in $S_i$ for $T = 228–218$ K. CC, cirrus cloud; OPC, optical particle counter; HINC, horizontal ice nucleation chambers.
the INP potential of the CFA particles decreased after a CC formation process and highlights that (cirrus) cloud processing can have opposing effects for different aerosol types. To further elucidate which properties or ice nucleation mechanisms cause the modified ice nucleation activity of the CC processed OA and CFA particles, we discuss these results in more detail in the following.

3.2. Impact of Cloud Processing on the Ice Nucleation Ability of OA

In this section, we discuss the ice nucleation results of CC processed raffinose particles for the CC regime temperatures tested. The \( AF \) curves as a function of \( S_w \) for the unprocessed and CC processed raffinose particles at all temperatures measured in HINC_IN are shown in separate panels in Figure 4. At \( T = 243 \text{ K} \), the CC processed and unprocessed raffinose particles show an activation onset above water saturation which are almost identical to the WDS line. As mentioned above, at these \( T \) and \( S_w \) conditions, ice crystals and liquid water droplets cannot be distinguished anymore from the 1 \( \mu \text{m} \) OPC bin data, because both hydrometer types reach diameters above this threshold based on theoretical calculations of pure diffusional growth (Lohmann et al., 2016; Yau & Rogers, 1996). The activation around \( S_w = 1 \), suggests that the OPC signal results from activation of the OA particles into supercooled liquid cloud droplets, as immersion/condensation freezing should result in ice crystals detectable in the larger OPC size bins (such as 4 \( \mu \text{m} \)), which was not the case here.

The activation onset for \( T = 228–218 \text{ K} \) (Figures 4b and 4d), as indicated by the steep increase in the \( AF \) curves, starts at or slightly above (within experimental uncertainty) the homogeneous freezing threshold (vertical dashed line) suggesting ice nucleation occurs due to homogeneous freezing. An exception is the \( AF \) of the CC processed raffinose particles at 218 K, where an increased \( AF \) signal below the homogeneous freezing threshold was observed. More specifically, the \( AF \) was found to range from 3 \( \times 10^{-3} \) to 0.3 for \( S_w \) of 0.68–0.82. At higher humidities, the \( AF \) decreases again to background concentrations (<\( 10^{-3} \)), causing a discontinuity of the \( AF \) signal, and only rises again strongly once the homogeneous freezing sets in. We interpret the increased \( AF \) as heterogeneous ice formation (by deposition nucleation) of the CC processed raffinose particles resulting from the cloud processed particles becoming increasingly glassy (amorphous, very high viscosity). This is in-line with previous results showing that highly viscous OA can act as heterogeneous INPs (Knopf et al., 2018; Murray et al., 2010; Wagner et al., 2012; Wilson et al., 2012).

We confirm this by the phase diagram of raffinose and levoglucosan, shown in Figure 5, where we immediately see that the onset of ice nucleation of all OA that nucleated ice homogeneously is in the liquid part of the phase diagram. In contrast, the onset of CC processed raffinose that nucleated ice heterogeneously is in the glassy part of the phase diagram (orange shaded region). The experimental trajectory of the CC processing pathway is indicated by the red arrows. The pathway starts at P1, which is the aerosol generation condition after the diffusion drier and the size selection in the DMA (see also Figures 1 and 2). According to the phase diagram in Figure 5, raffinose particles are in a glassy (viscous, semi-solid) state, as indicated by the light orange shading (\( T < T_{g}^{\text{raff}} \), with \( T_{g}^{\text{raff}} \) denoting 395.7 ± 21.6 K at \( a_w = 0 \)). The levoglucosan particles on the contrary are in a liquid state at P1, that is, \( T > T_{g}^{\text{levo}} \), where \( T_{g}^{\text{levo}} \) is 283.6 ± 18.7 K at \( a_w = 0 \). At P2, which refers to the conditions in HINC_CP (\( T_{CP} = 228 \text{ K} \), \( S_w = 1.04 \)) where the raffinose particles become CC processed, the OA particles are in a liquid state and freeze homogeneously, as expected for aqueous solutions droplets. Along the trajectory from P2 to P3, denoting the transition through CATZ, the ice crystals sublime, releasing highly viscous residual particles owing to the low temperature. It is important to note that P3 denotes the conditions at the end of CATZ, that is, before the particles enter HINC_IN. For the lowest cirrus temperature tested here (\( T = 218 \text{ K} \), the humidities of the RH-scan in HINC_IN range from \( S_w = 0.6 \) (P3.1) to 1.05 (P4). The value of 0.6 corresponds to the humidity at the start of the RH-scan in HINC_IN when both walls are held at the same temperature, that is, \( S_i = 1 \) across the chamber, and denotes the lowest relative humidity achievable in our experiment. The conditions at the start of the RH-scan in HINC_IN at \( T = 218 \text{ K} \) are indicated by the point P3.1. Upon increasing the humidity when testing the ice nucleation activity of the CC processed aerosol particles, the raffinose particles remain glassy over the range \( S_w = 0.6–0.84 \). This humidity range coincides with the ice nucleation onset of raffinose (IN\( ^{\text{raff}} \), orange dots in Figure 3) and where we observed an increased \( AF \) signal in Figure 4d), supporting our interpretation.
of deposition ice nucleation of the CC processed raffinose particles. This interpretation is further supported by the AF curve dropping sharply as soon as \( S_w > 0.84 \) is reached, coinciding with the glass to liquid transition of the raffinose particles (solid orange line in Figure 5), causing the particles to lose their heterogeneous ice nucleation activity. The pathways at 223 and 228 K differ during the respective RH-scan in HINC_IN (arrows not shown in Figure 5) and show ice nucleation onsets at \( S_w > S_{\text{levo}} \). As the temperatures in HINC_CP are 5 and 10 K higher than the RH-scans at 218 K, the particle viscosity is also lower. The \( S_w \)-range at which the processed raffinose particles exiting CATZ remain in a glassy state (light orange shading) during the RH-scan in HINC_IN is reduced for the 223 and 228 K scans compared to 218 K, as illustrated in Figure 5. At 223 K the CC processed raffinose particles turn liquid at \( S_w \approx 0.79 \) and at 228 K the particles already turn liquid at \( S_w \approx 0.75 \), considering the uncertainty in \( T^\text{eff}_{\text{raff}} \) (dashed-orange line). Levoglucosan requires much lower temperatures for turning from a liquid into a glassy state. As such it is not surprising that we did not observe deposition ice nucleation on the cloud processed levoglucosan particles (see \( T^\text{levo}_{\text{raff}} \) in Figures 5 and C.1), which is consistent with the results of Wilson et al. (2012). This is also the reason why a MPC processing of either raffinose and levoglucosan was not conducted in this study. \( T^\text{CATZ} = 253 \) K is too high for the MPC processed particles to be in a glassy state (see Figure 5) before entering HINC_IN. Another deviation of the AF curves of the processed particles from the unprocessed OA particles is that they reach values of almost unity at \( S_w \approx 1.05 \) (see Figures 4 and C.1). Furthermore, the CC processed AF curves at all temperatures are systematically shifted by about \( S_w \approx 0.03 \) to higher humidity (see also Figure 3). This systematic shift toward higher humidity, although within our reported uncertainty can likely be explained by the higher viscosity (lower temperature) of the processed particles. The water diffusion in the highly viscous particles is lower compared to the unprocessed particles and thus, they nucleate ice at slightly higher humidity.

A similar outcome was observed by Wagner et al. (2012) who exposed aqueous raffinose particles to a temperature-cycle in different cloud expansion runs before measuring their ice nucleation activity. In their experiment, Wagner and co-workers found that temperature-cycled glassy raffinose particles exhibited heterogeneous ice nucleation activity, whereas their reference measurements did not, similar to our results. The heterogeneous ice nucleation on raffinose particles only occurred below about 215 K, which is close to \( T = 218 \) K where we observe heterogeneous ice nucleation of the cloud processed raffinose particles. Wagner et al. (2012) attributed the altered ice nucleation behavior of the ultra-viscous/glassy raffinose particles to preactivation, where small ice embryos are retained in pores. This can likely be explained by the high water uptake capacity of the unprocessed glassy aqueous raffinose particles. In this work, at the higher (room) temperature of aerosol generation, the less viscous raffinose particles entering HINC_IN have much higher water diffusion rates, which suppresses the formation of ice by deposition or heterogeneous nucleation since the particle surface is able to liquefy rather than maintain any structural integrity to provide a surface for an ice germ to form. On the other hand, the CC processed glassy raffinose particles produced at much lower temperatures (65 K lower than room temperature) have a much higher viscosity, and lower water diffusion rates allowing for the aerosol particle to provide the solid surface necessary for ice germ formation within the 10 s residence time in HINC_IN. For the CC processed raffinose particles at 223 and 228 K we already discussed that the exposure to the glassy phase \( S_w \) within HINC_IN is limited before the glass-to-liquid transition is reached in HINC_IN during the RH-scan. Nonetheless, the CC processed particles are still exposed to a range of \( S_w \approx 0.08 \) (0.70 – 0.78) at 228 K and 0.1 (0.64 – 0.74) at 223 K corresponding to glassy conditions; however, we do not observe any heterogeneous ice nucleation for these temperatures in the CC processed case in HINC_IN. We support this by the data reported by Lienhard et al. (2015), demonstrating that the water uptake rates significantly increase for \( T > 220 \) K. This suggests that even for the CC

Figure 5. Phase diagram showing the glass transition temperature (\( T_g \)) of raffinose (\( T^\text{eff}_{\text{raff}} \), solid orange) and levoglucosan (\( T^\text{levo}_{\text{g}} \), solid blue) with the dashed lines representing the respective uncertainty ranges (one standard deviation) as a function of temperature (\( T \)) and water activity (\( a_w \)). The parameterizations are taken from Zobrist et al. (2008), with \( T^\text{eff}_{\text{raff}} = 395.7 \pm 21.6 \) K at \( a_w = 0 \) and \( T^\text{levo}_{\text{g}} = 283.6 \pm 18.7 \) K at \( a_w = 0 \) (see Appendix B). The dashed-black line illustrates the ice melting (\( T_m \)) curve and the solid-black line the homogeneous freezing curve for solution droplets (\( T_f \)) according to Koop et al. (2000). The red arrows illustrate the investigated CC processing pathway for HINC_IN at 218 K. The points P1–P4 refer to the location of the CC pathway in the cloud processing schematic in Figure 1 and to different humidity and temperature conditions in the laboratory setup in Figure 2. From P3.1 to P4, the RH-scan in HINC_IN takes place. It starts from \( S_w \approx 0.6 \) at 218 K to slightly supersaturated conditions (see Figure 2). The ice nucleation onsets of raffinose (\( T^\text{eff}_{\text{raff}} \), orange) and levoglucosan (\( T^\text{levo}_{\text{eff}} \), blue) at \( T = 228, 223 \) and 218 K are included here and are taken from Figure 3. HINC, horizontal ice nucleation chambers.
processed glassy raffinose particles at 223 and 228 K, the water uptake coefficients are high enough to liquefy the particles during the time scale of the experiments thus inhibiting heterogeneous ice nucleation on these particles and making way for the liquefied particles to freeze homogeneously as shown in Figures 3 and 4.

Similar to the enhancement reported here, Ladino et al. (2014) found that precooling to 233 K (similar to the CATZ temperature used here) lowered the $S_i$ required to form ice by about 0.2, for the water soluble fraction of secondary OA generated by dark ozonolysis of α-pinene. Ladino et al. (2014) attributed this to an increase in viscosity and solid-like particle morphology that promoted heterogeneous ice formation via deposition nucleation (Baustian et al., 2013; Murray et al., 2010; Wilson et al., 2012; Wagner et al., 2012; B. Wang et al., 2012). This suggests that the observations of raffinose nucleating ice heterogeneously is also applicable to more complex organic mixtures, as frequently found in the atmosphere.

An alternative explanation for the enhanced ice nucleation ability could be that cloud processing can lead to vitrification of the OA associated with an increase in particle size and the formation of highly porous aerosols (HPA, Adler et al., 2013). Specifically, Adler et al. (2013) observed a strong increase in the mean particle diameter after freeze-drying of natural organic matter (NOM) compared to the unprocessed NOM-particles. Such HPA could in turn promote ice nucleation via PCF (Marcolli, 2014; R. David et al., 2019). To detect a possible change in the particle size due to CC processing, we measured their size distributions at the two test-points indicated by TP1 and TP2 in Figure 2. In Figure 6, we show the ratio of the mode and the mean particle size measured at these two test points with an SMPS. The SMPS measurements revealed no increase (within standard deviation) in particle diameters due to a CC processing step. The absence of an increase in particle diameter (and ice nucleation activity) due to cloud processing is not surprising for levoglucosan because it is expected that at TP2, when the particles are scanned for their size distribution, the particles phase state could revert to those relevant to room conditions ($T = 298 \text{ K}$ and $R\varphi_w < 10\%$). For these conditions, levoglucosan remains in the liquid phase state and raffinose in the glassy state. As such observing an increase in ice nucleation activity for raffinose but no increase in particle diameter upon cloud processing rules out a size related morphological change or HPA formation as a cause for the enhanced ice nucleation activity. In contrast, a ratio of approximately 1.8 (ratio of freeze-dried/unprocessed) for NOM particles was observed by Adler et al. (2013) (data added to Figure 6). The absence of a size altering morphological change and HPA formation due to cloud processing of the OA types tested here further supports deposition nucleation onto the cloud processed OA and suggests that PCF is negligible. However, we cannot completely rule out PCF as microscopic defects may still exist on the highly viscous particles, that are not captured by our particle size comparison.

### 3.3. Effect of Wet-Versus Dry-Generation on the Ice Nucleation Ability of CFA

In Figure 7, we show the $AF$ curves of the CFA particles. It is immediately clear that at $T = 243 \text{ K}$ the onsets of the $AF$ curves ($S_w \approx 1$) of the unprocessed and processed samples cannot be differentiated and are similar within our experimental uncertainty. At $T = 243 \text{ K}$ the $AF < 10^{-2}$ is the background noise and does not signify ice crystals or water drop formation. Similar to the OA samples, the $AF$ of CFA does not indicate any heterogeneous freezing below water saturation at 243 K, making it unlikely to occur at warmer temperatures as well. The dry-generated unprocessed CFA particles have a similar ice nucleation onset and reach a higher maximum $AF \approx 0.1$ compared to the wet-generated particles ($AF \approx 4 \times 10^{-2}$). As explained in the case of OA, we cannot distinguish between ice crystals and liquid water above the WDS line, which in the case of CFA is calculated for the 2 µm OPC size bin. However, when comparing the CFA results at 243 K using the 4 µm OPC channel data (see Figure D.1a) with measurements of AN (see Figure E.1a), it becomes evident that the activation onset for the CFA takes place at lower humidities ($S_w \approx 1$) below the corresponding WDS line observed for AN ($S_w \approx 1.04$). In other words, at $S_w = 1$, water droplets cannot grow into the 4 µm OPC size bin, confirming that the $AF$ signal observed in the 4 µm data shown in Figure D.1
results from ice formation on the CFA and not from cloud droplet activation. Thus, ice crystals would also
be detected in the 2 µm OPC size bin shown in Figure 7. Overall, we interpret that in the MPC regime both
the dry- and wet-generated CFA particles formed ice heterogeneously via immersion freezing at/or slightly
above water saturation. Further, we did not detect differences between wet-and dry-generated CFA particles
regarding the ice nucleation onset. However, the unprocessed dry-generated CFA particles reach a higher
maximum AF compared to the wet-generated particles. This is in agreement with the results of Grawe
et al. (2018), who tested the ice nucleation ability of this CFA at \( T = 241\text{–}238 \) K. They reported a decrease in
the immersion freezing efficiency of wet-generated CFA particles compared to the dry-generated particles
(ice nucleation active surface site density decreased from \( 10^7 \) to \( 10^4 \) cm\(^{-2}\)).

Grawe et al. (2018) and Losey et al. (2018) proposed that the decrease in ice nucleation ability upon wet-gen-
eration compared to a dry-generation results from a change in the chemical properties of the CFA particles.
Specifically, Grawe et al. (2018) reported that the immersion freezing of some of the unprocessed CFA
samples (containing a mass percentage of CaO of 26%) correlated with the Ca and S content of the CFA
particles, which results from the anhydrite calcium sulfate (Ca(SO\(_4\)) on the CFA particle surface (Havlíček et al., 1993). In their study, Grawe et al. (2018) showed that dry-generated Ca(SO\(_4\)) (anhydrite) particles
are more active INPs than the hydrated wet-generated Ca(SO\(_4\)) \( \cdot 2\) H\(_2\)O (gypsum) particles in the im-
merison freezing mode. They attributed the decrease in INP activity to Ca(SO\(_4\)) becoming hydrated in the

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**Figure 7.** AF curves of the unprocessed dry- and wet-generated polydisperse CFA particles in the MPC (a) and cirrus
cloud regime (b, c, and d) with the corresponding temperatures (2 µm OPC bin, aerosol corrected). The value in
brackets for each data point refers to the number of conducted experiments for each aerosol proxy in the corresponding
cloud processing scenario. Blue-dashed line panel (a): water droplet survival condition explained in Figure 3 with
the corresponding uncertainty range in blue-shaded regions. Black-dashed lines: homogeneous freezing conditions
of solution droplets according to Koop et al. (2000). Gray-shaded regions: calculated \( S_w \) variation across the aerosol-
lamina that particles are exposed to in HINC_IN for the given homogeneous freezing conditions. Error bars are shown
for every fifth data point for clarity, and represent uncertainties in \( S_w \) in HINC_IN, for an aerosol to sheath flow ratio
of 1:10. The starting \( S_i \) of the RH-scans for each \( T \) was always set to \( \sim 1 \), which differs in \( S_w \) for \( T = 228\text{–}218 \) K. MPC,
mixed-phase clouds; CFA, coal fly ash; OPC, optical particle counter; HINC, horizontal ice nucleation chambers.
wet-generated sample, implying that active sites were associated with the anhydrite. Hence, we hypothesize that the same mechanism is true for the observed decrease in ice nucleation activity of our wet-generated particles in the cirrus regime since we used the same CFA sample. A similar decrease in immersion mode ice nucleation activity of acid-treated CFA samples reported by Losey et al. (2018) was attributed to the production of gypsum on the particle surface.

The AF at low $T = 228–218$ K are shown in Figures 7b–7d. The dry-generated unprocessed CFA particles showed strong heterogeneous ice nucleation activity at all investigated cirrus temperatures, as is evident from the low relative humidities required for ice formation around $S_w = 0.66–0.74$. The wet-generated CFA particles reveal a significantly weaker ice nucleation ability compared to the dry-generated unprocessed and processed particles. For instance, at 218 K and $S_w = 0.8$ ($AF = 10^{-3}$) the AF is around two orders of magnitudes higher for the unprocessed dry, compared to the wet-generated CFA particles ($AF = 10^{-5}$). We interpret the sharp, almost step-like onset of the AF curves for the dry-generated CFA particles as an ice nucleation event resulting from the PCF mechanism. This is also consistent with recent results of Umo et al. (2019), who showed that CFA can form ice via PCF at $T < HTT$. Additionally, a clear distinction is visible for all cirrus temperatures investigated here, suggesting an intrinsic difference in ice nucleation ability depending on dry- or wet-generation of the CFA particles.

3.4. Impact of Cloud Processing on the Ice Nucleation Ability of CFA

Based on these initial experiments, we decided to use the dry-generation method (see Section 2.2.2) for the CFA cloud processing experiments to test if a change in ice nucleation activity observed between the different aerosol generation methods can also result from cloud processing of these particles. In contrast to the OA particle types, for the CFA we also conducted a MPC processing scenario (see Figure 1), which is more similar to the wet-generation. The results of the CC and MPC processed CFA particles are also shown in Figure 7 and reveal slightly higher onset $S_w$ compared to the wet-generated unprocessed particles. However, the AF of the CC and MPC processed particles exhibit a steeper increase with humidity. Additionally, both types of cloud processed particles reach the highest maximum AF at 218–228 K, while at 243 K the maximum AF is as high as the dry- and wet-generated unprocessed CFA particles. Clearly, at $S_w < S_{hom}$ cloud processing decreased the heterogeneous ice nucleation potential of the CFA particles, as shown by the significantly lower AF of both the CC and MPC processed samples compared to the dry-generated unprocessed particles ($T = 228–218$ K). Given the AF of the wet-generated CFA particles is one to two orders of magnitudes lower than the AF of the MPC processed particles, we conclude that cloud processing has a different impact on the ice nucleation ability compared to generating the CFA from an aqueous suspension. In other words, wet suspension is not a proxy for cloud droplet processing, at least for the CFA particles investigated here. At the same time, these results highlight that great care must be taken when comparing the ice nucleation activity of an aerosol sample when using different particle generation methods.

The absence of ice nucleation below water saturation at $T = 243$ K for the cloud processed CFA samples, seems to be in conflict with the temperature-cycling measurements of Umo et al. (2019), who report an ice nucleation activity of CFA particles as warm as 263 K for the first time after they had been temperature-cycled to $T = 228$ K. Umo et al. (2019) concluded that a few temperature-cycled CFA particle types can contain ice-filled pores that cause the improved ice formation through preactivation. This correlates with the amount of anhydrite that the CFA particle types contain. The particles with a smaller amount of anhydrite (< 40 wt%) do not show improved ice nucleation activity (Umo et al., 2019). As we observe a lower INP potential of the cloud processed CFA particles compared to the dry-generated unprocessed particles, we cannot confirm any preactivation effect occurring on the cloud processed CFA sample. In line with the decrease in ice nucleation of CFA to result from a change in particle chemistry, we attributed the hydration of calcium sulfate to cause the decrease in active sites and thus, a decrease in the heterogeneous ice nucleation potential. We, therefore, observed a possible change in the CFA particle morphology upon cloud processing so that the chemical surface properties of CFA have been altered in the same way as it is observed for wet-generated particles, but to a lesser degree, given the smaller water volume and time scale of the droplets in the cloud processing experiments.
3.5. Atmospheric Implications

OA particles are ubiquitous in the atmosphere, comprising about 20–80% of the mass of submicron particulate matter, depending on the location (Hodzic et al., 2020; Jimenez et al., 2009; Kanakidou et al., 2005). Given that aerosols particles are on average cycled through multiple clouds during their atmospheric lifetime (Pruppacher & Jaenicke, 1995), a change in their INP potential upon processing at low temperatures, similar to the CC processing studied here, could have a considerable impact on subsequent CC formation. The temperature and humidity conditions investigated here occur at high altitudes in the upper troposphere (Wallace & Hobbs, 2006; P; Wang, 2013) and these heights can be reached in the mid-latitude (Hodzic et al., 2020) or close to the equator in the so-called tropical tropopause layer (TTL). Convection over land can transport aerosol particles directly into the TTL where these particles can contribute to ice nucleation. The cloud processing scenarios presented in this work are representative of most trajectories experienced by surface emitted aerosol particles which are transported to the mid to upper troposphere, typically through trajectories which involve formation of liquid droplets or ice crystals via the liquid phase (Wiacek et al., 2010). In fact, Wiacek et al. (2010) reported only very few trajectories where no cloud formation was encountered for aerosol particles reaching the upper troposphere. A significant number of trajectories reached cirrus-forming regions after processing in MPCs (Wiacek et al., 2010). Previous studies have demonstrated that OA is abundant in the upper troposphere (Froyd et al., 2009; Hodzic et al., 2020). If their viscosity is sufficiently increased during cold cloud processing, the processed particles can nucleate ice heterogeneously (Shiraiwa et al., 2017). Heterogeneous ice nucleation on INPs can then compete with homogeneous freezing and impact cirrus properties (DeMott et al., 1997). In fact, Baustian et al. (2013) found OA to be glassy more than 60% of the time in the mid-latitudes upper troposphere and 40% of the time in the TTL.

CFA particles are less abundant than OA in the troposphere. Nevertheless, the emission rates of 30 Tga⁻¹ CFA are not negligible (Smil, 2008). This is only two orders of magnitudes lower than the mineral dust annual emission between 1.6 and 1.96 × 10⁹ Tga⁻¹ with an atmospheric burden of ~20 Tg (Textor et al., 2006), which is regarded as the globally most important INP type (DeMott et al., 2010). The unprocessed CFA particles have ice nucleation activities at cirrus conditions that are comparable to mineral dust. For example, Welti et al. (2009) reported various dust particles including montmorillonite, kaolinite, illite and Arizona Test Dust to have ice nucleation onsets around $S_i = 1.05$–1.20 for $T = 218$–233 K for 200–800 nm particles, which is slightly lower compared the range of the CFA particles studied here (having onsets of $S_i = 1.15$–1.22 at $T = 218$–228 K). Considering these results, dry-generated CFA particles would be expected to compete with homogeneous freezing of solution droplets in regions influenced by CFA (anthropogenic emissions) rather than natural emissions of dust (Spichtinger & Cziczo, 2010). However, we show that both cloud processing scenarios, which are expected to be experienced by a vast number of aerosol trajectories (Wiacek et al., 2010), decreased the ice nucleation activity of the CFA particles investigated here. This highlights the need to know the atmospheric trajectory of INPs to predict their impact on cloud formation in models.

4. Summary and Conclusion

In this study, the impact of cloud processing on the ice nucleation ability of OA (raffinose, and levoglucosan) and CFA is presented. Ice nucleation experiments at CC ($T < 233$ K) and MPC (243 K) temperatures were performed on polydisperse CFA and on $d_m = 200$ nm size-selected OA. The cloud processing and ice nucleation was achieved using a laboratory setup where two HINCs are coupled in series (Mahrt et al., 2020). We determined the ice nucleation activity in terms of the $AF$ as a function of $S_a$ in the range of approximately 0.65–1.05 ($S_i \approx 1.00$–1.80), as determined by RH-scans in HINC_IN. The processing scenarios covered here include CC ($T = 228$ K at $S_w = 1.04$) and MPC ($T = 243$ K at $S_w = 1.08$) cycles.

Unprocessed OA particles nucleated ice at or above homogeneous freezing conditions. Heterogeneous ice nucleation of the CC processed OA particles at 228–223 K was not observed except in the case of the CC processed raffinose particles at 218 K. At 218 K a significant increase in $AF$ was observed for $0.68 \leq S_a \leq 0.82$. At these conditions raffinose is highly viscous (glassy) allowing these particles to act as deposition INP. The viscous state provides a better surface for deposition nucleation to take place. In contrast, CC processed levoglucosan, did not exhibit deposition nucleation owing to the lower glass transition temperature and
humidity compared to raffinose. Furthermore, particle size measurements did not show any increase of the raffinose particles after CC processing, suggesting the absence of highly porous OA formation as has been reported before through freeze-drying of natural organic matter (Adler et al., 2013). This further supports our interpretation that the enhancement in the case of raffinose results from a change in particle phase state.

We also showed that dry- and wet-generated CFA particles are both active INPs, but differ significantly in their potential to form ice. At \( T = 228-218 \) K and \( S_w < S_{\text{hom}} \), the dry-generated particles reached AF values that were a factor 100 larger than the wet-generated CFA particles. A similar decrease in ice nucleation activity upon wet-generation was observed by Gravé et al. (2018), when testing the immersion freezing activity of CFA at \( T < 241 \) K. Our results demonstrate that the observations by Gravé et al. (2018) are also valid at the lower cirrus temperatures studied here (\( T = 228-218 \) K). For \( S_i < S_{\text{hom}} \), all the CFA treatments indicate that ice formation via PCF is the likely ice nucleation pathway, confirming recent results by Umo et al. (2019). The CFA CC and MPC processing measurements had an altered ice nucleation activity compared to the dry- and wet-generated CFA particles by showing a factor of 10–100 higher AF at all cirrus temperatures compared to the wet-generated unprocessed CFA particles. However, their ability to act as INP was lower by two orders of magnitude compared to the dry-generated particles. This implies that a wet-generation of aerosols in laboratory studies, cannot necessarily be used to mimic cloud processing in liquid droplets, at least for the CFA particles studied here. Using wet-generation as a proxy for cloud processing should therefore carefully be considered for future studies with other aerosol types.

Overall, cloud processing leads to an altered INP potential in the case of OA and CFA particles, but with different general outcomes. In the case of OA, cloud processing may turn particles from aqueous to a very viscous, solid-like glassy state promoting deposition ice nucleation. In the case of cloud processing CFA particles, the particle surface was likely altered by changing the chemical properties of the CFA samples from anhydrite to hydrated calcium sulfate, which in turn led to a different ice nucleation ability. Finally, we note that pathways presented here are not exhaustive, but represent relevant trajectories that could be encountered by aerosol particles during transport in the atmosphere.

Appendix:

A. Humidity Calculations in CATZ

The specific \( S_i \) in CATZ (\( S_{i,CATZ} \)) for a given \( T \) in HINC_CP and CATZ (here \( T_{\text{HINC_CP}} = 228 \) K and \( T_{\text{CATZ}} = 233 \) K) was calculated according to:

\[
S_{i,CATZ}(T_{\text{CATZ}}) = \left( \frac{e_{\text{sat},i}(T_w) + e_{\text{sat},i}(T_c)}{2} \right) \frac{e_{\text{sat},i}(T_{\text{CATZ}})}{e_{\text{sat},i}(T_{\text{CATZ}})},
\]

(A.1)

where:

\( T_w = 237.1 \) K (warm wall temperature in HINC_CP)
\( T_c = 218.8 \) K (cold wall temperature in HINC_CP)
\( e_{\text{sat},i}(T_w) = 20.04 \) Pa (equilibrium vapor pressure with respect to ice at warm wall temperature)
\( e_{\text{sat},i}(T_c) = 2.31 \) Pa (equilibrium vapor pressure with respect to ice at cold wall temperature)
\( e_{\text{sat},i}(T_{\text{CATZ}}) = 18.62 \) Pa (average vapor pressure with respect to ice entering CATZ)

Evaluation of Equation A.1 results in \( S_{i,CATZ}(233 \) K) = 0.6 \( S_{i,CATZ}(233 \) K) ≈ 0.39 for the CC processing scenario and \( S_{i,CATZ}(253 \) K) ≈ 0.42 \( S_{i,CATZ}(253 \) K) ≈ 0.27 for the MPC scenario. The values for the saturation vapor pressure at each \( T \) were calculated according to Murphy & Koop (2005).
B. Parameterizations for Glass Transition, Freezing, and Melting Temperatures

The glass transition temperature at a specific solute weight fraction, \( T_g(w_2) \), can be expressed according to the Gordon-Taylor equation (Gordon & Taylor, 1953):

\[
T_g(w_2) = \frac{w_1 \cdot T_{g1} + \frac{1}{k} \cdot w_2 \cdot T_{g2}}{w_1 + \frac{1}{k} \cdot w_2}
\]  
(B.1)

where:

\( w_1 = \) weight fraction of water
\( w_2 = \) weight fraction of solute
\( k = \) constant of Gordon-Taylor equation (listed in Table B1)
\( T_{g1} = 136 \) K (glass transition temperature of water from Kohl et al. (2005))
\( T_{g2} = \) glass transition temperature of solute (listed in Table B1)

The water activity \( (a_w) \) can be expressed as a function of the solute weight fraction and temperature as follows:

\[
a_w(w_2, T) = \frac{1 + a \cdot w_2}{1 + b \cdot w_2 + c \cdot w_2^2} + \left( T - T^\Theta \right) \cdot \left( d \cdot w_2 + e \cdot w_2^2 + f \cdot w_2^3 + g \cdot w_2^4 \right)
\]  
(B.2)

where:

\( w_2 = \) weight fraction of solute
\( a, b, c, d, e, f, g = \) fit parameters (listed in Table B.1)
\( T^\Theta = 298.15 \) K
\( T = \) absolute (glass transition) temperature

The freezing and melting temperature curves \( (T_f, T_m) \) shown in Figure 5 are parameterized according to Koop et al. (2000):

\[
a_w(T) = e^{-\frac{210368 + 131.438 T - 3323730}{T - 41729.1 \ln(T)}}
\]  
(B.3)

where:

\( R = 8.314 \) kgm\(^2\)s\(^{-2}\)mol\(^{-1}\)K\(^{-1}\)

### Table B.1

| OA proxy |  |  |  |  |  |  |  |  |
|----------|------------|------------|------------|------------|------------|------------|------------|
|          | a          | b          | c          | d          | e          | f          | g          | T\(_{g2}\) |
| Levoglucosan | \(-0.99918\) | \(-0.90978\) | 0.021448   | \(-0.00045933\) | 0.0035813   | 0.00026549 | \(-0.0033059\) | 283.6      | 5.2        |
| Raffinose  | \(-1\)     | \(-1.0035\) | 0.1206     | 0.0005149  | \(-0.000263\) | 0.002451  | \(-0.002698\) | 395.7      | 5.33       |

*Note: The parameters are taken from Zobrist et al. (2008).*
C. Additional AF Plots – Levoglucosan

Figure C.1. AF curves of unprocessed and cirrus cloud (CC) processed levoglucosan particles ($d_{mm} = 200$ nm) for the temperature range 243–218 K. The value in brackets for each data point refers to the number of conducted experiments for each aerosol proxy in the corresponding cloud processing scenario. The AF is calculated according to Equation 1 using the data of the 1 µm OPC bin. Blue-dashed line panel (a): water droplet survival condition explained in Figure 3 with the corresponding uncertainty range in blue-shaded regions. Black-dashed lines: homogeneous freezing conditions for solution droplets according to Koop et al. (2000). Gray-shaded regions: calculated $S_w$ variation across the aerosol-lamina that particles are exposed to in HINC_IN for the given homogeneous freezing conditions. Error bars are shown for every fifth data point only for clarity, and represent uncertainties in $S_w$ in HINC_IN, for an aerosol to sheath flow ratio of 1:10. The starting $S_i$ of the RH-scans for each $T$ was always set to 1, which differs in $S_i$ for $T = 228–218$ K.
D. Additional AF Plots – Coal Fly Ash

Figure D.1. AF curves of the unprocessed dry and wet-generated polydisperse (50–600 nm) CFA particles in the MPC (a) and cirrus cloud regime (b, c, and d) with the corresponding temperatures (4 µm OPC bin, aerosol corrected). The value in brackets for each data point refers to the number of conducted experiments for each aerosol proxy in the corresponding cloud processing scenario. Blue-dashed line panel (a): water droplet survival condition explained in Figure 3 with the corresponding uncertainty range in blue-shaded regions and calculated for the 4 µm OPC bin. Black-dashed lines: homogeneous freezing conditions for solution droplets according to Koop et al. (2000). Gray-shaded regions: calculated $S_w$ variation across the aerosol-lamina that particles are exposed to in HINC_IN for the given homogeneous freezing conditions. Error bars are shown for every fifth data point only for clarity, and represent uncertainties in $S_w$ in HINC_IN, for an aerosol to sheath flow ratio of 1:10. The starting $S_i$ of the RH-scans for each $T$ was always set to 1, which differs in $S_w$ for $T = 228$-$218$ K.
E. Additional AF Plots - Ammonium Nitrate

![AF curves of unprocessed (d_m = 200 nm) ammonium nitrate (AN) particles in the MPC (a) and cirrus cloud regime (b, c and d) with the corresponding temperatures shown for the 1 µm and 4 µm OPC bin. The value in brackets for each data point refers to the number of conducted experiments for each aerosol proxy in the corresponding cloud processing scenario. Here, the blue dashed line represents the WDS line for the 1 µm and the green dashed line the WDS line for the 4 µm OPC bin with the corresponding uncertainty range in blue- or green shaded regions, respectively. Black-dashed lines: homogeneous freezing conditions for solution droplets according to Koop et al. (2000). Gray-shaded regions: calculated \( S_w \) variation across the aerosol-lamina that particles are exposed to in HINC_IN for the given homogeneous freezing conditions. Error bars are shown for every fifth data point only for clarity, and represent uncertainties in \( S_w \) in HINC_IN, for an aerosol to sheath flow ratio of 1:10. The starting \( S_i \) of the RH-scans for each \( T \) was always set to 1, which differs in \( S_w \) for \( T = 228–218 \) K.](image)

**Figure E.1.** AF curves of unprocessed \((d_m = 200 \text{ nm})\) ammonium nitrate (AN) particles in the MPC (a) and cirrus cloud regime (b, c and d) with the corresponding temperatures shown for the 1 µm and 4 µm OPC bin. The value in brackets for each data point refers to the number of conducted experiments for each aerosol proxy in the corresponding cloud processing scenario. Here, the blue dashed line represents the WDS line for the 1 µm and the green dashed line the WDS line for the 4 µm OPC bin with the corresponding uncertainty range in blue- or green shaded regions, respectively. Black-dashed lines: homogeneous freezing conditions for solution droplets according to Koop et al. (2000). Gray-shaded regions: calculated \( S_w \) variation across the aerosol-lamina that particles are exposed to in HINC_IN for the given homogeneous freezing conditions. Error bars are shown for every fifth data point only for clarity, and represent uncertainties in \( S_w \) in HINC_IN, for an aerosol to sheath flow ratio of 1:10. The starting \( S_i \) of the RH-scans for each \( T \) was always set to 1, which differs in \( S_w \) for \( T = 228–218 \) K.

Conflict of Interest
The authors declare no conflicts of interest relevant to this study.

Data Availability Statement
Data supporting the results are available in the appendix. Data used in this work are available at the following DOI: [https://doi.org/10.3929/ethz-b-000421826](https://doi.org/10.3929/ethz-b-000421826).
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References

Adler, G., Koop, T., Haspel, C., Taraniku, I., Moise, T., Koren, I., et al. (2013). Formation of highly porous aerosol particles by atmospheric freeze-drying in ice clouds. *Proceedings of the National Academy of Sciences*, 110(51), 20414–20419. https://doi.org/10.1073/pnas.1317209110

Aiken, A. C., De Foy, B., Wiedinmyer, C., Decarlo, P. F., Ulbrich, I. M., Wehrl, M. N., et al. (2010). Mexico city aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0); Part 2: Analysis of the biomass burning contribution and the non-fossil carbon fraction. *Atmospheric Chemistry and Physics*, 10, 5315–5341. https://doi.org/10.5194/acp-10-5315-2010

Archuleta, C. M., DeMott, P. J., & Kreidenweis, S. M. (2005). Ice nucleation by surrogates for atmospheric mineral dust and mineral dust/sulfate particles at cirrus temperatures. *Atmospheric Chemistry and Physics*, 5, 2617–2634. https://doi.org/10.5194/acp-5-2617-2005

Baustian, K. J., Wise, M. E., Jensen, E. J., Schill, G. P., Freedman, M. A., & Tollbert, M. A. (2013). State transformations and ice nucleation in amorphous (semi-solid) organic aerosol. *Atmospheric Chemistry and Physics*, 13(11), 5615–5628. https://doi.org/10.5194/acp-13-5615-2013

Berkemeier, T., Shiraiwa, M., Pischl, U., & Koop, T. (2014). Competition between water uptake and ice nucleation by glassy organic aerosol particles. *Atmospheric Chemistry and Physics*, 14(22), 12513–12511. https://doi.org/10.5194/acp-14-12513-2014

Boucher, O., Randall, D., Artaxo, P., Bretherton, C., Feingold, G., Forster, P., & others (2013). Clouds and aerosols. In *Climate change 2013: The physical science basis. contribution of working group i to the fifth assessment report of the intergovernmental panel on climate change* (pp. 571–657). Cambridge University Press. https://doi.org/10.1017/CBO9781107413528.016

Cappa, C., & Abbatt, J. P. (2010). Ice nucleation onto Arizona test dust at cirrus temperatures: Effect of temperature and aerosol size on heterogeneous nucleation of ice on surrogates of mineral dust. *Proceedings of the National Academy of Sciences*, 105(48), 18687–18691. https://doi.org/10.1073/pnas.0802144105

Christenson, H. K. (2013). Two-step crystal nucleation via capillary condensation. *Cryogenics*, 53, 2030–2039. https://doi.org/10.1016/j.cryogenics.2013.06.007

DeMott, P. J., Prenni, A. J., Liu, X., Kreidenweis, S. M., Petters, M. D., Twohy, C. H., et al. (2010). Predicting global atmospheric ice nucleation distributions and their impacts on climate. *Proceedings of the National Academy of Sciences*, 107(25), 11217–11222. https://doi.org/10.1073/pnas.0910818107

DeMott, P. J., Rogers, D. C., & Kreidenweis, S. M. (1997). The susceptibility of ice formation in upper tropospheric clouds to insoluble aerosol components. *Journal of Geophysical Research*, 102, 19575–19584. https://doi.org/10.1029/97JD01138

Floyd, K. D., Murphy, D. M., Sanford, T. J., Thomson, D. S., Wilson, J. C., Pfister, L., & Lait, L. (2009). Aerosol composition of the tropical upper troposphere. *Atmospheric Chemistry and Physics*, 9, 4363–4385. https://doi.org/10.5194/acp-9-4363-2009

Glatz, B., & Sarupria, S. (2018). Heterogeneous ice nucleation: Interplay of surface properties and their impact on water orientations. *Langmuir*, 34(3), 1190–1198. https://doi.org/10.1021/acs.langmuir.7b02859

Gordon, M., & Taylor, J. S. (1953). Ideal copolymers and the second-order transitions of synthetic rubbers. I. Noncrystalline copolymers. *Rubber Chemistry and Technology*, 26, 323–335. https://doi.org/10.5255/1.3539818

Grawe, S., Augustin-Bauditz, S., Clemen, H. C., Ebert, M., Eriksen Hammer, S., Lubitz, J., et al. (2018). Coal fly ash: Linking immersion freezing behavior and physicochemical particle properties. *Atmospheric Chemistry and Physics*, 18(19), 13903–13923. https://doi.org/10.5194/acp-18-13903-2018.10

Havlíček, D., Pitblad, R., & Škoulov, O. (1993). The chemical and mineralogical composition of the water-soluble fraction of power-plant ash and its effect on the process of crystallization of water. *Atmospheric Environment Part A. General Topics*, 27, 655–660. https://doi.org/10.1016/0960-1686(93)90018-Y

Hodzic, A., Campuzano-Jost, P., Bian, H., Chin, M., Colarco, P. R., Day, D. A., et al. (2020). Characterization of organic aerosol across the global remote troposphere: a comparison of ATom measurements and global chemistry models. *Atmospheric Chemistry and Physics*, 20, 4607–4635. https://doi.org/10.5194/acp-20-4607-2020

Hoose, C., & Möhler, O. (2012). Heterogeneous ice nucleation on atmospheric aerosols: A review of results from laboratory experiments. *Atmospheric Chemistry and Physics*, 12, 9817–9854. https://doi.org/10.5194/acp-12-9817-2012

Ignatius, K., Kristensen, T. B., Järvinen, E., Nichman, L., Fuchs, C., Gordon, H., et al. (2016). Heterogeneous ice nucleation of viscous secondary organic aerosol produced from ozonolysis of α-pinene. *Atmospheric Chemistry and Physics*, 16(10), 6495–6509. https://doi.org/10.5194/acp-16-6495-2016

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., et al. (2009). Evolution of organic aerosols in the atmosphere. *Science*, 326(5959), 1525–1529. https://doi.org/10.1126/science.1180353

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., et al. (2005). Organic aerosol and global climate modelling: A review. *Atmospheric Chemistry and Physics*, 5, 1053–1123. https://doi.org/10.5194/acp-5-1053-2005

Kanji, Z. A., & Abbott, J. P. (2010). Ice nucleation onto Arizona test dust at cirrus temperatures: Effect of temperature and aerosol size on onset relative humidity. *Journal of Physical Chemistry A*, 114, 935–941. https://doi.org/10.1021/jp908661m

Kanji, Z. A., Ladino, L. A., Wex, H., Boone, Y., Burkert-Kohm, M., Caizico, D. J., & Krämer, M. (2017). Overview of ice nucleating particles. *Atmospheric Chemistry and Physics Monographs*, 18, 1. https://doi.org/10.1017/AMSPHMONOGRAPHS-D-16-0006.1

Knopf, D. A., Alpert, P. A., & Wang, B. (2018). The role of organic aerosol in atmospheric ice nucleation: A review. *ACS Earth and Space Chemistry*, 2(3), 168–202. https://doi.org/10.1021/acsearthspacechem.7b00120

Knopf, D. A., & Koop, T. (2006). Heterogeneous nucleation of ice on surrogates of mineral dust. *Journal of Geophysical Research*, 111(D12). https://doi.org/10.1029/2005JD006094

Kohl, I., Bachmann, L., Hallbrucker, A., Mayer, E., & Loerting, T. (2005). Liquid-like relaxation in hyperquenched water at 140 K. *Physical Chemistry Chemical Physics*, 7, 3210–3220. https://doi.org/10.1039/b507651j

Koop, T., Bozköidel, J., Shiraiwa, M., & Pischl, U. (2011). Glass transition and phase state of organic compounds: Dependence on molecular properties and implications for secondary organic aerosols in the atmosphere. *Physical Chemistry Chemical Physics*, 13, 19238–19255. https://doi.org/10.1039/c3cp22817g
Koop, T., Luo, B., Tuia, A., & Peter, T. (2000). Water activity as the determinant for homogeneous ice nucleation in aqueous solutions. Nature, 406, 611–614.

Kreidenweis, S. M., Petters, M., & Lohmann, U. (2019). 100 years of progress in cloud physics, aerosols, and aerosol chemistry research. Atmospheric Chemistry and Physics, 19, 119–125. https://doi.org/10.5194/acp-19-8783-2019

Lohmann, U. (2015). Aerosols: Aerosol-cloud interactions and their radiative forcing. In G. R. North, J. Pyle, & F. Zhang (Eds.), Encyclopedia of atmospheric sciences (2nd ed., pp. 17–22). Academic Press. https://doi.org/10.1016/B978-0-12-382225-3.00052-9

Pruppacher, H. R., & Jaenicke, R. (1995). The processing of water vapor and aerosols by atmospheric clouds, a global estimate. Atmospheric Environment, 29(23), 173–182. https://doi.org/10.1016/1352-2310(95)00035-3

Mahrt, F., Marcolli, C., 119. https://doi.org/10.1038/nature09455

Simoneit, B., Schauer, J., Nolte, C., Oros, D., Elias, V., Fraser, M., et al. (1999). Levoglucosan, a tracer for cellulose in biomass burning and organic aerosol particles. Atmospheric Chemistry and Physics, 9(24), 9491–9522. https://doi.org/10.5194/acp-9-9491-2009

Spichtinger, P., & Cziczo, D. J. (2010). Impact of heterogeneous ice nuclei on homogeneous freezing events in cirrus clouds. Journal of Geophysical Research, 115(D14). https://doi.org/10.1029/2009JD012168

Textor, C., Schulz, M., Guibert, S., Kinne, S., Balkanski, Y., Bauer, S., et al. (2006). Analysis and quantification of the diversities of aerosol scales. Environmental Science: Processes and Impacts, 9, 1581–1592. https://doi.org/10.1039/c6em00319j

Virtanen, A., Joutsensaari, J., Koop, T., Kannosto, J., Yli-Pirilä, P., Leskinen, J., et al. (2010). An amorphous solid state of biogenic secondary organic aerosol particles. Nature, 467, 824–827. https://doi.org/10.1038/nature09455

Wagner, R., Kiselev, A., Möhler, O., Saathoff, H., Weidler, P. G., et al. (2019). Enhanced ice nucleation activity of coal fly ash aerosol particles initiated by ice-filled pores. Atmospheric Chemistry and Physics, 19(13), 7883–8000. https://doi.org/10.5194/acp-19-7883-2019

Vali, G., DeMott, P. J., Möhler, O., & Whale, T. F. (2015). Technical note: A proposal for ice nucleation terminology. Atmospheric Chemistry and Physics, 15, 10263–10270. https://doi.org/10.5194/acp-15-10263-2015

Wagner, R., Kiselev, A., Möhler, O., Saathoff, H., & Steinke, I. (2016). Pre-activation of ice-nucleating particles by the pore condensation and freezing mechanism. Atmospheric Chemistry and Physics, 16(4), 2025–2042. https://doi.org/10.5194/acp-16-2025-2016
