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The immersion freezing behavior of ash particles from wood and brown coal burning

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Abstract.

It is generally known that ash particles from coal combustion can trigger ice nucleation. However, data on the ice nucleation of ash particles from different sources, including both anthropogenic and natural combustion processes, is still scarce. As coal combustion still fuels the biggest proportion of electric power production worldwide and biomass burning contributes significantly to the global aerosol loading, further data is needed to better assess the ice nucleating efficiency of ash particles. In the framework of this study, we found that ash particles from brown coal (i.e., lignite) burning are more ice active than those from wood burning, with fly ash from a coal-fired power-plant being the most efficient at nucleating ice. Furthermore the effect of particle generation on the freezing behavior was studied. For this, particles were generated either by dispersion of dry sample material, or by atomization of ash-water suspensions, and then led into the Leipzig Aerosol Cloud Interaction Simulator (LACIS) where the immersion freezing behavior was examined. Whereas the immersion freezing behavior of ashes from wood burning was not affected by the particle generation method, it depended on the type of particle generation for ash from brown coal. It was also found that the common practice of treating prepared suspensions in an ultrasonic bath to avoid aggregation of particles led to an enhanced ice nucleation activity. The findings of this study suggest a) that ash from brown coal burning may influence heterogeneous ice nucleation on at least a regional scale and b) that the freezing behavior of ash particles may be altered by a change in sample preparation and/or particle generation.

1 Introduction

Gaining a comprehensive knowledge of the formation and behavior of ice particles in clouds is of the utmost importance to achieve a better representation of ice related processes in weather and climate models. Ice particles in clouds can be formed either by primary mechanisms, i.e., homogeneous and heterogeneous ice nucleation (Pruppacher and Klett, 1997), or by secondary mechanisms (e.g., Hallett and Mossop, 1974). In the atmosphere, homogeneous ice nucleation, i.e., the freezing of pure water or solution droplets, takes place at temperatures below -38 °C (Murray et al., 2012). This temperature limit is raised in the presence of so-called ice nucleating particles (INPs) acting as catalysts for ice formation which is then referred to as heterogeneous ice nucleation.

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Combustion aerosol, accounting for a large fraction of the global aerosol loading, has been frequently investigated concerning its freezing behavior. It was discovered that soot (DeMott, 1990; Diehl and Mitra, 1998), metal oxides from furnaces and smelters (Pruppacher and Klett, 1997), lead containing particles (Schäfer, 1975; Cziczo et al., 2009), and aerosol from biomass burning (Petters et al., 2009) are able to act as INPs. However, up to now only very few studies on the freezing behavior of ash particles have been conducted. Ash is defined as the solid material which remains after the combustion of organic substances (e.g., fossil fuels, biofuels, and plant parts). During the combustion process, a fraction of fine ash particles is directly emitted into the atmosphere together with flue gases whereas coarse ash particles mainly remain in the fireplace, boiler, or on the ground after a wildfire and may be lofted by the action of wind (Andreae et al., 2004). The former is termed "fly ash", the latter is referred to as "bottom ash".

The globally increasing electric power demand will continue to be covered by fossil fuels, making power generation by coal combustion grow faster than all renewable energy sources put together (International Energy Agency, 2012). As a result, coal ashes contribute a major proportion of anthropogenic aerosol emissions. Furthermore, ash is produced during biomass burning including wildfires. The impact of ash particles as potential INPs must be put into perspective by comparing with the concentrations of other INP containing aerosols, e.g., mineral dust which is present in the atmosphere in abundance. A rough estimate for fly ash from coal combustion yields global annual emissions of 30 Mt in the year 2000 (Smil, 2008). As there are no further values concerning the amount and distribution of different types of ash in the atmosphere, it is a difficult task to assess their impact on heterogeneous ice nucleation on a larger scale. However, DeMott et al. (2003) give a value of approximately 7 % of residues from cirrus ice particles which were formed under conditions favorable to heterogeneous nucleation to be fly ash particles. This shows that fly ash particles are able to reach high altitudes and can be suspended in the atmosphere for a long time. The large horizontal dispersion of these particles has been shown by Zhang et al. (2011) who found fly ash in surface snow crystal residues at a remote central Asian glacier. Backward air mass trajectories indicated that the particles originated from strongly populated areas to the west of the sampling site and were transported over thousands of kilometers through the high-level westerly jet stream. It must be mentioned that the chemical composition of mineral dust and ash is very similar (Cziczo et al., 2004) which is why DeMott et al. (2003) and Zhang et al. (2011) used the spherical shape of fly ash particles, originating from the combustion process in the furnace (Zhang et al., 2011), as a criterion to distinguish from other particle types.

Already in the 1960s, first presumptions arose that aerosol particles in the plumes of coal-fired power plants might be efficient at nucleating ice, as ice fog (Benson, 1965) and so-called "industrial snow" (Agee, 1971; Parungo et al., 1978b) were observed in close proximity to the stacks. Laboratory studies showed that coal fly ash particles are able to serve as INPs in the deposition (Parungo et al., 1978a; Havlíček et al., 1993) and immersion modes (Havlíček et al., 1989, 1993; Umo et al., 2015). Apart from untreated fly ash samples, Havlíček et al. (1993) also investigated the freezing behavior of the insoluble fraction and found that particles freed from water soluble components initiated freezing at lower temperatures. Additionally, it could be shown that water soluble components were responsible for differences in the ice nucleation ability of fly ash samples from different power plants. In comparison to coal fly ash, bottom ashes from coal and biomass burning have been poorly investigated. Recently, Umo et al. (2015) conducted first experiments on the immersion freezing behavior of bottom ash particles from coal and wood

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burning and compared the results to the ice nucleation ability of coal fly ash. With the help of a cold stage setup (Murray et al., 2010a), it could be shown that bottom ashes nucleate ice in the immersion mode. However, it was found that the fly ash particles are more efficient at nucleating ice than the bottom ash particles in a temperature range from -17 °C to -27 °C. The results for the bottom ashes were all rather consistent with a slight tendency of wood burning bottom ash being the most efficient and coal burning bottom ash being the least efficient at nucleating ice. Umo et al. (2015) assumed that the different fuels, combustion temperatures, compositions, and morphologies are the cause of the difference between bottom ashes and fly ash.

In the present study, the immersion freezing behavior of five different ash samples, similar but not identical to those investigated by Umo et al. (2015), was quantified at the Leipzig Aerosol Cloud Interaction Simulator (LACIS, Hartmann et al., 2011). It was possible to study the influence of particle generation on the measured ice fractions as particles were produced both by dispersion of dry sample material and atomization of ash-water suspensions. Suspensions were prepared according to the method described in Umo et al. (2015), which includes treatment in an ultrasonic bath and subsequent stirring. As similar procedures are often used in the sample preparation for ice nucleation experiments, the effect of ultrasonic treatment of the sample on the immersion freezing behavior was investigated as well.

2 Methods and materials

2.1 Experimental setup

2.1.1 Particle generation and size selection

Airborne ash particles were generated in two different ways: a) dispersion of dry sample material and b) atomization of ash-water suspensions. Airborne particles from dry ash were generated using an aerosol generator consisting of a tilted glass bottle which is connected to an electric imbalance motor. Dry ash particles being situated at the bottom of the bottle become airborne as particle free pressurized air streams into the bottle through a tube. Vibrations caused by the motor and the mounting of the bottle at a certain angle ensure that coarse material, which does not leave the bottle through the outlet at the top and deposits on its walls, is continually transported downwards. The efficiency of the aerosol generator can be enhanced by mixing some millimeter-sized glass beads into the samples which was done for the mostly fine sample material in this study. In addition to this herein called dry particle generation, particles were generated from an ash-water suspension using an atomizer (similar to TSI Model 3076) and a diffusion dryer unit. In the following, this procedure will be referred to as wet particle generation. For both dry and wet particle generation, the aerosol was brought to a bipolar charge equilibrium inside a neutralizer before 300 nm particles were selected by means of a differential mobility analyzer (DMA, Vienna type, medium, Knudson and Whitby, 1975). As for insoluble substances the ice activity depends on the surface area of the INP (Archuleta et al., 2005; Welti et al., 2009; Pinti et al., 2012; Hartmann et al., 2016), larger multiply charged particles which are present in the investigated aerosol are more efficient at nucleating ice. To account for the multiply charged particles, measurements were performed with an Ultra High Sensitivity Aerosol Spectrometer (UHSAS, DMT, Boulder, CO, USA). According to the UHSAS measurements, the number

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of particles with three or more negative charges was negligible, while the doubly charged fractions could be determined and accounted for in the immersion freezing measurements.

2.1.2 LACIS

The previously generated and size selected ash particles were fed into LACIS (Hartmann et al., 2011) to investigate their immersion freezing behavior. In comparison to cold stage methods, where a set of suspension droplets is brought onto a cooled surface, LACIS offers the opportunity to examine airborne droplets so that no surface influences the nucleation process. Furthermore, as water is brought into the system via the gas phase, water contamination which is known to cause the freezing of pure water droplets above the homogeneous freezing limit on cold stages, can be ruled out for our experiments. LACIS consists of seven connected 1 m long tube sections with an inner diameter of 15 mm. The 2 mm wide particle beam, being surrounded by humidified, particle free sheath air, is situated along the center line of the tube. As each of the seven sections can be temperature controlled individually with the help of thermostats, particles pass along defined temperature and saturation profiles. For the measurements presented here, LACIS was operated in a way that each particle was activated to a droplet in the second to last section. Further cooling caused a certain fraction of droplets, hereafter referred to as ice fraction f_{ice}, to freeze. The discrimination between supercooled droplets and ice particles was realized with the help of the Thermo-stabilized Optical Particle Spectrometer for the detection of Ice (TOPS-Ice, Clauß et al., 2013).

2.2 Sample preparation and characterization

Five different kinds of ashes were investigated concerning their immersion freezing behavior:

1. Bottom ashes from wood burning:
   (a) Spruce
   (b) Birch
   (c) Beech
2. Bottom ash from brown coal burning
3. Fly ash from brown coal burning

Bottom ashes from spruce, birch, and beech burning were examined to study the effect of wood type (deciduous vs. coniferous trees) on the freezing behavior of the respective ash particles. It has to be noted that the coal bottom and fly ashes were not produced from brown coal with identical compositions. All bottom ash samples were taken from commercially available domestic heaters after the combustion of the pure substances. The fly ash sample was extracted from the electrostatic precipitators of the Lippendorf power station which is situated 15 km south of Leipzig, Germany, and has a power output of 1840 MW.

Dry samples were placed in the aerosol generator without further preparations. The ash-water suspensions were prepared exactly as described in Umo et al. (2015) with bottom ashes from brown coal and spruce burning, as well as fly ash from

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brown coal burning. For this, a suspension of 0.05 wt% ash in Milli-Q® water was placed in an ultrasonic bath (RK100H Sonorex Super, BANDELIN electronic GmbH & Co. KG, Berlin, Germany) for 10 minutes. According to Umo et al. (2015), this step is necessary to break down ash aggregates. It has already been shown that the size distribution of soil particles in a suspension can be affected by ultrasonic dispersion (Oorts et al., 2005). To see whether a treatment with the ultrasonic bath influences the ice nucleation efficiency of the suspension particles as well, one fly ash suspension sample was prepared without ultrasonic treatment. Afterwards, all samples were stirred for ≈ 24 hours. Additionally to this procedure, part of the brown coal fly ash suspension sample was filtered using syringe filters (200 nm pore size, Millex™, Merck KGaA, Darmstadt, Germany) to remove fly ash particles from the suspension and leave water soluble material only.

Four of the dry samples (all except beech bottom ash) were investigated by means of atomic adsorption methods at ALS Scandinavia AB (Luleå, Sweden). Fig. 1 shows the results of the chemical composition analysis, i.e., the mass fractions of certain oxides (1) and elements (2). The former were obtained by recalculating the measured concentrations of the listed elements into their most common oxide forms. Fly ash from brown coal burning contains more SiO_2 (quartz) than any other sample which corresponds to findings by Umo et al. (2015). Also, bottom ash from brown coal burning includes a slightly higher fraction of SiO_2 than spruce bottom ash and significantly more than birch bottom ash. On the other hand, the wood bottom ashes contain more K_2O than those from coal burning. This is an important point as K in biomass burning ash, in contrast to K in coal ash, is largely water soluble (Andreae et al., 2004) and might influence its ice activity. As for single elements, it is most striking that the brown coal ashes include Hg which cannot be found in the wood ash samples. Suggestions on how these differences might affect the immersion freezing behavior of the different ash types can be found in Sec. 3.

To investigate particle shape and surface properties on a small scale, scanning electron microscope (SEM) images were taken. Exemplarily, bottom and fly ash particles with electrical mobility diameters of $D_{p,el}$ = 300 nm were generated as described in Sec. 2.1.1, collected on Nuclepore™ track-etched membrane polycarbonate filters (Sigma-Aldrich, St. Louis, MO, USA), and pictured by the SEM. Fig. 2 shows images of a) bottom ash and b) fly ash from brown coal burning. It can be seen that bottom ash particles have an irregular shape with sharp edges. In contrast, some fly ash particles are perfectly round and most show significantly less surface defects compared to the bottom ash particles. It is noticeable that there is a considerable fraction of particles in the size range of triply ($D_p \approx 700$ nm) and even quadruply ($D_p \approx 900$ nm) charged particles, although those were not observed in the UHSAS measurements during the ice nucleation experiments in such large fractions. It should be mentioned that care had been taken to set up the sampling lines from the DMA to both LACIS and the UHSAS in such a way that similar particle losses should have occurred. It is unresolved why these large particles are seen on the filter, but filter samples were not taken at the same time as LACIS and UHSAS measurements, as they were only meant to show the particle shape. Also, only a small fraction of the filter surface area was imaged by the SEM and the relations might have been different elsewhere.

Apart from a small number of spherical fly ash particles, the SEM image of brown coal fly ash particles from wet generation (see Fig. 3) shows a majority of particles that appear to be needle shaped crystals. Even though particles with $D_{p,el}$ = 300 nm were selected, the crystals are several microns long. The spherical particles, however, are close to 300 nm. It is reasonable to assume that the crystals consist of water soluble components which exist in the suspension separated from the fly ash particles. Inside the atomizer, droplets are formed which can consist of either only soluble material, or additional fly ash particles. The

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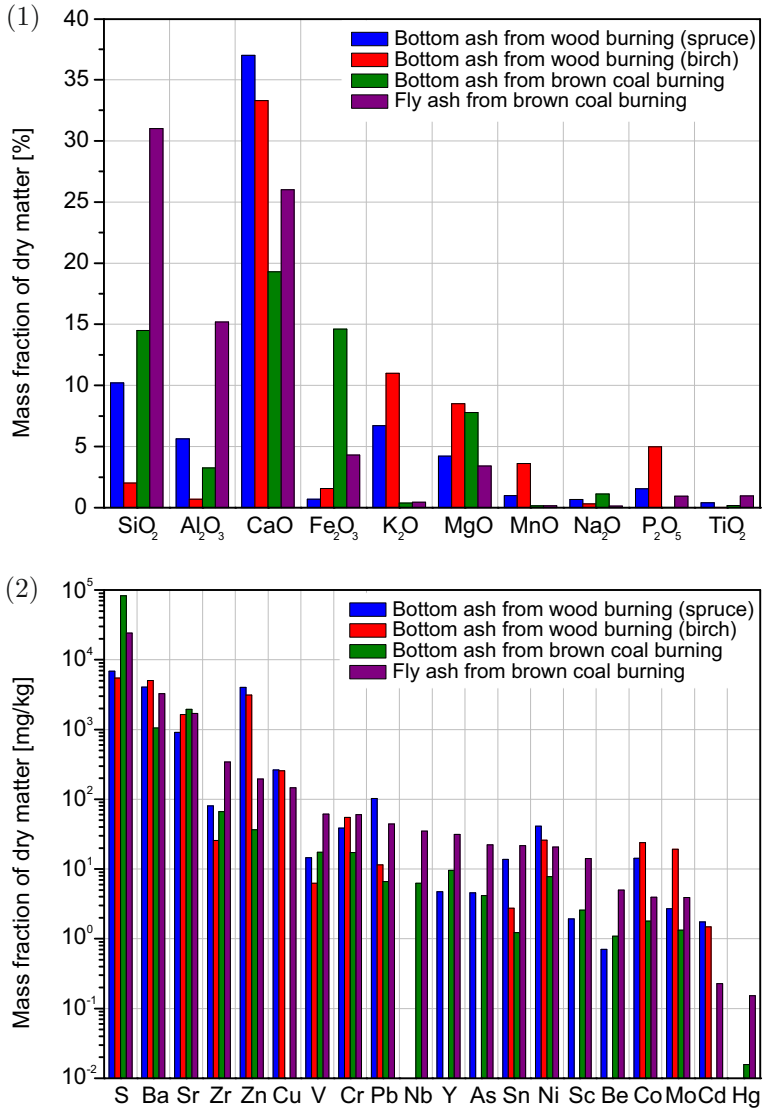

Figure 1. Mass fractions of certain minerals (1) and elements (2) in the dry matter of bottom ashes from spruce, beech and brown coal burning, as well as fly ash from brown coal burning. The analysis was performed by means of atomic adsorption methods at ALS Scandinavia AB (Luleå, Sweden).

subsequent drying process supposedly leads to a crystallization of the soluble components. Obviously, the formation of crystals does not take place in the experiments by Umo et al. (2015) as droplets are directly produced from the suspension. In this case, the components which are present in the crystals are dissolved in the droplets. There are several possible implications from the presence of crystals in the immersion freezing experiments with fly ash suspension particles which will be discussed in Sec. 3. Possibly, $CaCO_3$, which is known to be weakly soluble and form needle shaped crystals (Plummer and Busenberg, 1982), is the

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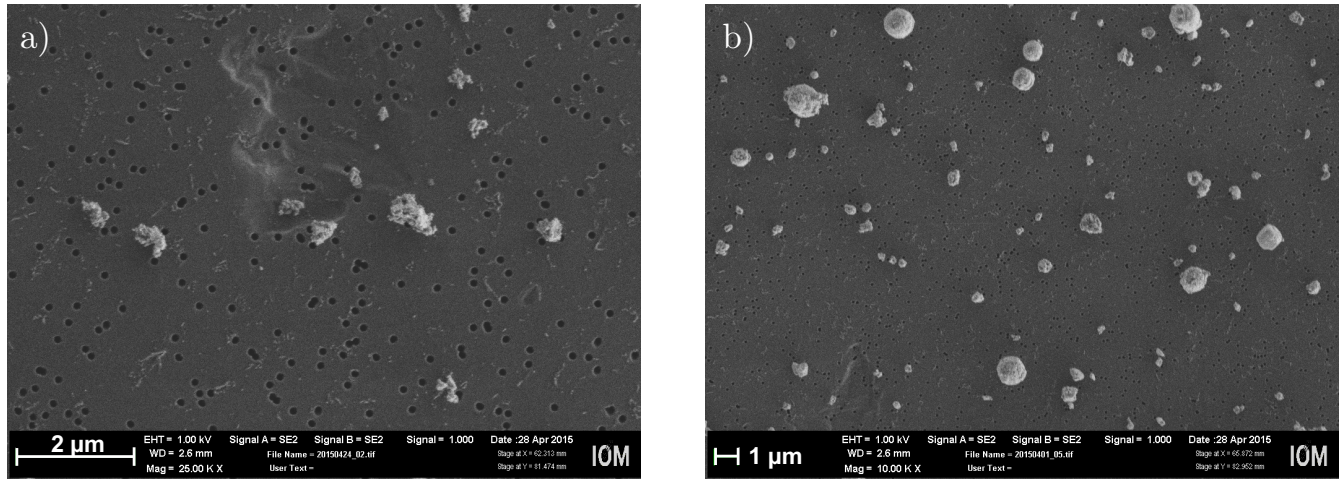

Figure 2. Scanning Electron Microscope (SEM) images of brown coal ash particles from dry generation with $D_{p,el}$ = 300 nm. a) Bottom ash particles, b) fly ash particles. Note the different magnification.

Figure 3. Scanning Electron Microscope (SEM) images of brown coal fly ash particles from wet generation with $D_{p,el}$ = 300 nm. Needle shaped crystals may have formed from water soluble components on fly ash particles in the drying process.

dominant phase of the water soluble fraction. During the combustion process, CaO is produced (present in the initial sample, see Fig. 1) which may react with H_2O to form $Ca(OH)_2$ (see Reac. R1). $CaCO_3$ may form from $Ca(OH)_2$ upon reaction with CO_2 from the air (see Reac. R2).

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad \text{(R1)}$$

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$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad \text{(R2)}$$

The presence of Ca in the needles could be confirmed by investigating filter samples by means of Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM/EDX) spectroscopy. However, there is no definite proof that $CaCO_3$ is the dominant phase of the water soluble fraction of fly ash particles from wet generation. It has to be mentioned that Havlíček et al. (1993) found a majority of $CaSO_4$ in the soluble fractions of most of their investigated fly ash samples. This can be ruled out for the sample from this work as the amount of S was below the detection limit of the EDX on all of the examined filter sections.

A filtered fly ash suspension sample was used to generate size segregated particles which were then also collected and examined under the SEM (not shown here). This was done to assure that the filtering process removed the spherical fly ash particles, which it did almost entirely.

3 Results and discussion

The immersion freezing behavior of the five ash samples was investigated in a temperature range from -24 °C to -40 °C. Fig. 4 shows the obtained f_{ice} for particles from dry (full circles) and wet generation (open circles). Four data sets were obtained for fly ash from brown coal burning which include f_{ice} values of dry particles, suspended particles with ultrasonic treatment (+US), suspended particles without ultrasonic treatment (-US), and the water soluble material remaining in the filtered ash-water suspension (+US, not shown). The data for ash particles from dry generation was multiple charge corrected according to the method presented in Hartmann et al. (2016). A multiple charge correction was not possible for ash from wet particle generation because of the two particle populations (crystals from soluble material and insoluble ash particles) causing overlapping signals in the UHSAS measurements.

Additionally, model calculations of three of the measured data sets (dry fly ash and bottom ash from brown coal burning, suspended fly ash from brown coal burning (+US)) are included in Fig. 4 which are based on the Soccer Ball Model (SBM) as described in Niedermeier et al. (2015). In the SBM, the ice nucleation activity of a sample is described using a contact angle distribution with μ and σ being its mean and standard deviation. The average number of INPs per droplet λ was determined according to Hartmann et al. (2013):

$$\lambda = -\ln(1 - f^*_{ice}). \quad (1)$$

with f^*_{ice} being the ice fraction in the saturation range. The values for λ, as well as μ and σ can be found in Tab. 1. All SMB fit curves are shown as thick lines in the measured temperature range and as thin lines in the extrapolation range.

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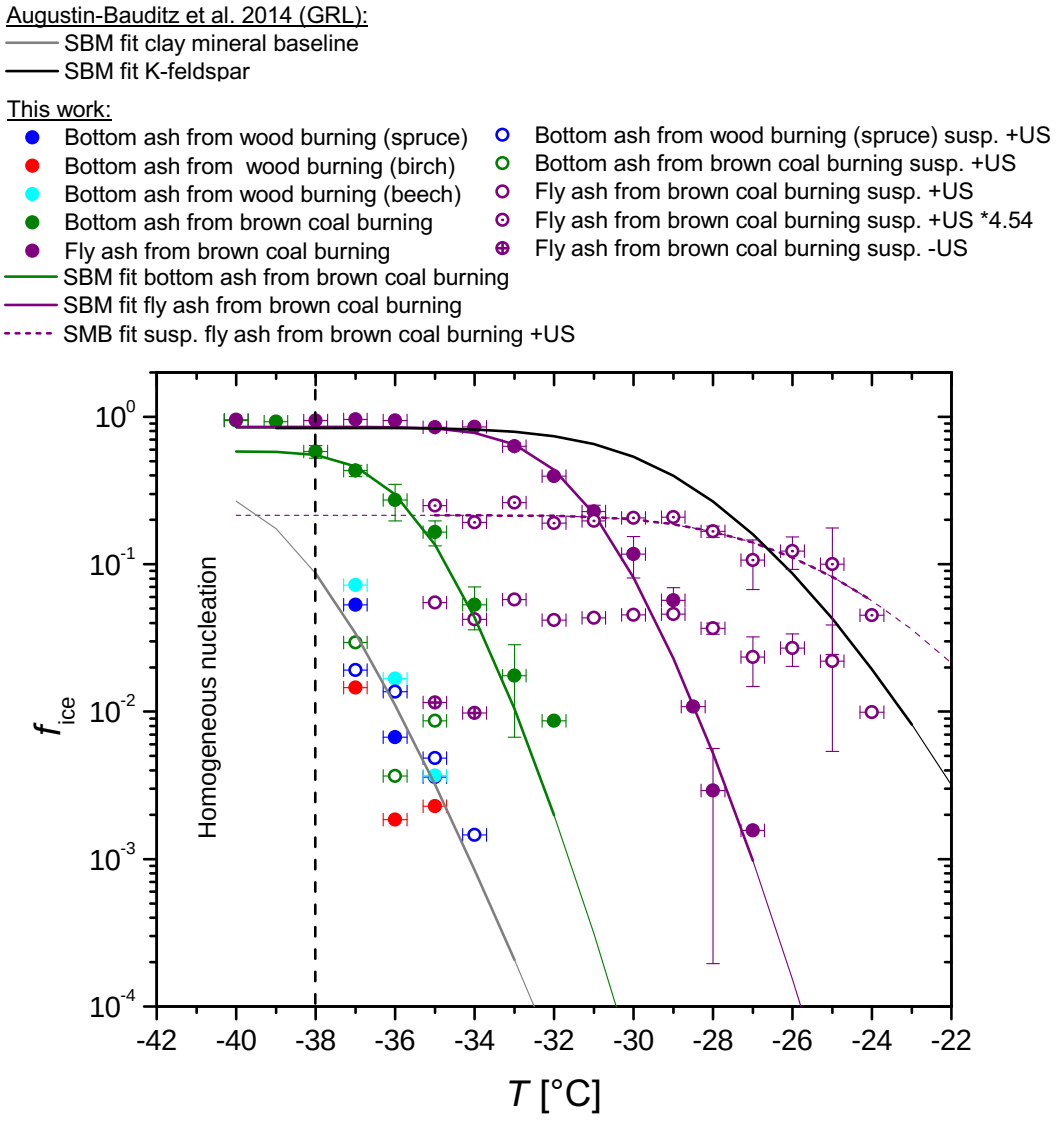

Figure 4. Ice fraction f_{ice} as a function of temperature T for ash particles from dry (full circles) and wet generation (open circles) with $D_{p,el}$ = 300 nm. Error bars represent the LACIS temperature error of 0.3 K and the f_{ice} standard deviation of at least three measurements, respectively. The solid and dashed lines represent the SBM fits to selected samples from this work and to data published in Augustin-Bauditz et al. (2014), all for $D_{p,el}$ = 300 nm. Parameters for the SBM fits are given in Tab. 1.

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Table 1. Parameters for the model calculations based on the SBM. λ is the ice fraction in the saturation range, μ the mean contact angle, and σ the standard deviation of the contact angle distribution.

	λ	μ (rad)	σ (rad)
Augustin-Bauditz et al. (2014)			
Clay Mineral Baseline	0.40	1.82	0.12
Microcline	1.84	1.30	0.10
This work			
Brown Coal Bottom Ash dry	0.87	1.60	0.08
Brown Coal Fly Ash dry	1.91	1.40	0.07
Brown Coal Fly Ash wet (+US) * 4.54	0.24	1.13	0.10

3.1 Dry particle generation

Fig. 4 shows a significant difference between wood ashes and brown coal ashes. The wood ash particles show a low ice activity in a temperature range where effects of homogeneous nucleation can be ruled out. There is a trend of beech bottom ash being the most effective and birch bottom ash being the least effective of the wood ashes. However, the rather similar pattern leads us to the conclusion that the influence of the burned wood type on the immersion freezing behavior of the bottom ash particles is small for the investigated samples. In comparison, bottom and fly ashes from brown coal burning are more effective INPs in the immersion mode. It is apparent that the fly ash particles are more efficient as they start nucleating ice at ≈ -29 °C, whereas we could not detect ice activity for bottom ash particles until ≈ -33 °C.

The chemical composition may influence the immersion freezing behavior and hence could be causing differences between the investigated samples. SiO_2 which is present in the brown coal ashes, and especially in brown coal fly ash, to a larger extent than in the wood bottom ashes has been shown to be ice active (Pruppacher and Sänger, 1955; Isono et al., 1959; Eastwood et al., 2008; Zimmermann et al., 2008; Atkinson et al., 2013). Consequently, it could be an important component influencing the immersion freezing behavior of the brown coal ashes in comparison to one another and to the wood bottom ashes. Also, Mason and van den Heuvel (1959) found that HgI has the potential to act as INP which might be relevant as Hg was detected in the brown coal ashes, but not in the wood bottom ashes. The fact that the wood ashes contain significantly more K than the brown coal ashes, which in this case is soluble, is a possible reason for the lower ice activity in comparison to the brown coal ashes. According to this, insoluble K could be the decisive element determining the freezing behavior of the brown coal ashes. Apart from the chemical composition, other properties such as ice active sites on the particle surface might affect the ice nucleation ability of a substance. Although studies dealing with the nature of active sites commonly investigated mineral dust particles, the findings might be transferable to other material systems such as ash. As for SiO_2 (Zolles et al., 2015), the brown coal ash particles might be more efficient at nucleating ice because of surface defects such as lattice dislocations caused by impurities or crystallographic dislocations. The high ice nucleation efficiency of the fly ash particles could be related to a

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large fraction of amorphous material (Umo et al., 2015, found more than 80 % in a coal fly ash sample). It has been shown that certain types of amorphous particles are able to nucleate ice (Murray et al., 2010b; Wilson et al., 2012), but it remains to be examined whether the amorphous components in fly ash are ice active as well.

To assess the ice nucleating ability of ash particles in comparison to mineral dust, Tab. 1 and Fig. 4 additionally show the parameters and fit curves to measurements with K-feldspar and mineral dust particles (K-feldspar, Arizona Test Dust, NX-illite, Fluka kaolinite) coated with sulphuric acid (clay mineral baseline, Augustin-Bauditz et al., 2014). As input for the SBM, results from measurements with 300 nm sized particles were used. Comparing the dry wood bottom ash particles to the clay mineral baseline shows similarities with a tendency of wood bottom ashes being slightly less ice active than clay minerals. On the other hand, the brown coal ashes are more efficient at nucleating ice than the clay minerals, yet not as efficient as K-feldspar (Augustin-Bauditz et al., 2014).

3.2 Wet particle generation

When comparing the results from dry and wet particle generation, it must be noted that a multiple charge correction was not possible for the latter. However, performing the multiple charge correction would lead to a reduction of f_{ice} depending on the multiple charge fractions. In Fig. 4, it can be seen that in the case of spruce bottom ash, the ultrasonic treatment and stirring process did not affect the ice nucleating ability considerably. The ice activity of the brown coal bottom ash suspension sample (+US), however, is reduced by several tens of percent due to the change in sample preparation and particle generation.

In case of the fly ash suspension sample, no further increase in f_{ice} is observable from ≈ -29 °C towards lower temperatures, meaning that 5 % of all generated particles are able to serve as INPs. The needle shaped crystals occurring during wet particle generation are unlikely to have an impact on the immersion freezing behavior of fly ash suspension particles as they are probably exclusively composed of water soluble material. These crystals can be expected to dissolve completely in the droplets and a solid substrate for heterogeneous nucleation would be missing. As a result, droplets containing a single crystal each, freeze due to homogenous nucleation only and the immersion freezing behavior of the sample originates solely from the spherical fly ash particles. To verify this hypothesis, immersion freezing experiments were conducted with the filtered fly ash suspension. The obtained f_{ice} values are comparable to what was found for similarly sized droplets containing one 300 nm ammonium sulfate particle each (Hartmann et al., 2011), i.e., droplets grown on these particles showed solely homogeneous freezing behavior. By counting ≈ 900 particles on SEM images, it was determined that ≈ 78 % of all particles are crystals. This value may be smaller in the flow tube as the fragile crystals could break upon impact on the filter leading to a multiplication. As only 22 % of the droplets contained a spherical fly ash particle during the experiments with the suspension sample (+US), the original data was corrected by a factor of 1/0.22 = 4.54 which is also shown in Fig. 4 for a direct comparability to the ice nucleation ability of dry particles from the same sample. The corrected f_{ice} was used for the calculation of the ice nucleation surface site density n_s (see Eq. 2 and Fig. 5). In the plateau region below -31 °C, a maximum of 25 % of all the spherically shaped fly ash particles from suspension is ice active, which is a clear lowering of the ice nucleation activity by a factor of 4 compared to dry particle generation, i.e., suspending the particles in water reduced their ice activity in the temperature range below -31 °C. However, fly ash suspension particles are more efficient at nucleating ice in the temperature range from -24 °C

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to -31 °C compared to fly ash particles from dry generation. These differences are, as for brown coal bottom ash particles, most likely related to a change of physical and/or chemical particle properties leading to a destruction of former active sites. In this context, water soluble components could play a role.

Furthermore, it is interesting to see that the f_{ice} values of the fly ash suspension which was not put in the ultrasonic bath are clearly lower than those of the fly ash suspension with ultrasonic treatment. Here, it is valid to compare to the uncorrected curve of the sample with ultrasonic treatment (open circles), assuming a similar, or smaller crystal fraction in the dispersed sample without ultrasonic treatment. This behavior could be related to an increased number of defects which could serve as active sites (Zolles et al., 2015) on the particle surface due to the redistribution to smaller grain sizes in the ultrasonic bath. It must be mentioned, that the enhancing effect of ultrasonic treatment on the immersion freezing behavior has been observed before during experiments with soil dust at LACIS (Hellner, 2015). As there are many publications describing the use of an ultrasonic bath during sample preparation in order to avoid aggregation and for resuspension purposes (e.g., Zobrist et al., 2008; Stetzer et al., 2008; Eastwood et al., 2009; Chernoff and Bertram, 2010; O'Sullivan et al., 2015; Umo et al., 2015) we recommend cautiousness, since this practice alters particle properties in a way that may lead to larger ice fractions in the immersion mode.

3.3 Comparison to previous results

In the next step, the ice nucleation surface site density n_s was determined from the measured f_{ice} according to the singular approach (DeMott, 1995):

$$n_s = -\frac{\ln(1 - f_{ice})}{A_n}. \quad (2)$$

For this, the particles were assumed to be spherical with a surface area of $A_n = 4\pi(D_p/2)^2$, with the diameter D_p of the sphere corresponding to the electrical mobility diameter of the selected particles (300 nm). In taking the particle surface area into account and assuming a time-independent behavior, a comparability to results obtained from other experimental setups than LACIS is made possible.

Fig. 5 shows n_s for ash particles from dry and wet generation in comparison to the results published by Umo et al. (2015). Similar to the measurements presented here, Umo et al. (2015) examined bottom ashes from wood and coal burning, as well as fly ash from coal burning. Here, a cold stage setup was used, where each droplet contains numerous ash particles, i.e., a large available INP surface area leading to an increase in freezing probability. As a result, Umo et al. (2015) investigated the immersion freezing behavior of ash particles in a higher temperature range (≈ -12 °C to -35 °C) and there is a limited overlap in comparison to our measurements. Apart from the contrasting measurement principle, another methodological difference is the determination of the particle surface area. Umo et al. (2015) used a standard Brunauer-Emmet-Teller (BET, Brunauer et al., 1938) nitrogen gas adsorption method which yields larger surface areas than assuming spherical particles with the electrical mobility diameter.

In Fig. 5, identical colors indicate similar fuels and combustion conditions. All wood bottom ashes, either from dry or wet particle generation, fit the data by Umo et al. (2015) (wood: commercially available solid wood fuel, domestic: unspecified soft

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and hard woods) within one order of magnitude. However, for brown coal bottom ash, the suspension particles yield n_s values close to what Umo et al. (2015) found for a comparable sample, while the respective dry generated particles show n_s values that are more than an order of magnitude larger at the same temperature. We ascribe this to a change caused by the particle generation, i.e., by the extended time (more than just some seconds) that the ash particles spent in suspension.

Although the shape of the nucleation spectrum of fly ash suspension particles from our measurements corresponds well to the findings by Umo et al. (2015), our results are up to three orders of magnitude higher. In order to explain the large discrepancy, the BET value corresponding to a monodisperse aerosol consisting of 300 nm spherical fly ash particles was calculated and compared to the value given by Umo et al. (2015) for bulk coal fly ash. It was found that the determined difference in surface area is a factor of 4 only, meaning that this is the factor by which our values were lowered had we used the BET surface area instead of the geometrical one. Hence, effects other than the difference in surface area determination must be responsible for the discrepancy in n_s. Time-dependence of the nucleation process could contribute, however, we expect this contribution to be small. The main contribution likely comes from the fact that the investigated samples were not completely identical concerning their chemical composition and morphology.

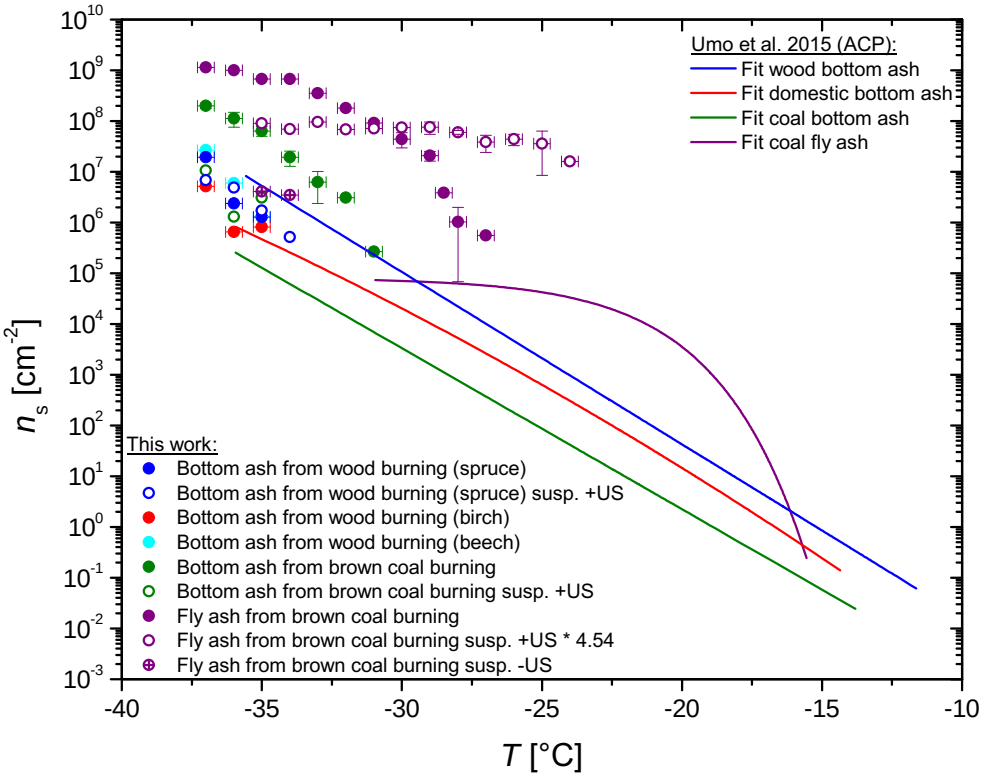

Figure 5. Comparison of ice nucleation surface site density n_s as a function of temperature T for ash particles from dry (full circles) and wet generation (open circles) with results by Umo et al. (2015).

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4 Atmospheric implications

Reliable information on the global emission of ash particles is scarce which is why it is difficult to evaluate their impact on heterogeneous ice nucleation on a large scale. However, it is possible to give a rough estimate on INP concentrations from fly ash emissions close to the source based on the findings presented in this work.

There are several studies investigating in-stack particle concentrations of coal-fired power plants. According to Ondrov et al. (1978) and Yi et al. (2006), the in-stack concentration of 1 μm sized particles may vary from 2×10^3 to 10^5 per cm^3. Airborne concentration measurements show that there are still 100 per cm^3 of 1 μm sized particles in a distance of $\approx$ 80 km downstream of the power plant (Parungo et al., 1978a) which corresponds to a dilution factor of up to 1000. With $n_s \approx 6 \times 10^5$ cm^{-2} at -27 °C (fly ash from dry particle generation, taken from Fig. 5) and assuming spherical particles, one can calculate the ice fraction to ≈ 0.02. On condition that the fly ash particles are the only component of the plume aerosol nucleating ice, this means that 2 particles per cm^3 are active INPs at a temperature of -27 °C at a distance of 80 km downstream of the power plant stack. This value is well above typical INP concentrations of 10^{-4} to 10^{-2} per cm^2 reported in the literature (Pruppacher and Klett, 1997; Rogers et al., 1998; DeMott et al., 2010; Petters and Wright, 2015). In conclusion, it can be said that the impact of fly ash particles on the heterogeneous ice nucleation in mixed-phase clouds can be significant on a regional scale. Of course, sufficiently low temperatures are needed to achieve relevant ice fractions. However, the results by DeMott et al. (2003), who found fly ash in cirrus cloud residues, prove that the particles may reach large altitudes where they experience suitable conditions and have an impact also on the synoptic scale.

5 Summary and conclusions

In the framework of this study, the immersion freezing behavior of ash particles has been investigated in a temperature range from -24 °C to -40 °C. Airborne aerosol particles of 300 nm in size were generated from five different combustion ash samples and analyzed atthe Leipzig Aerosol Cloud Interaction Simulator (LACIS). The samples included bottom ashes from spruce, birch, and beech burning, bottom ash from brown coal burning, and fly ash from brown coal burning.

It was found that there are differences between bottom ashes from wood burning and the two brown coal ash samples, the latter showing a significantly higher ice nucleating activity in the immersion mode. Bottom and fly ash from brown coal burning initiated freezing at temperatures as high as -33 °C and -29 °C, respectively. It was shown that the brown coal ashes are more efficient at nucleating ice than clay minerals, yet not as effective as K-feldspar (Augustin-Bauditz et al., 2014). The investigation of the chemical composition gave no definite indication of what exactly causes the differences between wood and coal ashes, however, a decisive factor could be the presence of insoluble K in the coal ashes. Investigating further particle properties which have been shown to influence freezing behavior such as lattice structure, surface chemical configuration, number and type of surface defects, and ability of the surface to participate in electrostatic interactions (Shen et al., 1977; Yakobi-Hancock et al., 2013; Zolles et al., 2015; Kulkarni et al., 2015) might be the key to understanding the differences between different kinds of ashes.

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Furthermore, measurements were conducted with ash particles from suspensions which were prepared by putting them in an ultrasonic bath followed by a 24 h stirring process. This was done for bottom ashes from spruce and brown coal burning, as well as fly ash from brown coal burning. LACIS measurements showed barely any change in the ice nucleation efficiency of bottom ash from spruce burning. On the other hand, a significant difference due to the change in particle generation could be observed for the brown coal ashes. SEM images of the fly ash suspension particles were taken on which we could observe a majority of needle shaped crystals and some insoluble fly ash particles. The crystals may have formed from soluble components, likely $CaCO_3$, in the drying process. After a potential ice nucleation activity of the crystals could be excluded, a correction of the determined n_s values was performed with respect to the fraction of insoluble fly ash particles. As the results do not match the nucleation spectrum of fly ash particles from dry generation, it can be concluded that the difference in immersion freezing behavior is caused by a change in particle properties from dry to wet particle generation which has been observed before for $CaCO_3$ containing mineral dusts (Sullivan et al., 2010). Eventually, another fly ash suspension sample without ultrasonic treatment was prepared for which we could only observe a very low ice nucleation activity below -34 °C. Hence, we advise to be cautious when using an ultrasonic bath for sample preparation prior to freezing experiments.

Regarding previous investigations on the immersion freezing of ash particles, we found that the wood bottom ashes, either from wet or dry particle generation, show similar nucleation spectra in comparison to the samples examined by Umo et al. (2015). However, brown coal bottom ash only shows a comparable immersion freezing behavior to the sample investigated by Umo et al. (2015) when particles are being generated from a suspension. It is striking that, although the shape of the nucleation spectrum of our brown coal fly ash suspension particles is similar to the one observed by Umo et al. (2015) in the overlap area, n_s is higher by up to three orders of magnitude. This discrepancy cannot be explained by the difference in particle surface area determination and therefore is most likely related to the physical and/or chemical properties of the two fly ash samples.

To summarize, we found the ice nucleation activity of brown coal bottom and fly ash to be similar to mineral dusts. However, ash is a very heterogeneous material containing several different particle types (Ramsden and Shibaoka, 1982; Umbría et al., 2004; Zhang et al., 2011) which complicates the interpretation of experimental results. More work has to be done in the field of sample characterization to identify features that cause differences in the immersion freezing behavior of different kinds of ashes. Complementary to experimental data on the freezing behavior of ash particles, more information is needed about the atmospheric abundance of these particles. As reliable estimates of global ash emissions are missing, this knowledge can only be acquired by developing feasible methods to clearly distinguish between mineral dusts and ash particles in the framework of in situ measurements. A long-term objective is the implementation of parameterizations of ash particles as INPs into weather and climate models.

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