

Kaolinite particles as ice nuclei: learning from the use of different kaolinite samples and different coatings

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Abstract. Kaolinite particles from two different sources (Fluka and Clay Minerals Society (CMS)) were examined with respect to their ability to act as ice nuclei. This was done in the water subsaturated regime where often deposition ice nucleation is assumed to occur, and for water supersaturated conditions, i.e. in the immersion freezing mode. Measurements were done using a flow tube
5 (LACIS) and a continuous flow diffusion chamber (CFDC). Pure and coated particles were used, with coating thicknesses of a few nanometer or less, where the coating consisted of either levoglucosan, succinic acid, or sulfuric acid. In general, it was found that the coatings strongly reduced deposition ice nucleation. Remaining ice formation in the water subsaturated regime could be attributed to immersion freezing, with particles immersed in concentrated solutions formed by the
10 coatings.

In the immersion freezing mode, ice nucleation rate coefficients j_{het} from both instruments agreed well with each other, particularly when the residence times in the instruments were accounted for. Fluka kaolinite particles coated with either levoglucosan or succinic acid showed the same IN activity as pure Fluka kaolinite particles, i.e. it can be assumed that these two types of coating did not
15 alter the ice active surface chemically, and that the coatings were diluted enough in the droplets that were formed prior to the ice nucleation, so that freezing point depression was negligible. However, Fluka kaolinite particles which were coated with either pure sulfuric acid or which were first coated with the acid and then exposed to additional water vapor both showed a reduced ability to nucleate ice, compared to the pure particles. For the CMS kaolinite particles, the ability to nucleate ice in
20 the immersion freezing mode was similar for all examined particles, i.e. for the pure ones and the ones with the different types of coating. Moreover, j_{het} derived for the CMS kaolinite particles was comparable to j_{het} derived for kaolinite particles coated with sulfuric acid. This is suggestive for the Fluka kaolinite possessing a type of ice nucleating surface feature which is not present on the

CMS kaolinite, and which can be destroyed by reaction with sulfuric acid. This might be potassium
25 feldspar.

1 Introduction

Ice in clouds is a research topic which has received interest already before the 1950's (see e.g. Vonnegut, 1947). Despite many decades which have gone by since scientists started to work on ice in clouds, our understanding of even the basic related processes is still incomplete (Murray et al.,
30 2012). In the atmosphere, ice containing clouds (meaning both pure ice clouds and mixed phase clouds) play important roles. They cover a significant fraction of the Earth at any time and hence influence radiative processes and also the formation of precipitation. Of the latter, the majority is produced via the ice phase in mixed phase clouds, particularly outside of the tropics.

The first step on the way to having ice in clouds is ice formation, and therefore this process is
35 of large interest. It is known that ice can form by primary or secondary processes, an example for the latter being e.g. rime-splintering (Hallett and Mossop, 1974). The primary processes are either homogenous or heterogenous ice nucleation, where heterogeneous ice nucleation involves ice nuclei (IN) which lower the energy barrier that has to be overcome to form a stable ice cluster. Mixed phase clouds form at temperatures above those for which homogenous ice nucleation can occur. And as
40 these clouds are also the ones responsible for forming much of the globally occurring precipitation, the heterogenous ice nucleation mechanisms are of particular interest. Additionally, it has been claimed that maybe even for cirrus clouds, heterogenous formation mechanisms might be of large importance (Spichtinger and Cziczo, 2010; Cziczo et al., 2013).

There are different pathways for heterogenous freezing, generally discriminated into immersion,
45 condensation and contact freezing and deposition ice nucleation. For mixed phase clouds, it has been stated that immersion freezing is the most important ice forming mechanism (Ansmann et al., 2009; Wiacek et al., 2010; de Boer et al., 2011), while for cirrus clouds deposition ice nucleation and condensation/immersion freezing are considered as ice forming mechanisms, too. For the fourth heterogenous ice nucleation process, contact freezing, little data is available, but new results on this
50 topic are currently emerging as e.g. in Hoffmann et al. (2013) and Ladino Moreno et al. (2013).

The difference between condensation and immersion freezing is poorly defined, and in the Appendix (App. A), a more detailed description of different definitions is given, based on Fukuta and Schaller (1982), Vali (1985), Pruppacher and Klett (1997) and Hoose and Möhler (2012). In our study, we will use the term immersion freezing for all cases when an insoluble particle is immersed
55 in a diluted droplet. Condensation freezing will denote the case when an insoluble particle is immersed in a concentrated solution (i.e. in the case of haze particles), which principally can occur for $S_w < 1$ as long as the deliquescence RH of the soluble material which was on the insoluble core prior to forming a solution is overcome. This is similar to the “immersion freezing of solu-

tion droplets” from Hoose and Möhler (2012) or e.g. to a term called “deliquescent-heterogenous
60 freezing” in Khvorostyanov and Curry (2004).

Much has been learned about the nature of IN (see the two reviews given by Hoose and Möhler
(2012) and Murray et al. (2012)). However, on a process scale, it is still not known what exactly it is
that makes a particle act as IN. Mineral dust particles are known to be an important IN source in the
atmosphere (e.g. DeMott et al., 2003; Sassen et al., 2003; Cziczo et al., 2004; Hoose and Möhler,
65 2012; Murray et al., 2012; Atkinson et al., 2013). Particularly desert soils but also fertile soils of
the Earth are abundant sources for mineral dust, and the respective aerosol is distributed world wide,
with a stronger abundance in the Northern Hemisphere (see e.g. Atkinson et al., 2013; Burrows et al.,
2013). Different minerals have been examined with respect to their role as IN (see the summary in
Murray et al., 2012), among them atmospherically relevant minerals like clay and feldspar and also
70 quartz. Quartz was found to act as IN for deposition ice nucleation by Zimmermann et al. (2008) and
for immersion freezing by Atkinson et al. (2013) but did not act as good IN for immersion freezing
in measurements done with the Leipzig Aerosol Cloud Interaction Simulator (LACIS, unpublished
results). There, quartz particles nucleated ice clearly less efficiently than particles from different
kaolinite samples. In Zolles (2013), quartz samples bought from different companies were found to
75 vary much in their ice nucleation ability for immersion freezing, showing median freezing tempera-
tures between -24°C and -37°C . Silicates generally are ice active (see e.g. Archuleta et al., 2005;
Kanji et al., 2008; Zimmermann et al., 2008; Welti et al., 2009), and e.g. Sullivan et al. (2010a)
and Niedermeier et al. (2011) explicitly mentioned that it might be the aluminosilicate minerals
which are the most efficient ice active component in the test dust examined in their studies (Arizona
80 Test Dust). Recently it has been proposed that the potassium feldspar content may play the most
important role for the IN ability of mineral dusts worldwide (Atkinson et al., 2013).

A uniform description or parameterization which would enable an easy incorporation of the het-
erogenous freezing processes in models still needs to be developed, if this will be possible at all.
Understanding the processes underlying the freezing and learning about the nature of IN can help
85 shed light onto this. Particularly for the deposition ice nucleation, the review by Hoose and Möhler
(2012) shows that reported onset temperatures scatter over a large range with respect to both ob-
served temperature and water vapor saturation ratios. Some of this scatter can be explained by
different thresholds, i.e. by different frozen fractions, that were reported for the different mea-
surements which have been included in the comparison or by other issues specific to the different
90 instruments. However, open issues remain for the understanding of heterogeneous ice nucleation.
A new suggestion concerning deposition ice nucleation was recently discussed in Marcolli (2013),
viewing this particular heterogenous ice nucleation mode as either homogeneous or as immersion
freezing in pores and cavities. A part of this present study will be devoted to a related discussion.
It has been already described that coatings, particularly of sulfuric acid, on mineral dust particles
95 containing aluminium-silicates can largely reduce their ice nucleation ability for deposition ice nu-

cleation (e.g. in Archuleta et al., 2005; Cziczo et al., 2009; Eastwood et al., 2009; Sullivan et al., 2010b; Tobo et al., 2012), and for immersion freezing (e.g. Zuberi et al., 2002; Koop and Zobrist, 2009; Niedermeier et al., 2010; Sullivan et al., 2010b; Niedermeier et al., 2011; Tobo et al., 2012). However, a coating of nitric acid inhibited deposition ice nucleation for relative humidities below
100 $\sim 97\%$ but not for immersion freezing (Sullivan et al., 2010a), and the observed sharp increase in ice nucleation ability at $\sim 97\%$ was interpreted as a change in the heterogenous ice nucleation mode, namely from deposition ice nucleation to condensation/immersion freezing. In the present study, we will explicitly show that the ice nucleation for some coated mineral dust particles can be described as immersion freezing, with the mineral dust particle being immersed in a concentrated solution for
105 which then a freezing point depression has to be assumed.

In the present work we will show results for heterogenous ice nucleation measured with either LACIS (Leipzig Aerosol Cloud Interaction Simulator) in its immersion freezing mode (Hartmann et al., 2011) and a CFDC (Continuous flow Diffusion Chamber, Rogers et al., 2001; DeMott et al., 2010) measuring both, deposition ice nucleation and condensation/immersion freezing. Examined
110 particles consisted of two different kaolinites with and without coatings (details are described in Section 2). In all cases, size segregated particles were examined.

A subset of the data presented here was already shown in Tobo et al. (2012), where data from the CFDC for Fluka kaolinite particles (pure and coated with H_2SO_4 or levoglucosan) were described. It was found that both coatings reduced the IN ability for the deposition ice nucleation while only the
115 H_2SO_4 coating reduced the IN ability for condensation/immersion freezing in the CFDC. Therefore the levoglucosan coating was similar in its effect than nitric acid in Sullivan et al. (2010a) in inhibiting deposition ice nucleation but allowing for condensation/immersion freezing once the coating is dissolved at relative humidities close to 100%.

The present study extends from Tobo et al. (2012). It includes a comparison of the measured
120 immersion freezing by LACIS and the CFDC, additional data on CMS kaolinite and also data on coatings with succinic acid. Furthermore, it discusses a model for describing the heterogeneous ice formation of particles with sufficiently thick coatings at relative humidities below 100%, interpreting this type of freezing as immersion freezing of IN immersed in concentrated solutions.

2 Samples, set-up and instrumentation

125 In this study, two different kaolinites were examined. The samples were provided by Fluka and by the Clay Minerals Society (CMS, KGa-1b). In general, kaolinite belongs to the group of clay minerals. It is a phyllosilicate (Deer et al., 1992) and occurs in atmospheric samples in amounts on the order of a few up to a few 10% (see Murray et al., 2012). However, the Fluka kaolinite additionally contains about 5% of potassium feldspar, while CMS kaolinite does not contain a detectable amount
130 (Atkinson et al., 2013).

Besides pure, also coated particles were studied, where the coatings consisted of either sulfuric or succinic acid or levoglucosan. Sulfuric acid is known to be a reactive substance with the potential to decrease the IN ability of dust particles, as mentioned above. It is of atmospheric relevance as atmospheric SO₂ can be oxidized to H₂SO₄ during wet phase chemistry. Succinic acid was chosen
135 as it is a slightly soluble substance with a high deliquescence relative humidity which is present in the atmosphere (Wex et al., 2007), while levoglucosan is an organic substance known to be a tracer for biomass burning (Simoneit et al., 1999) with a much higher solubility.

A sketch of the general set-up can be seen in Fig. 1. To disperse kaolinite particles, a fluidized bed generator (TSI 3400A, TSI Inc., St. Paul, Minnesota, USA) was used. In order to reduce the
140 number of charges carried on the particles, and therewith to reduce the loss of charged particles to walls within the particle generation set-up, a corona discharger was put in line behind the fluidized bed. The corona was produced on top of a needle to which high voltage (4 kV) was applied. It has been tested previously, that the corona discharger did not influence the IN ability of the particles (Niedermeier et al., 2010). We wanted to examine size selected particles, and to facilitate the size
145 selection, a rough pre-selection was done, i.e. particles with aerodynamic diameters above 560 nm or 1000 nm (for the generation of 300 nm or 700 nm particles, respectively) were separated with a MOUDI impactor (Micro Orifice Uniform Deposition Impactor, Model 100R, MSP Corporation, Shoreview, Michigan, USA). Downstream of the MOUDI, a neutralizer established a bipolar equilibrium charge distribution on the particles.

150 When a coating was applied to the particles, the aerosol was then sent through one of three thermostated glass tubes, which contained either a reservoir filled with succinic acid (C₄H₆O₄, SuccA will be used as abbreviation for it from here on), levoglucosan (C₆H₁₀O₅, abbreviated LG) or with sulfuric acid (H₂SO₄). The temperature of the tubes was controlled via thermostats (HAAKE C25P, HAAKE GmbH, Karlsruhe, Germany). The glass tubes were set to temperatures between 45 °C
155 and 90 °C, depending on the material and the desired coating thickness. For particles coated with H₂SO₄ at 70 °C, a further treatment was sometimes applied, i.e. water vapor was added to the aerosol by sending it over a water bath at room temperature and subsequently sending it through a second diffusion drier (not shown in the sketch).

The coating section could also be bypassed, but whether coated or not, particles were then sent
160 through a DMA (Differential Mobility Analyzer, Type Vienna Hauke medium, aerosol to sheath air flow ratio of 1 : 10) to select particles with one mobility. Selected mobility diameters were either 300 nm or 700 nm throughout the experiments described herein. The aerosol was then distributed to the different instruments. In this part of the set-up, two additional flows of particle free air were added, where the particle number concentration was roughly halved in each of the steps. The differ-
165 ent flows were controlled frequently, using a bubble flow meter, to enable the calculation of particle concentrations delivered to the different instruments. It was also ensured that a small excess of aerosol was produced. The small excess flow was vented in order to maintain the pressure in the

whole particle generation set-up close to laboratory pressure.

170 Directly downstream of the DMA, the aerosol was fed into LACIS (Leipzig Aerosol Cloud Inter-
action Simulator), which was used to measure immersion freezing (Hartmann et al., 2011). LACIS
consists of a 7 m long flow tube where each 1 m section can be temperature controlled separately.
Temperatures can go down to -50°C . Before entering the flow tube, by use of a humidifier (PH-
30T-24KS, Perma Pure), the sheath air stream is hydrated such that droplets form on the aerosol
175 particles upon cooling, i.e. during the passage of the flow tube. These droplets can subsequently
freeze, depending on the nature of the immersed aerosol particle and the adjusted temperature. A de-
tailed analysis of thermodynamic profiles in LACIS can be found in Hartmann et al. (2011). At the
LACIS outlet, a self built optical particle spectrometer (TOPS-Ice, Clauss et al., 2013) determines if
the arriving hydrometeors are liquid droplets or frozen ice crystals, resulting in the determination of
a frozen fraction, f_{ice} , i.e. the number of frozen droplets divided by the total number of liquid and
180 frozen droplets.

Particle number concentrations were measured with a Condensation Particle Counter (CPC,
TSI 3010), which was operated in parallel to a Cloud Condensation Nucleus counter (CCNc, Droplet
Measurement Technologies) to determine the activation of the particles to cloud droplets and from
that the coating thicknesses. Using both data from CPC and CCNc, the fraction of all particles acti-
185 vated was determined. During the measurements, the supersaturation in the CCNc was scanned such
that full activation curves, i.e. from none to all particles activated, were obtained.

Ice nucleation was also measured using a CFDC (Continuous Flow Diffusion Chamber, Rogers
et al., 2001; DeMott et al., 2010). The particle number concentrations delivered to this instrument
were a few tens per cubic centimeter. The CFDC is operated with ice covered walls which are
190 kept at different temperatures. Temperatures can be set such that both, sub- or supersaturation with
respect to water vapor can be achieved for a focused aerosol lamina within the instrument. Evap-
oration of only liquid particles within the last section of the instrument facilitates optical detection
of nucleated ice crystals. In this study, the IN number concentrations were determined as a func-
tion of water vapor saturation by stepwise scanning experimental conditions from ice saturation to
195 a relative humidity (with respect to liquid water, RH_w) of about 107 %. It is assumed that although
all ice formation mechanisms are possible in the regime above 100 % RH_w , this condition favors
condensation/immersion freezing nucleation. Particularly close to 100 % RH_w , it might be possible
that the particles are not activated to diluted droplets but form haze particles, instead, and the term
condensation freezing should be understood correspondingly. To obtain frozen fractions, f_{ice} , from
200 the CFDC measurements, measured total particle number concentrations were used together with
the IN number concentrations, i.e. the same parameter was derived that was also obtained from the
LACIS measurements.

3 Results and discussion

3.1 Coating thicknesses

205 We first discuss the amount of coatings present on the examined particles. Besides examining
300 nm particles from either Fluka or CMS kaolinite samples, also 700 nm Fluka kaolinite parti-
cles were used. Different coating temperatures were applied for all three coating substances, SuccA,
LG and H₂SO₄, where for the latter additionally water vapor was added in some cases. Particle
generation was operated such that for the course of one experiment, which usually lasted around 2 h,
210 one type of particle with one type of coating was produced, while the different instruments examined
the particles. The need for CFDC and LACIS to either re-ice or defrost, respectively, determined the
length of an experiment. Some particle types were generated repeatedly for more than one of these
2 hourly time-spans.

Scans of activated fractions vs. supersaturation were measured with the CCNc for all the different
215 particle types. The critical supersaturations for droplet activation, i.e. the supersaturation at which
50 % of all particles were activated, were derived applying an error function fit to the measured
activated fraction curves.

The critical supersaturation for the pure particles were found to be 0.29 % and 0.44 % for the
300 nm Fluka and CMS kaolinite particles, respectively, and 0.17 % for Fluka particles of 700 nm.
220 These critical supersaturations are lower than expected for purely insoluble particles. Still, when
using κ -Köhler theory (Petters and Kreidenweis, 2007), these values correspond to κ below 0.005.
Comparable or even larger κ has been reported for different mineral dusts e.g. in Herich et al. (2009)
and Koehler et al. (2009), i.e. mineral dust particles generally were observed to be more easily
activated to a droplet than expected. Kumar et al. (2011) attributed this fact to adsorption of water
225 on the insoluble component of the dust particle. However, Herich et al. (2009) and Koehler et al.
(2009) both also found that κ of the mineral dust particles increased when the particles had been
sprayed from an aqueous solution (instead of dispersing them from a dry powder), and argued that
this was due to a redistribution of small amounts of soluble material which had to have been present
already on the dry particles. We follow that line of argument, i.e. we assume that a small amount
230 of soluble impurities was present on the kaolinite particles examined in this study. Based on the
observed critical supersaturations it can be estimated that this amounts to less than 1 % of the mass
of the examined particles.

Coated particles activated at lower supersaturations than the pure ones, due to the larger soluble
mass available. This decrease in supersaturation between uncoated and coated particles was used
235 to derive the amount of soluble material which had been added to the particle during coating. We
assumed that the particles were spherical with an insoluble core and a mantle of soluble material of
either SuccA, LG or H₂SO₄ around them, depending on the coating. Derived coating thicknesses are
given in Table 1. The corresponding κ for the coated particles is < 0.02 for thin and medium thick

coatings and to up to 0.05 for the thickest coatings. Coatings < 2 nm correspond to hygroscopic
240 growth factors at 90% relative humidity below 1.1, a value generally observed for the hydrophobic
fraction of atmospheric aerosols. For a dryly dispersed Saharan mineral dust sample taken from
a surface soil layer, Koehler et al. (2009) found a κ of 0.054. Herich et al. (2009) reported 0.02
and < 0.01 for dryly dispersed mineral dust samples from the Sahara and the Takla Makan desert,
respectively. In general, coated particles used in our study, particularly those with thin and medium
245 thick coatings, are comparable in their hygroscopicity to naturally occurring mineral dust particles.

It should be mentioned that at least the H_2SO_4 coating most likely will have chemically reacted
with the dust particles. Reitz et al. (2011) examined ATD (Arizona Test Dust) particles coated
with H_2SO_4 , where the coating procedure was similar to the one in the present study, and it was
reported that both sulfuric acid as well as sulfates were present on the particles. This suggests
250 a reaction between the H_2SO_4 coating and the ATD. As the derived amount of coating depends on
the hygroscopicity of the coating material, and as sulfates commonly have a lower hygroscopicity
than sulfuric acid, coating thicknesses derived from our data could be up to a factor of 2 above those
given in Table 1 for the H_2SO_4 coatings. Nevertheless, the derived coating thicknesses still can give
a rough estimate and should only be viewed as such.

255 With sizes of the molecules of SuccA, LG and H_2SO_4 roughly in the range of 0.5 nm, and with
the shape of the particles likely being rather flaky than spherical, the coatings that were obtained
for the lowest coating temperatures can be expected to not cover the whole particle surface, while
the highest coating temperatures are much more likely to having produced a complete coating in all
cases.

260 3.2 Immersion freezing

Figure 2 shows exemplary freezing results from both, CFDC and LACIS, for two particle types.
Shown are values for f_{ice} , directly inferred from the measurements, and also for j_{het} , the heteroge-
neous freezing rate coefficient, calculated assuming pure stochastic freezing. The latter was obtained
following e.g. Murray et al. (2012):

$$265 f_{\text{ice}} = 1 - \exp(-j_{\text{het}} \cdot s \cdot t) \quad (1)$$

with the surface area of the examined particles s and the freezing time t . While t was 1.6 s for the
LACIS measurements (see Hartmann et al., 2011), a residence time of 5 s was used for the CFDC,
based on the maximum time for immersion freezing (104–106 % RH_w) in the CFDC, following the
model of Rogers (1988) (see ?).

270 A stochastic approach for the description of immersion freezing induced by kaolinite has e.g. also
been used in Murray et al. (2011), where a single type of active site was sufficient to describe the
observed immersion freezing for a suite of different experimental conditions for a CMS kaolinite
sample, pointing towards homogeneity of active sites on CMS kaolinite. For Fluka kaolinite, Pinti

et al. (2012) reported two separate heterogeneous freezing peaks for measurements done with a differential scanning calorimeter. Wheeler and Bertram (2012) examined the onset of ice nucleation for deposition ice nucleation of Fluka kaolinite. They found that a model using a single contact angle did not reproduce their data well, while models using contact angle distributions as well as a simple deterministic model using a surface density of active sites were both able to describe their data. The latter results are consistent with Broadley et al. (2012), a study on immersion freezing of illite particles, which are considered as a more representative surrogate for atmospheric dusts. There, the use of a multi-component stochastic model was required or, alternatively, the data could be approximated as freezing deterministically (without time dependence) for the purpose of atmospheric modeling. Therefore, while we mainly present and interpret our data based on a stochastic approach, in App. B the same data will be shown additionally when evaluated based on a deterministic approach.

Values for f_{ice} given in Fig. 2 were fitted separately for the data from CFDC and from LACIS, and the curves are shown as black and red lines in the upper panels. An apparent shift in the data from CFDC to LACIS of up to 2 K could be interpreted from these curves. The fact that an analysis of j_{het} brings the data into better alignment in the lower panel of Fig. 2 is consistent with the assumption of stochastic freezing for kaolinite particles, i.e. with the assumption that freezing is a time dependent process, corroborating the results by Murray et al. (2011).

The two experiments shown in Fig. 2 are similar to what was found for all coated and uncoated kaolinite particles examined in this study. That is, analysis of j_{het} always led to merger of data from CFDC and LACIS. Hence data from the two instruments were combined and fitted as one data-set. This was done using:

$$j_{het} = A \cdot \exp(B \cdot T) \quad (2)$$

where T is the temperature (expressed in °C), A and B are the fitting parameters. Examples for the resulting fitting curves are included as grey lines in the two lower panels of Fig. 2. A and B were derived for all particle types for which data from both, the CFDC and LACIS, were available. All resulting fitting curves are displayed in Fig. 3, while resulting values for A and B are shown in Fig. 4.

It has to be added that A and B were derived for the temperature range in which the measurements had been done (indicated by the grey shaded area in Fig. 3) and for residence times on the order of a few seconds. Hence the parameterizations underlying the curves shown for kaolinite IN in Fig. 3 are not necessarily valid outside the grey shaded area, nor for much longer time scales. It should also be added, that the approach of parameterizing j_{het} using the simple fit function given in Eq. (2) differs from calculation of nucleation rates based on Classical Nucleation Theory (CNT) together with a single contact angle. We parameterize j_{het} and therefore describe its temperature dependence as obtained from the measurements. Using CNT together with a single contact angle tends to deliver temperature dependencies of nucleation rates which are too steep, unless all examined IN are identical. This can be seen e.g. in Augustin et al. (2013): a parameterization of nucleation rates similar

to the one done in our study described measured frozen fractions almost as good as calculations based on CNT using a contact angle distribution, while calculations based on CNT with a single contact angle could not reproduce the measured data at all (compare Figs. 5 and A1 in Augustin et al. (2013)).

315 The curves displayed in Fig. 3 roughly split into two groups, with the grey curve, i.e. the one for 300 nm Fluka kaolinite particles coated with the thinnest H_2SO_4 coating, applied at only 45°C , belonging to neither. The first group of curves includes data for pure Fluka kaolinite and data for all Fluka kaolinite particles which were pure or coated with either SuccA or LG (corresponding to the top 10 curves given in the legend). Error bars depicting one standard deviation were added
320 exemplarily to the curve for the pure 300 nm Fluka kaolinite particles (shown in red). The second group contains all CMS kaolinite particles, regardless of the coating, and additionally also the Fluka kaolinite particles which had been coated with H_2SO_4 at 70°C (with or without additionally water vapor) (corresponding to the lowest 8 curves given in the legend). Here, the two black curves in this
325 group have error bars added to them, exemplarily. (It should be pointed out that the lowest black curve almost completely coincides with the next lower blue curve, hence only 3 different blue curves are clearly visible.) It can be seen that the CMS kaolinite particles and particles coated with H_2SO_4 are generally less ice active than particles belonging to the first group for temperatures above about -34°C . Among all 300 nm Fluka kaolinite particles coated with H_2SO_4 , those with the thinnest coating (grey curve) are clearly still the most ice active, indicating that the respective smaller amount
330 of coating did not destroy the ice nucleation ability as thoroughly as did the thicker coatings.

We will now turn to Fig. 4, which resolves details better than Fig. 3. It can be seen that A and B show the same tendencies, i.e. when lower values were obtained for A , also lower values were obtained for B . When results were available for both, 300 nm and 700 nm Fluka kaolinite, they were always similar, as to be expected since the particle size is accounted for when deriving j_{het} .

335 One of the most noticeable features in Fig. 4 is, that the parameters obtained for the CMS kaolinite particles are clearly lower than those for the Fluka kaolinite for all particles except for those coated with H_2SO_4 . This agrees with literature available on immersion freezing of kaolinites, where generally CMS kaolinite was found to be less ice active than the Fluka kaolinite: Murray et al. (2011) used CMS kaolinite in their study and reported that they found a lower ice nucleation ability than
340 Löönd et al. (2010), a study in which Fluka kaolinite has been used. Pinti et al. (2012) examined CMS kaolinite and kaolinite distributed by Sigma Aldrich (which is the same as that provided by Fluka) and found the Sigma Aldrich kaolinite to be more ice active. We will return to discussing the differences in the two types of kaolinite later in this section.

Coatings of SuccA or LG for all examined coating temperatures had no remarkable influence on
345 the immersion freezing, i.e. A and B derived for the particles coated with SuccA or LG are similar to those for the respective uncoated particles. This holds true for Fluka and CMS kaolinite particles. This is not surprising, as SuccA and LG are both soluble substances, and for immersion freezing the

droplets generated in the CFDC and in LACIS, had maximum sizes above $2\ \mu\text{m}$ (Hartmann et al., 2011; ?), i.e. the soluble material on the particles was strongly diluted and freezing point depression is negligible. These results also suggest that SuccA and LG did not alter the surface of the particles chemically.

Concerning coatings of H_2SO_4 , the data as shown in Fig. 4 reiterates and expands the point that this type of coating reduces the immersion freezing ability of Fluka kaolinite particles, visible in the lower A and B values. The addition of water vapor was intended to intensify the reaction between the acid and the kaolinite, as it had been observed previously for Arizona Test Dust (ATD, Niedermeier et al., 2011), but this was not observed, here.

Differently than for the Fluka kaolinite, a considerable decrease in the immersion freezing ability due to H_2SO_4 coating was not observed for the CMS kaolinite particles. A data-set sufficient for evaluation exists only for the CMS kaolinite particles coated at $70\ ^\circ\text{C}$ with additional water vapor, which, however, should have been the most reactive coating produced.

The group of Fluka kaolinite particles of both sizes, either uncoated or coated with SuccA or LG, shows average values of $A_{\text{Fluka}} = 155.4\ \text{m}^{-2}\ \text{s}^{-1}$ and $B_{\text{Fluka}} = -0.57\ ^\circ\text{C}^{-1}$. The second group including all CMS kaolinite particles, regardless of the coating, and the Fluka kaolinite particles which had been coated with H_2SO_4 at $70\ ^\circ\text{C}$, with or without added water vapor have average values of $A_{\text{CMS}} = 1.21 \times 10^{-5}\ \text{m}^{-2}\ \text{s}^{-1}$ and $B_{\text{CMS}} = -1.03\ ^\circ\text{C}^{-1}$.

The grouping of the data shows that although we used a strong acid we were not able to destroy ice nucleation sites on the CMS kaolinite much while we were able to do so on the Fluka kaolinite. It can be assumed that the H_2SO_4 coating causes a chemical reaction which alters the Fluka kaolinite, making the remaining particles similar in their IN ability to CMS kaolinite.

These results can be further interpreted when considering a recent publication by Atkinson et al. (2013). In that study, potassium feldspar is considered to be the most efficient ice nucleating dust under mixed-phase cloud conditions, globally. Atkinson et al. (2013) give the amount of potassium feldspar present in Fluka kaolinite to be roughly 5 %, while CMS kaolinite is reported to not contain any detectable amount. In general, common clay minerals are the weathering product of feldspar (Blum, 1994), and one transformation occurring in the field is the reaction of e.g. potassium feldspar with H^+ and H_2O to form quartz and kaolinite. Therefore, the different fractions of feldspar in the two examined kaolinite samples hint towards the fact that the Fluka kaolinite is not weathered quite as thoroughly as the CMS kaolinite. The additional natural weathering likely is the reason for the reduced IN ability of the CMS kaolinite particles, and the feldspar contained in Fluka kaolinite might be responsible for the larger IN ability of this sample. In our experiments, it could be the altering of this feldspar when coating Fluka kaolinite with H_2SO_4 , which causes the observed lowering in the IN ability.

The above presented results on immersion freezing of the two different kaolinites are consistent with a corroboration of the claim by Atkinson et al. (2013), i.e. that it might indeed be the potassium

385 feldspar which is responsible for an increased IN ability in some dusts.

3.3 Ice nucleation under water subsaturated conditions

Now we will introduce measurements of ice nucleation in the regime below water saturation where deposition nucleation or freezing of haze particles may occur. These measurements were done only with the CFDC. Figure 5 shows f_{ice} as determined with the CFDC for 300 nm Fluka, 300 nm CMS
390 and 700 nm Fluka kaolinite particles for water subsaturated conditions, for pure particles and those with medium thick and thick coatings. Measurements for Fluka kaolinite were done at -26°C , -30°C and -34°C , while the CMS kaolinite measurements were made at -30°C , -34°C and -38°C . At the highest temperatures used for measurements for both kaolinites, ice was generally not detected. Compared to Fluka kaolinite particles, the CMS kaolinite particles were less active for
395 ice nucleation in the water subsaturated regime, similar to what was observed for immersion freezing of particles in dilute solutions above water saturation.

Results for 300 nm Fluka, 300 nm CMS and 700 nm Fluka kaolinite share some features in the observed ice nucleation in the water subsaturated regime: (1) the uncoated kaolinite particles showed ice nucleation at a water vapor saturation ratio (S_w) below 0.95 clearly occurring at temperatures be-
400 low -34°C and even already at -30°C for the 700 nm Fluka kaolinite particles. (2) The coated particles examined here, which all had coating thicknesses above 0.5 nm, lost the ability to induce apparent deposition ice nucleation at S_w below 0.95. (3) These particles all started to induce ice at S_w above 0.95, with a steep increase in the measured ice fractions towards saturation. The following paragraphs will show that for these particles with coating thicknesses above 0.5 nm deposition ice
405 nucleation likely can not take place any more, but that instead the measurements follow quantitatively what can be expected when immersion freezing in a concentrated solution takes place.

It is known that soluble material in a solution lowers the ice melting temperature of that solution (ΔT_m) compared to pure water, and that this lowering depends on the concentration, i.e. on the water activity (a_w), of the solution. This lowering is reflected in a lowering of the homogeneous
410 freezing temperature (ΔT_{hom}). It was observed that there is a proportional relationship between ΔT_{hom} and ΔT_m , yielding the so called λ -approach: $\Delta T_{hom} = \lambda_{hom} \Delta T_m$. This approach has first been described by MacKenzie et al. (1977) and Rasmussen (1982) and was applied to model atmospheric homogenous freezing of droplets as early as in Sassen and Dodd (1988). Following Koop and Zobrist (2009) and literature citetd therein, λ_{hom} can be expected to be on the order of 2 to 2.5
415 for the soluble substances we examined in our study.

The λ -approach can be extended to solutions with immersed IN, as suggested already in DeMott (2002) and applied e.g. in Zuberi et al. (2002), Archuleta et al. (2005) and Koop and Zobrist (2009) (where the latter gives an overview of publications on this topic). The extended λ -approach results in a relationship between ΔT_m and the freezing point depression for heterogeneous freezing (ΔT_{het}):
420 $\Delta T_{het} = \lambda_{het} \Delta T_m$, where generally $1 < \lambda_{het} < \lambda_{hom}$.

For our study, values for ΔT_m vs. a_w were taken from Koop and Zobrist (2009). For the CFDC data, Köhler theory was used to convert S_w as adjusted during the measurements to a_w . This was done based on particle hygroscopicities known from the CCNc measurements. With these, the Köhler equation was solved separately for each particle type and at the different values of S_w at
 425 which CFDC measurements had been done. This yielded the Kelvin term (K) and the corresponding a_w (where $S_w = K \cdot a_w$). As the examined dry particles were already at least 300 nm and 700 nm in diameter, the Kelvin term was below 1.006 and 1.003, respectively, and the difference between S_w and a_w was correspondingly small.

For a coated kaolinite particle exposed to water vapor, the soluble material on the particle will dis-
 430 solve as soon as S_w in the surroundings is above the deliquescence point of the soluble material, and (providing equilibrium is reached) a solution with a_w close to S_w will then be present on the particle surface. For a_w of e.g. 0.95 (where $\Delta T_m = 5.3$, Koop and Zobrist, 2009), the respective solution will cause a ΔT_{het} of 10.6 K or 13.3 K for a λ_{het} of 2 or 2.5, respectively. Figure 6 illustrates what follows from this: the ice nucleation rates and likewise j_{het} need to be shifted to lower temperatures.
 435 j_{het} can be calculated based on Eq. (2), using the values of A and B as given in Fig. 4 and assuming that the ice nucleation takes place at a temperature which is increased by ΔT_{het} compared to the temperature of the surrounding. This causes j_{het} to be shifted in the direction of the arrow in Fig. 6. The black curve shows j_{het} for uncoated 300 nm Fluka kaolinite particles, based on the respective A and B given in Fig. 4. The curves in different shades of grey show this same curve for such particles
 440 immersed in solutions with $0.99 \leq a_w \leq 0.94$ for a λ_{het} of 2. The black vertical line indicates which values for j_{het} would be expected at -34°C for differently concentrated solutions, showing that e.g. at an a_w of 0.95, j_{het} is reduced by roughly three orders of magnitude.

For our further analysis, a combination of Eqs. (1) and (2), including the freezing point depression, was used:

$$445 \quad f_{ice}(a_w) = 1 - \exp(-A \cdot \exp(B \cdot (T + \Delta T_{het}(a_w)))s \cdot t) \quad (3)$$

The average values A_{Fluka} and B_{Fluka} were used, together with the residence time in the CFDC of 5 s, to calculate f_{ice} at -34°C for the 300 nm and 700 nm Fluka kaolinite particles, as a function of water activity. Results are shown in Fig. 7 as grey shaded areas (panels A and B). These areas cover results for λ_{het} between 1 (left edge) and 2.5 (right edge) and a grey line in their middle represents
 450 $\lambda_{het} = 1.7$. λ_{het} of 1 and 2.5 are a conservative lower and upper bound, where for $\lambda_{het} = 1$ it would be $\Delta T_{het} = \Delta T_{hom} = \Delta T_m$, and therefore this bound can be expected to underestimate the freezing point depression and likewise the suppression of freezing. A λ_{het} of 1.7 was chosen as this value was found in Zuberi et al. (2002) to fit their data for freezing of kaolinite and montmorillonite particles in aqueous solutions containing $(\text{NH}_4)_2\text{SO}_4$. Also shown in Fig. 7 in panels A and B is f_{ice} measured
 455 with the CFDC for medium and thickly coated particles with SuccA or LG coating.

The grey shaded areas now represent the range where freezing induced by the pure particles can be expected when they are immersed in a solution. And indeed, both the observed temperature range

and slope of the measured freezing behavior for the Fluka kaolinite particles coated with SuccA and LG are well captured. It should be noted here that the CFDC has an uncertainty in relative humidity of roughly 3 %, i.e. about 0.03 in water activity, so that measured and calculated values all agree within uncertainty.

It has to be noted here explicitly, that the parameters A_{Fluka} and B_{Fluka} determined from the immersion freezing are valid for the Fluka kaolinite in our experiments as long as it is not coated with H_2SO_4 , i.e. as long as it is not altered. Applying the above described model to Fluka kaolinite coated with H_2SO_4 or to CMS kaolinite requires use of the average values of A_{CMS} and B_{CMS} . When this is done, the red striped areas in Fig. 7 (panels C to E) are obtained. Again, a grey line represents results for $\lambda_{\text{het}} = 1.7$. For the Fluka kaolinite particles, the location of the red striped areas, compared to the grey areas, reflect the fact that these particles showed a reduced immersion freezing ability upon coating with H_2SO_4 , hence they are shifted to lower f_{ice} (or seemingly larger water activities).

When comparing the measured values for the two different groups of IN, indeed, the 300 nm Fluka kaolinite particles coated with either SuccA or LG show an increased freezing ability compared to these particles coated with H_2SO_4 (with or without additional water vapor). Such a clear difference in f_{ice} between SuccA and LG coating to the two coatings with H_2SO_4 is not seen for the 300 nm CMS kaolinite particles, where it would not have been expected. All in all, when considering the above mentioned measurement uncertainty of the CFDC and including all particles and coatings, measured and calculated values are well in agreement within uncertainty in the examined λ_{het} range and even with λ_{het} of 1.7. Unfortunately, the measurement uncertainties do not allow for a more constrained determination of λ_{het} .

Our results support that particles with medium thick and thick coatings examined in our study did not show deposition ice nucleation behavior any more, in the whole range of $S_w < 1$. At relative humidities below the deliquescence point of the coating material, ice nucleation sites were covered and freezing was inhibited. Above the deliquescence relative humidity, additional water was added to the coating and a solution shell formed around the particles, causing them to rather nucleate ice from concentrated solutions via the immersion freezing pathway. The solutions were so concentrated that immersion freezing was quenched due to freezing point depression. This is well in line with observations reported in Archuleta et al. (2005), Eastwood et al. (2009) and Sullivan et al. (2010a), where it was concluded for the heterogenous freezing of coated particles in the water vapor subsaturated range that freezing could only be initiated once the coating was dissolved.

An open issue is, why also SuccA, a slightly soluble substance, seems to form a solution at water activities below 0.99, where it should not dissolve. Deliquescence relative humidity (DRH) of SuccA is 0.99% at room temperature (Wex et al., 2007) and can be expected to be lower in our experiments due to a decrease of solubility of SuccA with temperature. However, as stated above, likely the applied coatings were not the only soluble materials on the particle surfaces. Mixtures tend to deliquesce at lower S_w than the pure substances (Marcolli et al., 2004), and the co-existence

495 of the coating material with impurities on the kaolinite surfaces might be an explanation for the observations. Another explanation would be that during the coating SuccA did not condense in its crystalline form, but in a glassy state. In this case, deliquescence of the coating might have occurred at a lower DRH than if the SuccA had been crystalline (Mikhailov et al., 2009).

Figure 8 shows the relation of S_w to the water vapor saturation ratio above ice (S_i) as function
500 of temperature, in a way which is typical for displaying results particularly for deposition ice nucleation. A black, grey and light grey line correspond to S_w of 1, 0.9 and 0.8, respectively. For reference, a green line is shown for homogeneous freezing of solution droplets taken from Koop et al. (2000). Furthermore, lines are inserted which are based on the above presented parameterization (Eq. (3)) for 300 nm and 700 nm Fluka kaolinite particles with SuccA or LG coatings, assuming
505 a λ_{het} of 1.7. The lines correspond to a frozen fraction (f_{ice}) of 0.1 % and 1 %. These lines and the one for $S_w = 1$ limit the range in which the above described effect, i.e. immersion freezing of concentrated solution droplets, can occur in our study. This range will become larger for larger nucleation rates ($j_{\text{het}} \cdot s$), i.e. either for larger particles (as can e.g. be seen by comparing the data for 300 nm and 700 nm in Fig. 8), or for more ice active IN (e.g biological IN, see Murray et al.,
510 2012). Deposition ice nucleation can still occur within this range when a potential IN is not completely coated. However, in literature the range of freezing onsets (temperature and S_w) reported for deposition ice nucleation is very large for any one IN particle type (Hoose and Möhler, 2012), and besides instrumental and experimental issues, some of this scatter might be explained by wrongly attributing immersion freezing in concentrated solutions to deposition ice nucleation instead.

515 The above described results support the hypothesis that condensation and immersion freezing (i.e. the ice nucleation of an insoluble core immersed in a haze particle or in a diluted droplet) might basically be the same process, with the only distinction that a freezing point depression has to be accounted for in the subsaturated regime (i.e. for the haze particles). Eq. (3) (and likely also other temperature dependent parameterizations, see e.g. App. B) could be used to describe both, the freezing
520 of droplets consisting of either concentrated or of dilute solutions with an immersed ice nucleus, where only care has to be taken to include the freezing point depression for the concentrated solutions correctly, whereas $\Delta T_{\text{het}} = 0$ for diluted solutions. In e.g. Khvorostyanov and Curry (2004) it is argued that atmospheric IN are not necessarily insoluble but that rather a significant fraction is mixed with soluble material, motivating the development of a model describing “deliquescent-
525 heterogenous freezing” following a concept comparable to the one we used here. Recently, Knopf and Alpert (2013) developed a model for describing immersion freezing of water and aqueous solution droplets, depending on the suspended IN types and a_w , similar to an approach given in Koop and Zobrist (2009). In principle, this approach is comparable to the approach described in the present study, and in App. C this is discussed in more detail. It hence is not a new idea when we argue that
530 condensation and immersion freezing are similar, but by including a comparison of measured and modeled data for both, the sub- and supersaturated regime, we corroborated this assumption. Future

work should aim at testing our hypothesis, making maybe a discrimination between the two modes, condensation and immersion freezing, unnecessary.

4 Summary and conclusions

535 In the present study, we examined immersion freezing and ice nucleation in the water subsaturated regime for size segregated particles from two types of kaolinite, provided by Fluka and CMS. Pure particles were examined, and also particles with coatings of below up to a few nanometers of sulfuric acid (H_2SO_4), succinic acid (SuccA) and levoglucosan (LG). Freezing measurements were done using two different instruments, LACIS (Hartmann et al., 2011) and a CFDC (DeMott et al., 2010),
540 where both instruments measured in the water supersaturated regime, while deposition ice nucleation or other mechanisms possible in the water subsaturated regime were only examined by the CFDC.

Frozen fractions observed by the two instruments in the immersion freezing regime differed, being seemingly apart by up to 2 K. However, when considering a time dependence of the freezing process based on a stochastic approach, i.e. when comparing nucleation rate coefficients, these differences
545 were diminished, i.e. the data observed by LACIS and the CFDC were in good agreement. However, as we used a simple formulation for describing the time dependence of the nucleation rate coefficients, our approach may not be generally valid for all types of IN. For example, in Broadley et al. (2012) heterogenous freezing induced by NX-illite particles could not be characterized by a single component stochastic model but instead by either a multi component stochastic model or a deterministic model. Also, DeMott et al. (2014) discuss other instrumental factors for the CFDC that require
550 clarification before all caveats may be removed in interpreting data from this instrument stochastically. Therefore, data analysis in this study was also done using a deterministic approach and it was found that both, the time dependent and the deterministic approach yielded the same results.

Our results concerning the IN ability of the pure minerals corroborate earlier findings, i.e. CMS
555 kaolinite generally was found to be less ice active than Fluka kaolinite in both, immersion freezing and in deposition ice nucleation, and deposition ice nucleation generally was found to be the less effective heterogenous freezing process, compared to immersion freezing.

In case of immersion freezing, the organic coatings used in our study did not reduce the IN ability of either kaolinite, i.e. these coatings did not alter the surface of the particles irreversibly and formed
560 a very dilute solution when the particles were activated to droplets prior to freezing. On the other hand, H_2SO_4 coatings did reduce the IN ability of the Fluka kaolinite remarkably, but left the IN ability of the CMS kaolinite almost unchanged. This observation could potentially be explained by attributing the higher IN ability of the Fluka kaolinite to its content of potassium feldspar, a mineral which is not present in the CMS kaolinite and which likely is destroyed on contact with H_2SO_4 .
565 This hypothesis aligns with a recent publication by Atkinson et al. (2013), where potassium feldspar was found to be the most important mineral dust for atmospheric ice nucleation.

Ice nucleation at below water saturation was found to be impeded by all coatings with coating thicknesses above 0.5 nm for S_w below about 0.95, while at $S_w \geq 0.95$ a steep increase in the observed freezing was seen. Consistent with previous hypotheses, we showed that these observations
570 can be explained by assuming that deposition ice nucleation likely does not take place any more for the examined particles, but that instead the measurements follow what can be expected when immersion freezing in a concentrated solution takes place. The coatings examined in this case correspond to a hygroscopicity parameter κ of the overall dust particle of about 0.05, showing that the amount of soluble material present on a particle which suffices to hinder deposition ice nucleation is small.
575 This might explain some of the observed scatter in the data for deposition ice nucleation reported in literature in the past, i.e. some of the observation might not have been deposition ice nucleation but immersion freezing in a concentrated solution, instead. This also points towards the possibility that deposition ice nucleation might play an even smaller role in atmospheric processes than so far expected.

580 The fact that the parameterization we derived for the immersion freezing regime could also be used to model the freezing behavior of the IN immersed in concentrated solution droplets indicates that maybe all freezing processes which include a (more or less concentrated) solution shell which formed around an IN prior to freezing might be treated as being the very same process. The term immersion freezing has generally been used for all cases when an insoluble particle is immersed
585 in a diluted droplet, and e.g. Koop and Zobrist (2009) and Hoose and Möhler (2012) additionally used it for immersion freezing in (more concentrated) aqueous solutions. Although the definition of condensation freezing has previously been less well defined, we argue that this should include all cases when an insoluble particle is immersed in a concentrated solution (i.e. in the case of haze particles), which principally can occur for $S_w < 1$ as long as the deliquescence RH of the soluble
590 material which was on the insoluble core prior to forming a solution is overcome. We show in the present study, that these two heterogenous freezing modes, i.e. condensation and immersion freezing, can be treated similarly, only by accounting for a freezing point depression for the haze particles. This potentially reduces the number of heterogenous freezing processes which need to be considered separately in atmospheric models to three, namely deposition ice nucleation, contact
595 freezing and the here examined condensation/immersion freezing. This is in line with what was already said by Fukuta and Schaller (1982), i.e. that there are three main mechanisms of heterogenous ice nucleation.

Appendix A

Fukuta and Schaller (1982) wrote that there "are presently three main mechanisms of heterogeneous
600 ice nucleation known by aerosol particles - deposition, condensation-freezing including immersion
freezing, and contact-freezing". Nevertheless they try to distinguish between condensation and im-
mersion freezing as follows: "In the process of condensation-freezing nucleation, liquid water forms
on the ice nucleus surface before freezing nucleation takes place in it. If the liquid has existed for
some time on the nucleus surface before the freezing nucleation starts, the process is considered as
605 immersion-freezing." Vali (1985) listed four different heterogeneous ice nucleation mechanisms and
distinguished between condensation and immersion freezing, defining immersion freezing as "nucle-
ation of supercooled water by a nucleus suspended in the body of water", where the "body of water"
is not defined more precisely and could hence include both, diluted droplets as well as haze particles
(with haze particles being particles with at least some soluble material on them, which are in an envi-
610 ronment where the relative humidity (RH) is above the deliquescence RH of the soluble material but
below the value needed for activation to a cloud droplet, see also Vali (1985)). Also following Vali
(1985), condensation freezing occurs when "a cloud condensation nucleus (CCN) initiates freezing
of the condensate". However, no further refinement of the definition is given, e.g. with respect to the
amount of the condensate. It should also be pointed out here that this definition overlaps with the one
615 for immersion freezing as cloud droplet activation is one way of getting a nucleus suspended in wa-
ter. Following Pruppacher and Klett (1997) (p. 309 in the second edition), where also four distinct
modes are described for heterogeneous ice nucleation, condensation freezing denotes the process
during which an IN is activated to a droplet below 0°C and subsequently freezes (it is not clarified
if this happens with or without further cooling), while during the immersion freezing process the IN
620 enters the droplet above 0°C and the droplet then freezes once it is cooled sufficiently. A schematic
in Hoose and Möhler (2012) (Fig. 1 *ibidem*) suggests that immersion freezing represents a process
by which a droplet with an immersed IN freezes upon further cooling (seemingly independent from
the temperature at which the droplet formed). Condensation freezing in this schematic is indicated as
a process during which condensation of water onto the IN occurs at water vapor saturation, leading
625 to ice nucleation possibly upon further cooling. A separate process is indicated in this schematic as
"immersion freezing of solution droplets" (i.e. haze particles).

Appendix B

Data in this study has been evaluated and interpreted based on Eq. (1), i.e. using an stochastic
approach. Here, now, it is shown how it influences the results of our study when a deterministic

630 approach (surface site densities n_s) is used instead:

$$f_{\text{ice}} = 1 - \exp(-n_s \cdot s) \quad (\text{B1})$$

Fig. B.1 is a reproduction of Fig. 2, additionally showing data for n_s in the two lowest panels, obtained using Eq. (B1). As before, for each of the 19 different particle types CFDC and LACIS data were always combined to one dataset, and fitted using $n_s = A' \cdot \exp(B' \cdot T)$. The corresponding fit is shown as a grey line in the two lower panels of Fig. B.1. For the two particle types shown in Fig. B.1 and also for all others, the slope of n_s versus temperature is slightly less steep than that of j_{het} .

A' and B' for all 19 different particle types are shown in Fig. B.2. This figure is comparable to Fig. 4, only now the fit parameters describe n_s instead of j_{het} . Grouping of the data is similar as observed for j_{het} , i.e. similar values of A' and B' are obtained for all Fluka kaolinite particles which were either uncoated or coated with SuccA or LG, and others but again similar values of A' and B' are obtained for all CMS kaolinite particles and Fluka kaolinite particles which were coated with sulfuric acid (with or without water vapor). Grey lines in Fig. B.2 represent average values for A' and B' for these two groups ($A'_{\text{Fluka}} = 5.07 \times 10^4 \text{ m}^{-2}$, $B'_{\text{Fluka}} = -0.44 \text{ }^\circ\text{C}^{-1}$, $A'_{\text{CMS}} = 0.00127 \text{ m}^{-2}$ and $B'_{\text{CMS}} = -0.91 \text{ }^\circ\text{C}^{-1}$).

These average values of A' and B' obtained for the two groups were used to estimate the freezing that should be observed for sub-saturated conditions, with an equation based on Eq. B1 together with a freezing point depression:

$$f_{\text{ice}}(a_w) = 1 - \exp(-A' \cdot \exp(B' \cdot (T + \Delta T_{\text{het}}(a_w))) \cdot s) \quad (\text{B2})$$

650 Fig. B.3 shows the respective results, comparable to what was obtained when the data analysis was based on j_{het} (see Fig. 7). Measured values (symbols) again agree with the calculated ones (see grey and red striped areas) within measurement uncertainty. Hence, results are similar to those described in the main body of the text, i.e. the ice nucleation observed at sub-saturated conditions for particles immersed in a concentrated solution droplet can be described using a parameterization of the observed immersion freezing when regarding for the freezing point depression caused by the solution.

Overall, the same results are obtained, based on our measured data, no matter if the data evaluation is based on a stochastic approach (j_{het}) or a deterministic one (n_s).

Appendix C

660 In the present study, we described the ice nucleation induced by kaolinite particles in concentrated solution droplets by using a parameterization obtained from immersion freezing measurements, together with a temperature shift that depended on the melting point depression, and thus water activity

of the solution. This method has been applied by a number of previous investigators, as summarized by Koop and Zobrist (2009). Koop and Zobrist (2009) and studies referenced therein also compared
665 and contrasted this approach to one directly relating immersion freezing nucleation rate to the water-activity of solution droplets in dependence on the type of ice nucleus.

Knopf and Alpert (2013) have now comprehensively examined to what extent it is possible to model immersion freezing based on a_w . Fig. C.1 reproduces a part of Fig. 4 A from Knopf and Alpert (2013) and shows nucleation rate coefficients j_{het} as a function of Δa_w , where Δa_w is the
670 observed shift in a_w between the melting curve and the measurement. Fig. C.1 shows data for CMS kaolinite particles measured by Murray et al. (2011) and Pinti et al. (2012) and an additional linear fit through the data, as given in Knopf and Alpert (2013). Additionally included are CFDC data measured in our study for coated particles at water subsaturated conditions, separately for coated
300 nm CMS and Fluka kaolinite particles in the left and right panel of Fig. C.1.

Data for coated CMS kaolinite particles are close to or even overlay both the data from Murray et al. (2011) and Pinti et al. (2012). This also applies for data for Fluka kaolinite particles when they are coated with H_2SO_4 (with and without water vapor). Data for Fluka kaolinite particles coated with either succinic acid (SuccA) or levoglucosan (LG) show somewhat larger values for the nucleation rate coefficient j_{het} with a tendency to form a group of their own. This corroborates the
680 results obtained in our study: a parameterization describing coated CMS kaolinite also represents Fluka kaolinite particles well when they have been chemically altered due to a coating with H_2SO_4 . On the other hand, Fluka kaolinite particles coated with either SuccA or LG are better described by a separate parameterization, due to their larger ice nucleation ability. A need for different parameterizations for different particle types can also be inferred from Fig. 4 of Knopf and Alpert (2013),
685 where different types of IN presented in different panels (kaolinite, aluminum oxide, iron oxide and fungal spores) show a different dependency of j_{het} on Δa_w .

This all corroborates what was found earlier by, e.g. Koop and Zobrist (2009) and Knopf and Alpert (2013) and again in this study, i.e. that immersion freezing of solution droplets can be modeled when a_w is known, based on a parameterization of j_{het} for the respective type of IN.

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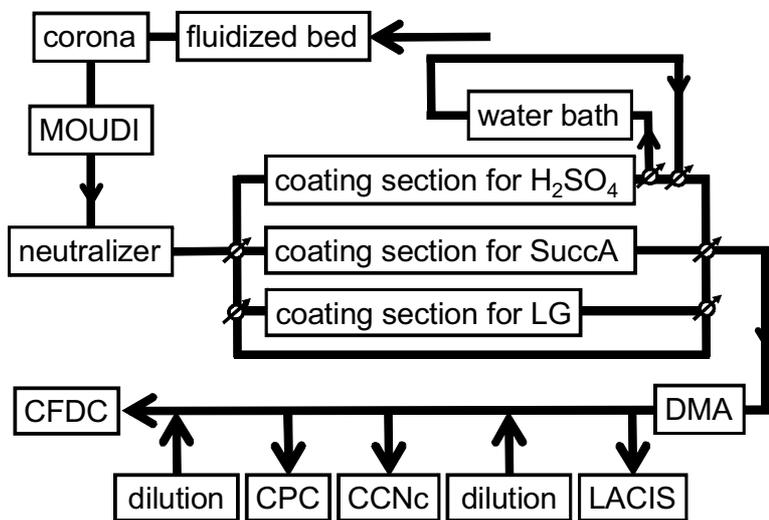


Fig. 1. Set-up of the particle generation.

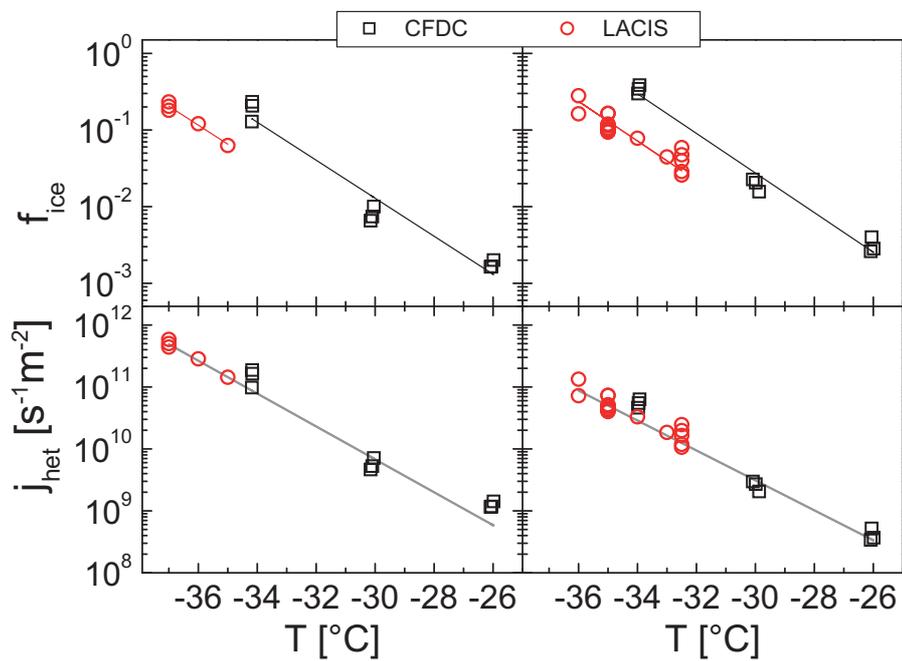


Fig. 2. Measured f_{ice} and derived j_{het} for CFDC (at $104\% \leq RH_w \leq 106\%$) and LACIS (i.e. for immersion freezing) for two particle types. Left panels: 300 nm Fluka kaolinite coated with LG at 80 °C; right panels: 700 nm Fluka kaolinite (no coating).

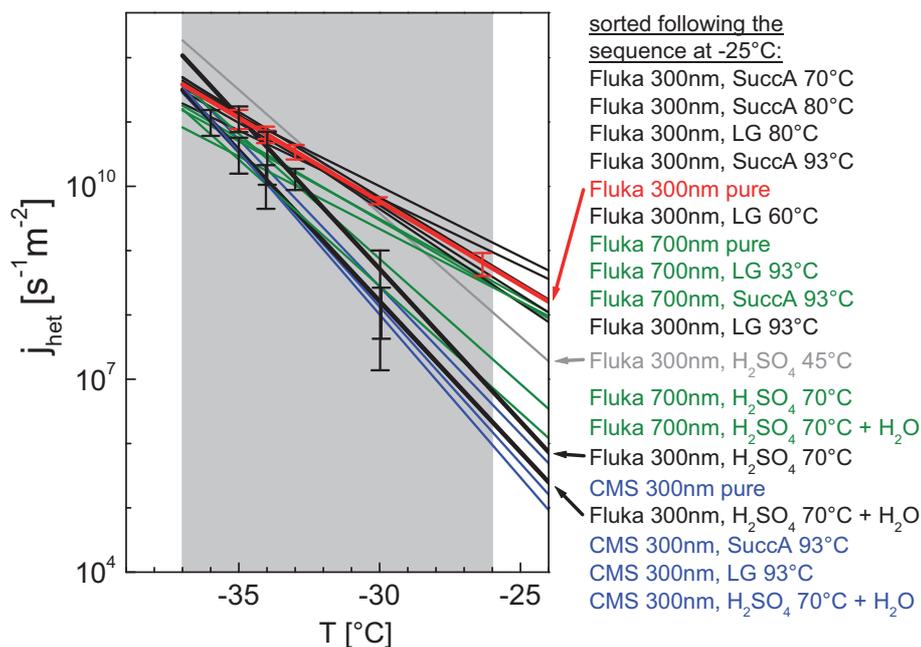


Fig. 3. Fitting curves for j_{het} for the different particle types, following Eq. (2). Corresponding values of the fit parameters A and B are shown in Fig. 4. j_{het} for pure 300 nm Fluka kaolinite particles is shown in red, while black lines show j_{het} for coated 300 nm Fluka kaolinite particles. A grey line indicates 300 nm Fluka kaolinite particles coated with H₂SO₄ at 45°C coating temperature. Pure and coated 700 nm Fluka kaolinite are shown in green, while blue lines depict j_{het} for all CMS kaolinite particles. Error bars are given exemplarily for the red line and two black lines (for particle type see legend to the right of the plot).

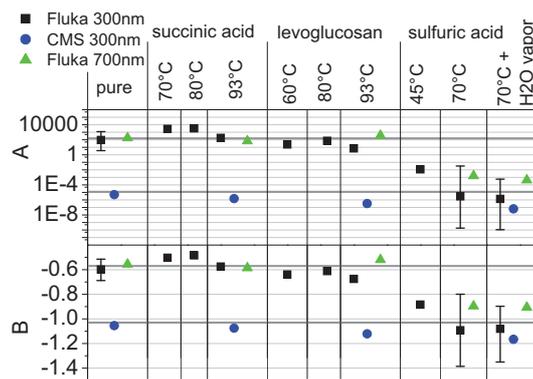


Fig. 4. Overview over fit parameters A and B for j_{het} for the different particle types. Error bars are given for the same datasets for which they were shown in Fig. 3. Grey horizontal lines give the average values for A_{Fluka} , B_{Fluka} , A_{CMS} and B_{CMS} as given in the text.

Table 1. Effective coating thicknesses, derived assuming spherical particles with a homogenous coating. (Dots indicate, if data for particles with the respective coating are presented in Fig. 5. Two dots indicate that data is displayed at both temperature shown there, one dot indicates that data was only measured at the lowest temperature at which measurements were made.)

| type of coating | Fluka-kaolinite, 300 nm coating thickness [nm] | CMS-kaolinite, 300 nm coating thickness [nm] | Fluka-kaolinite, 700 nm coating thickness [nm] |
|------------------------------------|---------------------------------------------------|-------------------------------------------------|---------------------------------------------------|
| H₂SO₄ | | | |
| 45 °C | 0.44 | | |
| 70 °C | 1.32 • | 0.87 •• | 0.87 • |
| 70 °C + H ₂ O | 1.77 • | 1.48 • | 1.57 |
| LG | | | |
| 60 °C | 0.20 | | |
| 80 °C | 1.36 •• | | |
| 93 °C | 3.27 •• | 1.85 • | 1.22 •• |
| SuccA | | | |
| 70 °C | 0.11 | | |
| 80 °C | 0.54 •• | | |
| 93 °C | 4.78 •• | 3.17 •• | 1.58 •• |

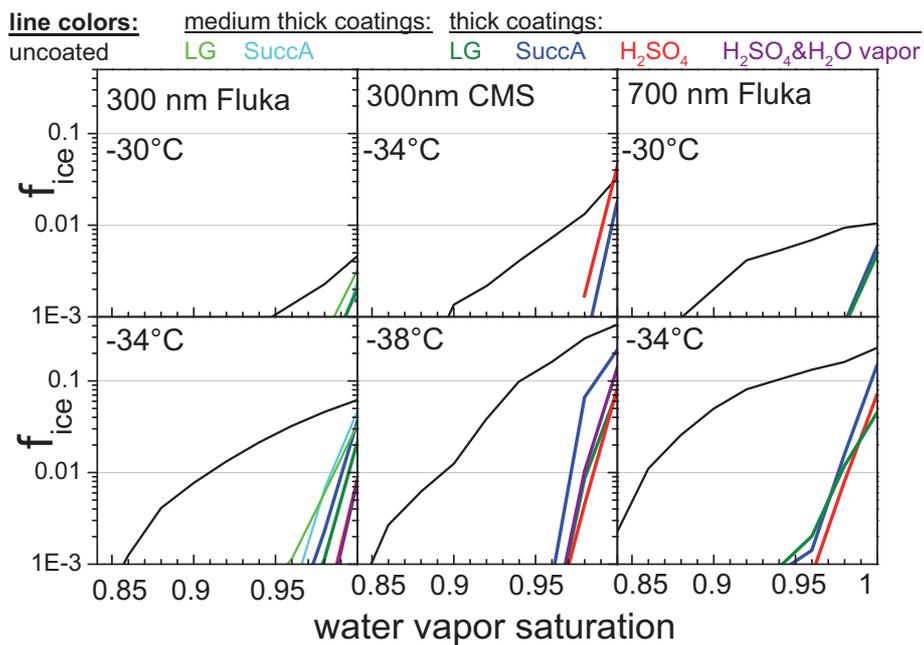


Fig. 5. f_{ice} measured with the CFDC for $S_w < 1$. Thinner lines indicate medium thick coatings, thicker lines represent thick coatings. The type of coating is indicated by colors, the color coding can be seen above the panels. Some lines cover others, therefore it is additionally indicated in Table 1, for which of the particle types deposition ice nucleation was detected and is hence shown here.

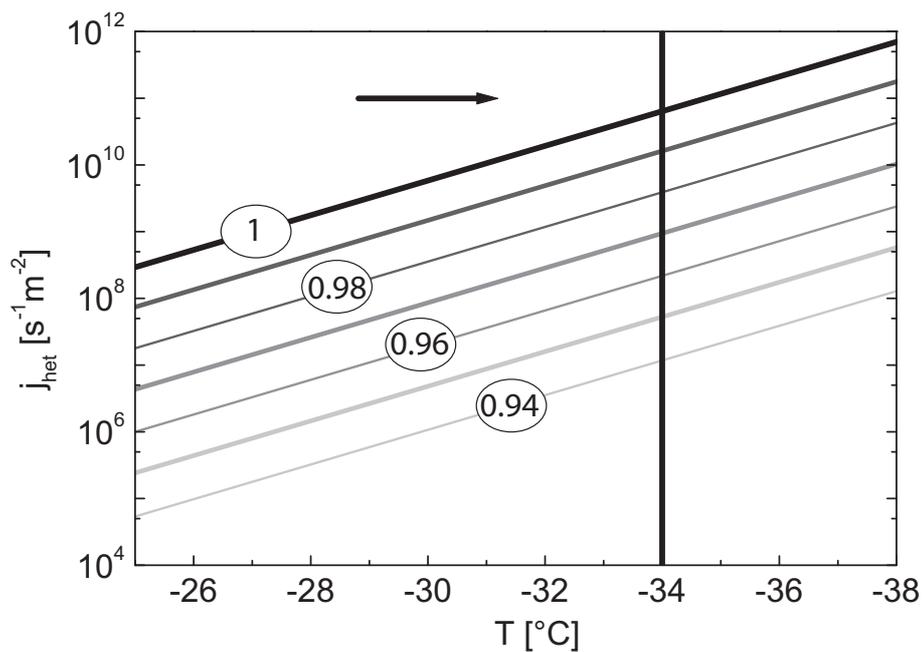


Fig. 6. j_{het} estimated for different water activities a_w in a solution droplet surrounding a particle. The black line labeled "1" is the one for the uncoated 300 nm Fluka kaolinite particles. The different grey lines indicate the curves for j_{het} for such particles immersed in a solution with $0.94 \leq a_w \leq 0.99$ (values for a_w indicated on every other line). The vertical black line at -34 $^{\circ}\text{C}$ was drawn as a guide for the eye, to indicate how much j_{het} changes for different a_w at a fixed temperature (i.e. when measurements were done at a fixed temperature but for differently concentrated solutions).

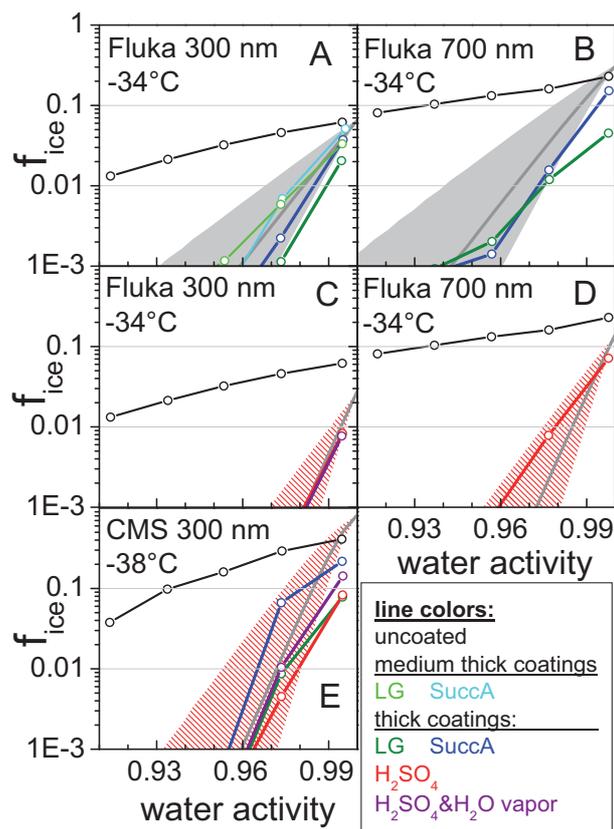


Fig. 7. Measured f_{ice} for deposition ice nucleation and expected ice nucleation behavior for particles which are completely coated by a solution (grey areas for Fluka kaolinite coated with SuccA or LG, and red striped areas for CMS kaolinite and Fluka kaolinite coated with H_2SO_4). The color code for the measured data with respect to the type of coating is similar to that used in Fig. 5.

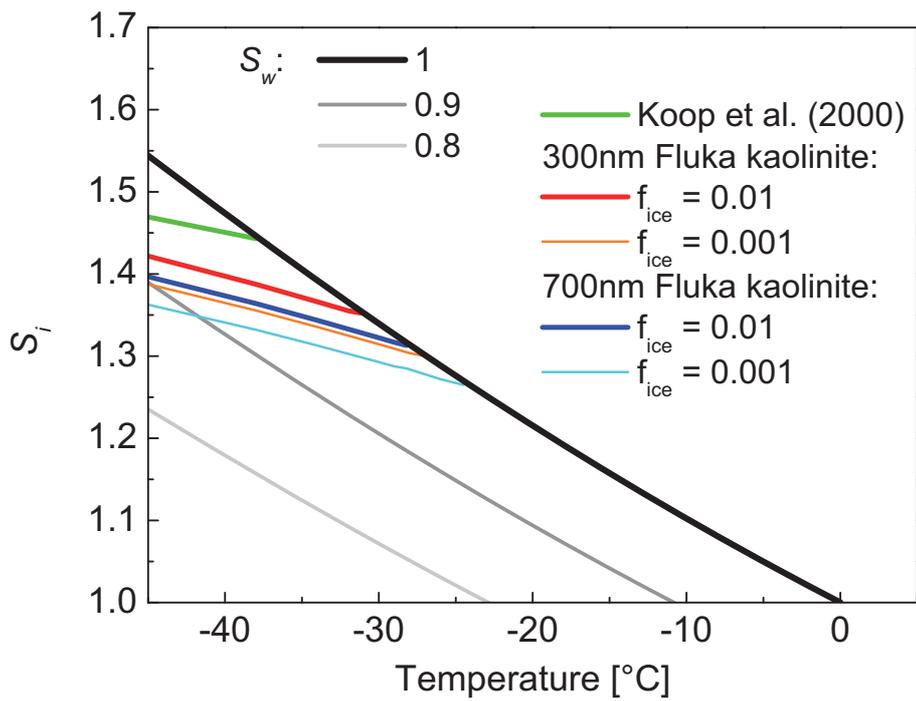


Fig. 8. The plot shows the relation between the water vapor saturation ratio above ice (S_i) to that above water S_w . Lines are shown for S_w of 0.8, 0.9 and 1. Also shown is a line for homogeneous freezing taken from Koop et al. (2000) and lines indicating an f_{ice} of 1% and 0.1% for the 300 and 700 nm particles with SuccA or LG coating examined in this study, calculated using Eq. (3).

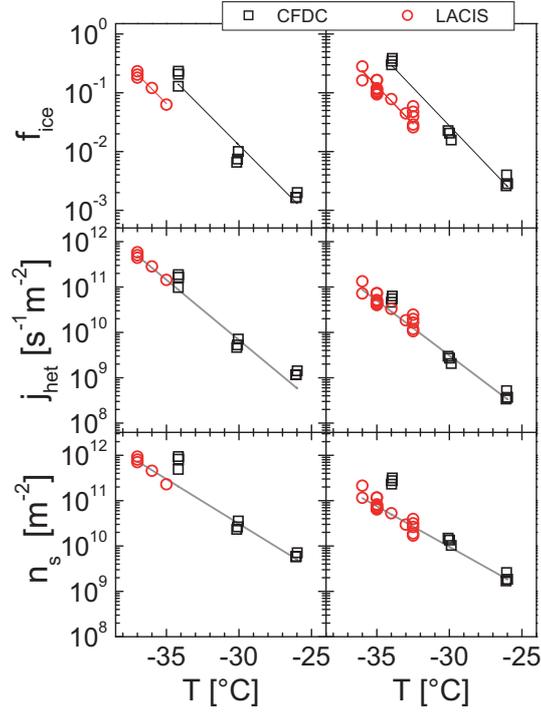


Fig. B.1. Measured f_{ice} and derived j_{het} for CFDC (at $104\% \leq RH_w \leq 106\%$) and LACIS (i.e. for immersion freezing) for two particle types. Left panels: 300 nm Fluka kaolinite coated with LG at 80 °C; right panels: 700 nm Fluka kaolinite (no coating).

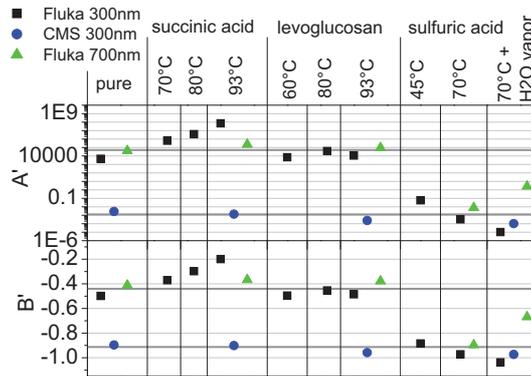


Fig. B.2. Similar to Fig. 4 in the main text, but values for A' and B' were obtained by fitting n_s obtained from measured f_{ice} . A separate fit was done for each of the 19 different particle types, each time accounting for all data available from both LACIS and the CFDC. Similar to the fit done for j_{het} , the following equation was used: $n_s = A' \cdot \exp(B' \cdot T)$.

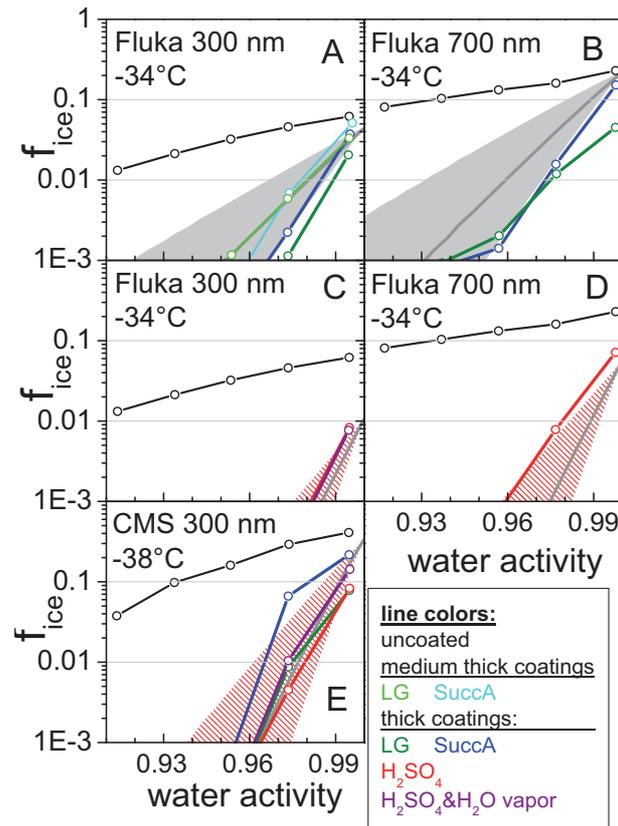


Fig. B.3. Similar to Fig. 7 in the main text, i.e. showing measured f_{ice} for deposition ice nucleation and expected ice nucleation behavior for particles which are completely coated by a solution. The difference to Fig. 7 is, that the calculations done to obtain the grey and red striped areas were based on average values for A'_{Fluka} , B'_{Fluka} , A'_{CMS} and B'_{CMS} as shown in Fig. B.2, i.e. based on n_s , and on Eq. B1.

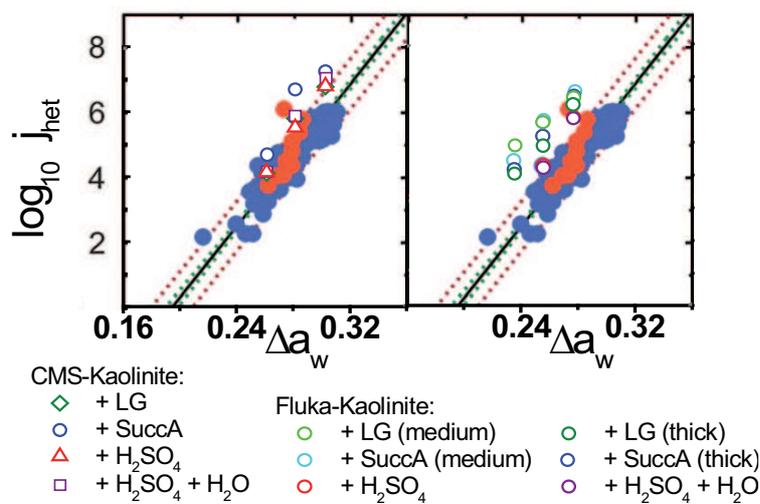


Fig. C.1. This figure reproduces a part of Fig. 4 A from Knopf and Alpert (2013), showing data from Murray et al. (2011) (filled blue dots) and Pinti et al. (2012) (filled red dots). The solid black line is a linear fit through the data, the dashed green and red lines represent confidence intervals and prediction bands, respectively, at a 95% level, as calculated by Knopf and Alpert (2013). The figure additionally includes the data measured in our study for coated particles with the CFDC for water subsaturated conditions. The left and right panel include data for 300 nm CMS and Fluka kaolinite, respectively. The figure is discussed in the text in this supplement.