

## Our answer to the review by the anonymous Referee #2 on our manuscript:

Wex et al. "Kaolinite particles as ice nuclei: learning from the use of different types of kaolinite and different coatings"

Dear Referee!

We thank you for your comments and suggestions. In the following, your review text is given in italic letters, while we used regular letters for our answers. Text which now appears in the manuscript is given in quotation marks ("..."). We changed the sequence of your comments regarding the issue of the definition of freezing modes: you commented on that several times and we address all of the respective comments first, in our answers below, before then addressing all your other comments in the sequence as you made them.

*In this study, kaolinite samples from two different sources (Fluka and CMS) were examined with respect to their ability to act as ice nuclei. Kaolinite particles were either investigated uncoated or with levoglucosan, succinic acid or sulfuric acid coatings. Measurements were carried out with two different setups (CFDC and LACIS) in subsaturated and supersaturated conditions with respect to water. The observed heterogeneous freezing of the coated particles below water saturation is interpreted as immersion freezing of solution droplets. This study provides an important contribution to the understanding of heterogeneous ice nucleation of coated particles. The authors have performed a profound evaluation of the data. Nevertheless, there are some questions regarding the evaluation procedure that should be resolved prior to publication in ACP (see general and specific comments). Also, I think that the new definition of condensation freezing proposed by the authors is not needed and might lead to more confusion than a clarification.*

General comments:

*I have a mature concern with the way condensation freezing is first redefined in the introduction section and then – based on this new definition – rejected as a separate nucleation mode in the summary and conclusions section. The generally accepted view of condensation freezing refers to the sequence of events of condensation of liquid water on an IN directly followed by freezing (e.g. Fukuta and Schaller, J. Atmos. Sci., 39, 648-655, 1982). It is thought to occur when starting from subsaturated conditions, water saturation or supersaturation is reached. This is in contrast to the new definition suggested in this article, where condensation freezing is considered to occur below water saturation in haze droplets. It might be the case that condensation freezing is a special case of immersion freezing with a comparable nucleation efficiency, but this conclusion should not be reached by the artifice of a redefinition of condensation freezing.*

and

*Page 30314, lines 2-14: This seems to be a new definition of condensation freezing (see general comments). I advise the authors to stick to the common notion of condensation freezing and to use for heterogeneous freezing of solution droplets containing an IN the term immersion freezing (of solution droplets) as has been done in other studies before (e.g. Hoose and Möhler (2012); Zobrist et al., 2006, Atmos. Chem. Phys., 6, 3115–3129; Zobrist et al., 2008, J. Phys. Chem. A, 112, 3965-3975; Koop and Zobrist, 2009).*

and

*Page 30331, lines 15-17: The second part of this sentence should be removed (see general comments).*

and

*Page 30333, line 18 - page 30334, line 2: I do not agree with the statement that the term immersion freezing has so far been reserved for insoluble particles immersed in diluted droplets. Hoose and Möhler (2012), Zobrist et al. (Atmos. Chem. Phys., 6, 3115–3129, 2006), Zobrist et al., (J. Phys. Chem. A, 112, 3965-3975, 2008) and Koop and Zobrist (2009) have used the term immersion freezing for dilute and concentrated solutions. I agree with the authors that there is indeed no need to distinguish between immersion freezing of dilute and concentrated solutions and that for both cases the term immersion freezing should be used. The term condensation freezing should therefore be kept for the process that implies the sequence of condensation of liquid water and freezing (see general comments).*

You are correct when stating that the term immersion freezing has been used for immersion freezing of solution droplets before. Therefore, concerning the last of your above comments, a part was added to the sentence you refer to (repeated below in blue print):

“The term immersion freezing has generally been used for all cases when an insoluble particle is immersed in a diluted droplet, and e.g. Koop & Zobrist (2009) and Hoose & Möhler (2012) additionally used it for immersion freezing in (more concentrated) aqueous solutions.”

However, we do not agree that the terms immersion and condensation freezing have been well defined in the past. In e.g. Fukuta & Schaller (1982), the difference between the two depends on a time span, the length of which is left undiscussed (“if the liquid has existed for some time ..., the process is considered as immersion-freezing.”) In Pruppacher & Klett (1997), the difference between these two modes is defined based on whether a droplet is nucleated on an IN above or below 0°C. And there are other definitions.

Therefore, we added a section to the appendix (Appendix A) in which we explicitly describe how immersion and condensation freezing have been described in the past by different authors (Fukuta & Schaller (1982), Vali (1985), Pruppacher & Klett (1997) and Hoose & Möhler (2012)), clearly showing that there indeed is a lack of a clear definition. (The Appendix added newly to the manuscript, which includes this and other texts is attached at the of this review.)

It is correct that we define condensation freezing in the introduction of our manuscript and later redefine it as “immersion freezing of concentrated solution droplets”. Our definition of condensation freezing closely follows that given in Vali (1985), where condensation freezing is said to occur when “a CCN initiates freezing of the condensate”. Also, we feel that we cannot use the term “immersion freezing of a concentrated solution” until we show that this is reflected in our results. Therefore we stick to the definition we used previously.

And finally, as can be read in Appendix A, already Fukuta & Schaller (1982) mentioned that there “are presently three main mechanisms of heterogeneous ice nucleation known by aerosol particles - deposition, condensation-freezing including immersion freezing, and contact-freezing”. Based on that, we added as finishing line at the end of the “Summary and Conclusion”:

“This is in line with what was already said by Fukuta & Schaller (1982), i.e. that there are three main mechanisms of heterogeneous ice nucleation.”

Other than the here mentioned additions, nothing was changed.

*General comments continued:*

*Another major point is the application of a stochastic approach to the Fluka kaolinite. This approach might be well justified for the CMS kaolinite but not for the Fluka kaolinite sample. Pinti et al. (2012) observed more than one freezing peak for this kaolinite sample for emulsions investigated by DSC. Moreover, Atkinson et al. (2013) revealed that this sample contained 5% feldspar which might be responsible for a frozen fraction < 5%. All these facts are discussed in the manuscript. Nevertheless, a stochastic formulation of the nucleation rate is applied for the analysis of the data. This seems to be inconsistent.*

Following your remark, we added a section in the appendix (Appendix B), where it is shown, that the deterministic approach yields the same results as the approach we had already used previously (see Appendix attached to the end of this review), and we also added the following text (in the section following equation 1):

“For Fluka kaolinite, Pinti et al. (2012) reported two separate heterogeneous freezing peaks for measurements done with a differential scanning calorimeter. Wheeler & Bertram (2012) examined the onset of freezing 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 Appendix B the same data will be shown additionally when evaluated based on a deterministic approach.”

*The physical basis of Eq. 2 ( $J_{het} = A \exp(BT)$ ) is unclear. It seems to be just a fitting function and does not show the temperature dependence expected for an activated process given by the Arrhenius equation ( $J_{het} = A \exp(-B/kT)$ ). Nevertheless, this equation*

*is inserted in Eq. 3 as if it described a physical correct temperature dependence of the nucleation rate. In view of this shortcoming, an analysis of the data as suggested in the comment from Alpert and Knopf is highly recommended.*

You are correct, and it has been explicitly stated in the manuscript, that this is just a fitting function. It can be seen in Figure 2 of the manuscript discussed here, that this simple fitting function is clearly capable of fitting nucleation rate coefficients in the whole range in which measurements were made. Also, we have successfully used this approach in the past to describe nucleation rates for biological ice nuclei which then reproduced measured data well (Hartmann et al., ACP, 2013 and Augustin et al., ACP, 2013). Augustin et al. (2013) also gave a comparison of the performance of this approach with that of Classical Nucleation Theory (CNT) together with a single contact angle or with a contact angle distribution, where this approach performed almost as well as the latter.

This justifies the use of this simple approach to describe nucleation rate coefficients, also when using it e.g. for the determination of frozen fractions using Eq. 3. The following text was added to the manuscript, following Eq. 2:

“It should also be added, that the approach of parameterizing  $j_{\text{het}}$  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  $j_{\text{het}}$  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)).“

Concerning an analysis following the comment from Alpert and Knopf, Figures similar to Fig. 2 in that comment (i.e. similar to Fig. 4A in Knopf and Alpert (2013)) are now shown and discussed in the appendix (Appendix C), showing both data for CMS kaolinite and Fluka kaolinite and how they compare with the kaolinite data from Murray et al. (2011) and Pinti et al (2012). Conclusions which can be drawn from these figures are similar to the conclusions we reach with our analysis.

*Specific comments:*

*Page 30314, lines 13- 14: also refer to the recent review by Ladino et al. (Atmos. Chem. Phys., 13, 9745–9769, 2013) about contact freezing.*

done

*Page 30317, lines 12-17: Can you comment on the effect of the discharger? This might be interesting information for other groups using similar setups.*

We tested our particle generation set-up in the past, producing particles when the corona discharger was turned on or off, and the number of particles we produced increased when the corona was turned on. We explain this with the fact that particles are highly charged when they leave the fluidized bed, due to friction occurring in the fluidized bed. These particles are then likely lost to the walls of the fluidized bed. Also, maybe the typical bipolar charge distribution is not reached in the neutralizer when the aerosol is very highly charged, which might lead to less of the particles in the size range we are aiming at (300nm) carrying a single charge, hence reducing the number of particles passing the DMA.

With respect to an influence of the corona towards our freezing measurements, we did immersion freezing measurements using Arizona Test Dust particles when the corona was on and when it was off, and results of the measurements were the same in both cases.

As much of the above is speculative, we prefer to not ponder on it in the manuscript. But we did add the following remark:

“It has been tested previously, that the corona discharger did not influence the IN ability of the particles (Niedermeier et al., 2010).“

*Page 30327, lines 19-21: It should be explained in more detail how Koehler theory was used to convert from Sw to aw.*

Particle hygroscopicity ( $\kappa$ ) was known from the CCNc measurements and had been derived to determine coating thicknesses. Using these  $\kappa$  values, calculations with Köhler theory were made to determine the particle size and hence also the Kelvin term (K) at the RH at which CFDC measurements had been made. Then:  $aw = Sw/K$

Values for  $a_w$  were roughly 0.6% lower than the respective  $S_w$  for the 300nm particles and 0.3% for the 700nm.

The following text was added to the manuscript:

“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 which CFDC measurements had been done. This yielded the Kelvin term (K) and the corresponding  $a_w$  (where  $S_w = K * a_w$ ). As the examined dry particles were already at least 300nm and 700nm 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.”

*Page 30329, line 5: Inspecting Fig. 4, it does not seem to be justified to use the same A and B average values (ACMS and BCMS) for Fluka kaolinite treated with sulfuric acid and CMS kaolinite.*

We do not agree with your statement here. Instead, we would argue that within measurement uncertainty (see e.g. error bars in Fig. 3 and 4), it is justified to treat CMS kaolinite particles similar to those from Fluka kaolinite treated with sulfuric acid. We consider it as one of the major results of this work that reaction with sulfuric acid changes the Fluka kaolinite particles such that they resemble those from CMS kaolinite in their IN ability. Therefore, regarding this remark, nothing was changed.

*Figure 2: The RH conditions for the data shown in this figure should be explicitly stated.*

done

*Figure 3: The color code should be improved. CMS particles should be given a different color from Fluka particles. Fluka 300 nm and Fluka 700 nm particles should be given different colors.*

Done, together with a few rewordings in caption and text which were required due to that change.

*Figure 4: The average values AFluka, BFluka, ACMS, BCMS should be given as lines in Fig. 4.*

done

*Figure 5: it is difficult to assign freezing curves to the specific experimental conditions given in Table 1. Either the readability of the figure has to be improved or the data should be in addition given in a Table for selected nucleated fractions.*

The readability of the figure was improved by removing the upper panels which had contained almost no data, enabling an enlargement of the remaining panels. The color legend is given in larger print above the panels, now. Additionally, in Table 1 it is indicated for which of the coating types data is to be expected in this figure. Caption and text were changed accordingly where needed.

*Technical comments:*

*Page 30314, line 15: second end bracket is missing.*

done

*Page 30330, line 8: “deliquesce” instead of “deliquescence”.*

done

*Figure 1: spelling error: “dilution” instead of “dillution”.*

done

## Appendix A

Fukuta and Schaller (1982) wrote that there "are presently three main mechanisms of heterogeneous ice nucleation known by aerosol particles - deposition, condensation-freezing including immersion freezing, and contact-freezing". Nevertheless they try to distinguish between condensation and immersion 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 immersion-freezing." Vali (1985) listed four different heterogeneous ice nucleation mechanisms and distinguished between condensation and immersion freezing, defining immersion freezing as "nucleation 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 environment 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 for immersion freezing as cloud droplet activation is one way of getting a nucleus suspended in water. 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 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 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

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

$$40 \quad f_{\text{ice}} = 1 - \exp(-n_s \cdot s) \quad (\text{B1})$$

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  
 45 Fig. B.1 and also for all others, the slope of  $n_s$  versus temperature is slightly less steep than that of  $j_{\text{het}}$ .

$A'$  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  $j_{\text{het}}$ . Grouping of the data is similar as observed for  $j_{\text{het}}$ , i.e. similar values of  $A'$  and  $B'$  are obtained for all Fluka kaolinite particles which  
 50 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  $B'_{\text{CMS}} = -0.91 \text{ }^\circ\text{C}^{-1}$ ).

55 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:

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

Fig. B.3 shows the respective results, comparable to what was obtained when the data analysis  
 60 was based on  $j_{\text{het}}$  (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  
 65 solution.

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

## Appendix C

In the present study, we described the ice nucleation induced by kaolinite particles in concentrated  
 70 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 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  $j_{\text{het}}$  as a function of  $\Delta a_w$ , where  $\Delta a_w$  is the 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.

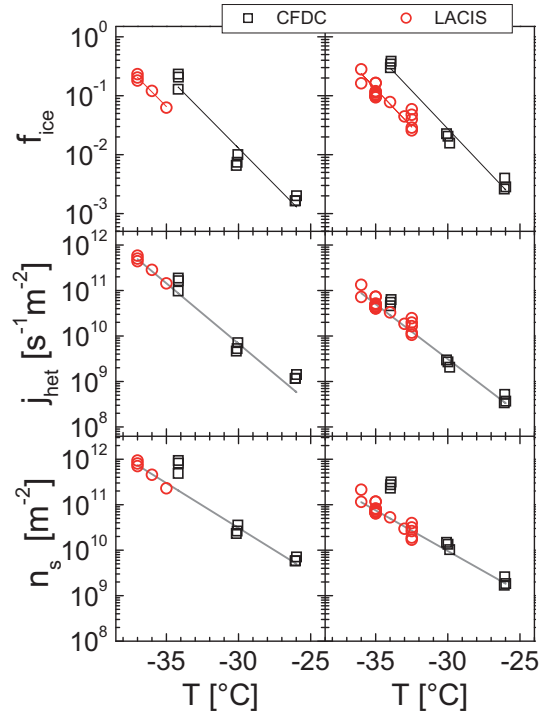
Data for coated CMS kaolinite particles are close to or even overlay both the data from Murray et al. (2011) and Pinti et al. (2012). This also applies for data for Fluka kaolinite particles when they are coated with  $\text{H}_2\text{SO}_4$  (with and without water vapor). Data for Fluka kaolinite particles coated with either succinic acid (SuccA) or levoglucosan (LG) show somewhat larger values for the nucleation rate coefficient  $j_{\text{het}}$  with a tendency to form a group of their own. This corroborates the 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  $\text{H}_2\text{SO}_4$ . 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), where different types of IN presented in different panels (kaolinite, aluminum oxide, iron oxide and fungal spores) show a different dependency of  $j_{\text{het}}$  on  $\Delta a_w$ .

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  $j_{\text{het}}$  for the respective type of IN.

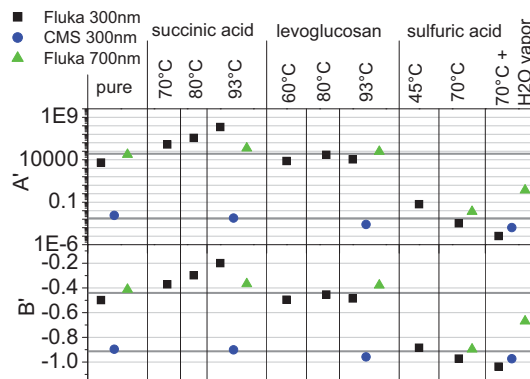
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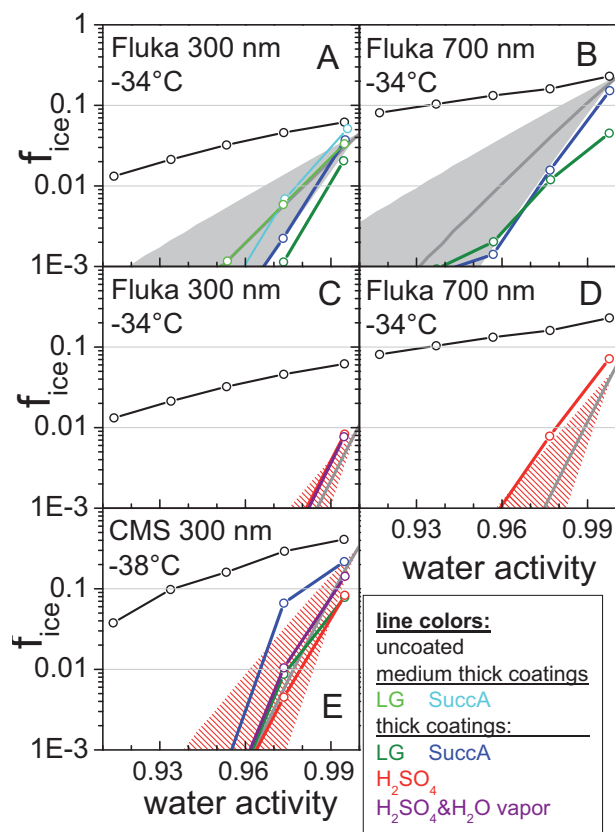




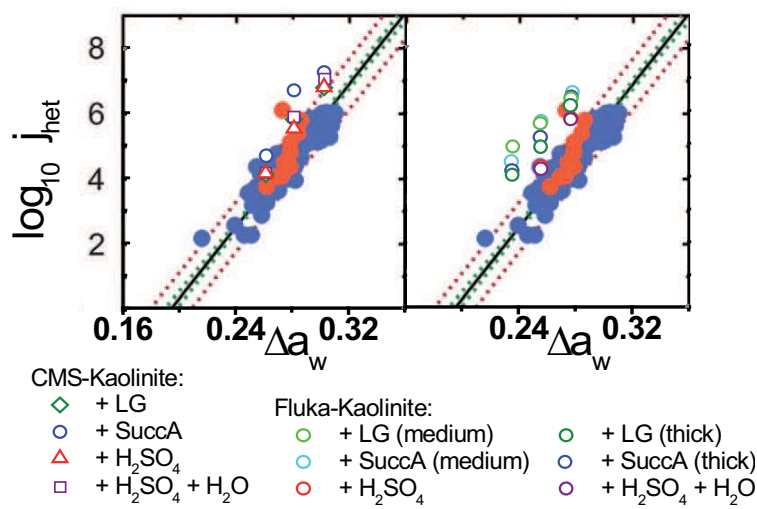
**Fig. B.1.** Measured  $f_{ice}$  and derived  $j_{het}$  for CFDC (at  $104\% \leq RH_w \leq 106\%$ ) and LACIS (i.e. for immersion freezing) for two particle types. Left panels: 300 nm Fluka kaolinite coated with LG at 80 °C; right panels: 700 nm Fluka kaolinite (no coating).



**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.