Our answer to the review by Dr. Ben Murray (Referee) on our manuscript:

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

Dear Ben!

We thank you for your corrections and constructive comments, which we appreciated. 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 by quotation marks (“…”).

In this article Wex et al. present a study of the effects of coatings of levoglucosan, succinic acid and sulphuric acid on two different kaolinite samples. They show that in the immersion mode only one kaolinite sample is affected by sulphuric acid and neither sample is affected by the other coatings. They also show that nucleation below water saturation is shifter to higher RH for all coatings. The authors then go on to suggest that nucleation of ice by coated particles is simply a form of immersion nucleation in solution droplets. The paper is well presented, the experimental methodology is sound and once the following comments are addressed I recommend it for publication in ACP.

Comments

1. Title: The phrase ‘types of kaolinite’ implies the kaolinite mineral was somehow variable. The word kaolinite refers to a mineral with a specific chemical formula and a specific crystal structure, so by definition there is only one kaolinite. But, kaolinite samples from different locations have different impurities. I suggest replacing ‘types of kaolinite’ with ‘kaolinite samples’.

done

2. I agree with the definitions presented on p30314. They are fairly close to Vali’s (1985), which could be cited explicitly. The definition obviously contrasts with the rather rigid definitions presented by Pruppacher and Klett (1997), which could also be stated clearly.

We added a description of the definitions of condensation and immersion freezing as given in Fukuta & Schaller (1982), Vali (1985), Pruppacher & Klett (1997) and Hoose & Möhler (2012) to a new section in an appendix (see Appendix A), which, due to its length, is not given here but at the end of this review, where the complete appendix can be found.

3. p30314 ln 20. Define ‘top soils’. Do you mean fertile soils as well as desert soils?

Indeed we meant that desert soils as well as fertile soils both are sources of mineral dust (while particularly fertile soils deliver much organic matter in addition). We are aware of the fact that for fertile soils the organic matter can influence the ice nucleation of the respective particles, and that they deliver a smaller amount of particles into the atmosphere, and therefore we could simply only mention desert soils, here, if you preferred. But for the time being, unless you object, we simply changed the wording to:

“Particularly desert soils but also fertile soils of the Earth are abundant sources for mineral dust, …”

4. p30314 ln25. The statement about quartz not being a good ice nucleus is not supported by Atkinson et al. (2013) in the immersion mode or Zimmerman in the deposition mode (JGR, VOL. 113, D23204, doi:10.1029/2008JD010655, 2008). In the immersion mode it is far more active than the clay minerals.

We have done measurements on the ice nucleation ability of quartz particles in the immersion freezing mode using LACIS. The results of these measurements are, unfortunately, unpublished. There, the quartz particles were really bad ice nuclei (only a bit of ice nucleation very close to the homogeneous freezing level). Also, there is a Master-thesis published at the university Vienna, where quartz samples bought from different companies varied much in their ice nucleation ability for immersion freezing. Hence we’ve changed the text as follows:

“Quartz was found to act as IN for deposition ice nucleation (Zimmermann et al., 2008) and immersion freezing (Atkinson et al., 2013), but did not act as good IN 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 vary much in their ice nucleation ability for immersion freezing, showing median freezing temperatures between -24°C and -37°C."

5. P30316 ln 27. 'In general, kaolinite belongs to the group of clays, consists largely of aluminium-silicates.' This is incorrect. Kaolinite is a clay mineral and is a phyllosilicate. Refer to Deer et al. (An Introduction to Rock forming minerals, Longman, 1966).

The text is now as follows:
"In general, kaolinite belongs to the group of clay minerals. It is a phyllosilicate (Deer et al., 1992) and occurs …"

6. P30322 ln17. Wheeler and Bertram (Deposition nucleation on mineral dust particles: a case against classical nucleation theory with the assumption of a single contact angle. Atmos. Chem. Phys. 12(2):1189-1201, 2012) should also be cited here. Kaolinite from the clay mineral society (KGa1b) seems to be a special case!

Following your remark and remarks from Reviewer #2, we added a section in an appendix (Appendix B) (see end of this review), where it is shown, that the deterministic approach yields the same results as the approach we had already used previously. 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. "

7. P30326. Ln 5: 'hint towards'. Revise. I suggest something like 'are consistent with. . .'

done

8. P30330. ln 5. In this argument there is an implicit assumption that the succinic acid is deposited as a crystalline material. Yes, if it were crystalline and given the high DRH then it would be strange to see immersion freezing like behaviour. I suspect that the vapour deposition of succinic acid onto kaolinite particles results in an amorphous coating and I'd expect that crystallisation of this amorphous material to be inhibited as it is for other aqueous organic systems (e.g. Price et al. Quantifying water diffusion in high-viscosity and glassy aqueous solutions using a Raman isotope tracer method, Atmos. Chem. Phys. Discuss., 13, 29375-29411, 2013). Also, a citation for the high DRH should be included.

Yes, it was implicitly assumed that succinic acid deposited as a crystalline material. We added the following to the end of this paragraph:

"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)."

As a citation for the high DRH we added the following:
"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."

9. P30331, para 1. In this discussion a recent article by Knopf and Alpert needs to be discussed (A water activity based model of heterogeneous ice nucleation kinetics for freezing of water and aqueous solution droplets, Faraday Discuss., 2013, 165, 513, DOI: 10.1039/c3fd00035d). They reach a similar conclusion to the present authors, i.e. that the freezing of solution droplets can be described as immersion freezing by taking *into account water activity.*

We cite this work here, now. Based on your remark here and the review for our manuscript submitted by Alpert and Knopf, we also added a section in the appendix, (see Appendix C) including a new figure (similar to Fig. 4 A from Knopf and Alpert (2013)), together with some discussion.

10. P30332, ln 26. Atkinson et al. did not 'assume' that K-feldspars are most important, this was a conclusion based on experiments. They used experimental evidence to argue that K-feldspar is the most important mineral in desert dusts for ice nucleation. This finding was recently reinforced by O'Sullivan et al. (Ice nucleation by soil dusts: relative importance of mineral dust and biogenic components, Atmos. Chem. Phys. Discuss., 13, 20275-20317, 2013. doi:10.5194/acpd-13-20275-2013).

Sorry for this mis-formulation, "assumed" was exchanged to "found".

11. How do the coatings and hygroscopicity of coated dusts compare to natural dusts?

We added the following text to the manuscript:

"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 < 2nm correspond to hygroscopic growth factors at 90% relative humidity below 1.1, a value generally observed for the hydrophobic fraction of the atmospheric aerosol. For a dryly dispersed Saharan mineral dust sample taken from a surface soil layer Köhler 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 thick coatings, are comparable in their hygroscopicity to naturally occurring mineral dust particles."

12. Fig. 6. Say what the vertical black line is in the caption. Can this be distinguished from the other black line by making it dotted or dashed?

The following text was added to the caption:
"The vertical black line at -34°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)."

13. Fig 7. There is a lot of detail in this plot which makes it difficult to read. Could the sulphuric acid results be presented in different plots to the other coatings?

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

Minor comments

1. P30314, ln 4: 1950's

done

2. P30315, ln 3. 'often blurry' is inappropriate terminology. I suggest something like: 'The difference between condensation and immersion freezing is poorly defined'.

done

3. P30329. Ln 10. 'redly'. Change to 'red'.

done

4. Fig. 5. Should SA in the key be SuccA?

done

5. Fig. 8. Use some colour to distinguish groups of line.

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 hererogenous 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:

$$f_\mathrm{ice} = 1 - \exp(-n_\mathrm{s} \cdot s) \tag{B1}$$

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 $n_\mathrm{s} = A' \cdot \exp(B' \cdot T)$. 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 ($A'_\mathrm{Fluka} = 5.07 \times 10^4\,\mathrm{m}^{-2}$, $B'_\mathrm{Fluka} = -0.44\,°\mathrm{C}^{-1}$, $A'_\mathrm{CMS} = 0.00127\,\mathrm{m}^{-2}$ and $B'_\mathrm{CMS} = -0.91\,°\mathrm{C}^{-1}$).

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:

$$f_\mathrm{ice}(a_\mathrm{w}) = 1 - \exp(-A' \cdot \exp(B' \cdot (T + \Delta T_\mathrm{het}(a_\mathrm{w}))) \cdot s) \tag{B2}$$

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

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 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 $\Delta\ a_\mathrm{w}$, where $\Delta\ a_\mathrm{w}$ 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 $\mathrm{H_2SO_4}$ (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 results obtained in our study: a parameterization describing coated CMS kaolinite also represents Fluka kaolinte particles well when they have been chemically altered due to a coating with $\mathrm{H_2SO_4}$. 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), 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 $\Delta\ a_\mathrm{w}$.

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.

References

Fukuta, N. and Schaller, R. C.: Ice nucleation by aerosol particles: Theory of condensation-freezing nucleation, J. Atmos. Sci., 39, 648–655, 1982.

Hoose, C. and Möhler, O.: Heterogeneous ice nucleation on atmospheric aerosols: a review of results from laboratory experiments, Atmos. Chem. Phys., 12, 9817–9854,

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Koop, T. and Zobrist, B.: Parameterizations for ice nucleation in biological and atmospheric systems, Phys. Chem. Chem. Phys., 11, 10839–10850, 2009.

Murray, B. J., Broadley, S. L., Wilson, T. W., Atkinson, J. D., and Wills, R. H.: Heterogeneous freezing of water droplets containing kaolinite particles, Atmos. Chem. Phys., 11, 4191–4207,

Pinti, V., Marcolli, C., Zobrist, B., Hoyle, C. R., and Peter, T.: Ice nucleation efficiency of clay minerals in the immersion mode, Atmos. Chem. Phys., 12, 5859–5878, 2012.

Pruppacher, H. R. and Klett, J. D.: Microphysics of Clouds and Precipitation, Kluwer Academic Publishers, Dordrecht, the Netherlands, 1997.

Vali, G.: Nucleation terminology, J. Atmos. Sci., 16, 575–576, 1985.

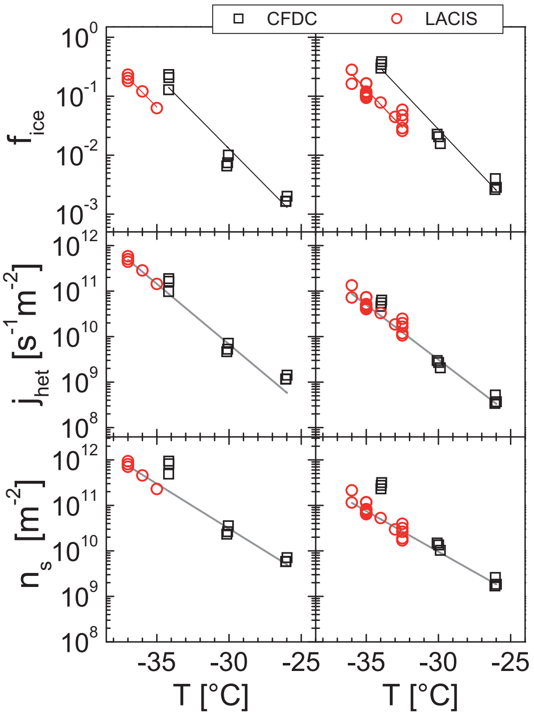

Fig. B.1. Measured f_{ice} and derived j_{het} for CFDC (at $104\% \leq \text{RH}_{\text{w}} \leq 106\%$) and LACIS (i.e. for immersion freezing) for two particle types. Left panels: 300 nm Fluka kaolinite coated with LG at 80 °C; right panels: 700 nm Fluka kaolinite (no coating).

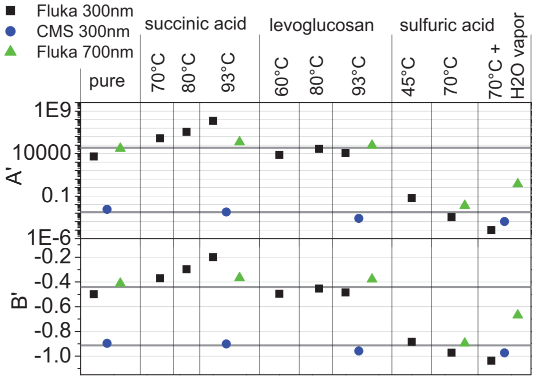

Fig. B.2. Similar to Fig. 4 in the main text, but values for A' and B' were obtained by fitting n_s obtained from measured f_{ice}. A separate fit was done for each of the 19 different particle types, each time accounting for all data available from both LACIS and the CFDC. Similar to the fit done for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

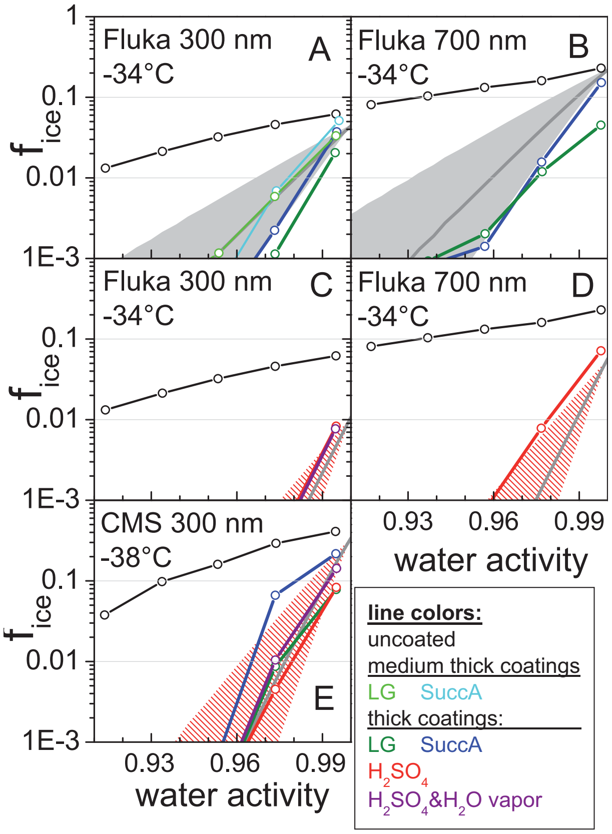

Fig. B.3. Similar to Fig. 7 in the main text, i.e. showing measured f_{ice} for deposition ice nucleation and expected ice nucleation behavior for particles which are completely coated by a solution. The difference to Fig. 7 is, that the calculations done to obtain the grey and red striped areas were 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.

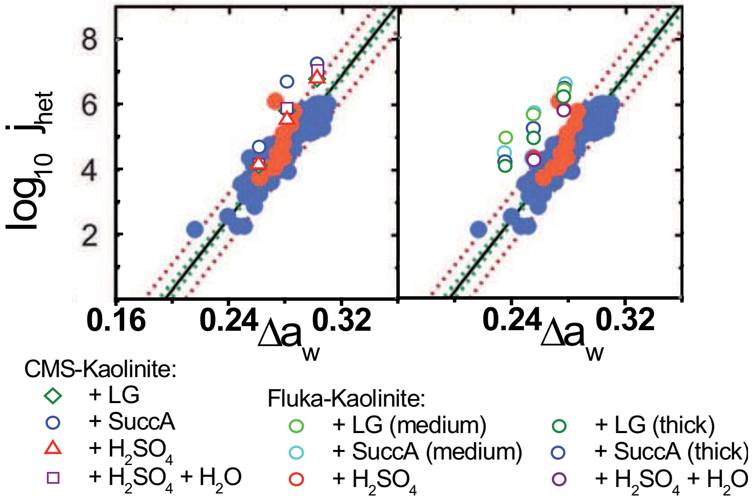

Fig. C.1. This figure reproduces a part of Fig. 4 A from Knopf and Alpert (2013), showing data from Murray et al. (2011) (filled blue dots) and Pinti et al. (2012) (filled red dots). The solid black line is a linear fit through the data, the dashed green and red lines represent confidence intervals and 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.

Our answer to the review by P. A. Alpert and D. A. Knopf on our manuscript:

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

We thank Peter Alpert and Daniel Knopf for their comment on our manuscript and apologize for not having cited their work, which had happened simply due to the fact that we had not been aware of it at the time of submitting our manuscript. We have included it now.

As this comment was mostly describing and summarizing the model presented in Knopf and Alpert (2013), together with evaluating a fraction of our data with the method presented therein, we do not answer to this review point by point but instead answer here directly.

Following your recommendation in the review, we added a figure similar to Fig. 2 from your review to the supplemental material of the manuscript (shown as Fig. C.1 below). It shows our measurements for coated particles in the water sub-saturated regime, compared with data from Murray et al. (2011) and Pinti et al. (2012). With respect to the nature of the IN immersed in the droplets, our data follows your theory “C” (we pasted the text of your review below our answer and marked the respective part in yellow and also cite it here): “freezing temperatures for these modified particles would also follow predicted freezing curves as a function of a_w … only that two different parameterizations would be required to describe the freezing kinetics of these two different particle types.” You remarked that: “There may or may not be limitations when applying the ABIFM to particles in which their surface is chemically or physically altered, e. g. by reactions of Fluka kaolinite with sulfuric acid.” Fig. C.1, right panel, shows a deviation of the data for Fluka kaolinite particles when they are coated with succinic acid (SuccA) or Levoglucosan (LG) from the bulk of the data for CMS kaolinite. Fluka kaolinite particles coated with sulfuric acid, however, are rather similar to CMS kaolinite particles, which seems to reflect that altering Fuka kaolinite particles with sulfuric acid changes their character. This corroborates our results.

The following discussion and figure are now given in an appendix of the manuscript:

“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 & Zobrist (2009). Koop & 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 & Alpert (2013) have now comprehensively examined to what extent it is possible to model immersion freezing based on a_w. Fig. A4 reproduces a part of Fig. 4A from Knopf & Alpert (2013) and shows nucleation rate coefficients j_{het} as a function of Δa_w , where Δa_w is the observed shift in a_w between the melting curve and the measurement. Fig. A4 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 & 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. A4.

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 results obtained in our study: a parameterization describing coated CMS kaolinite also represents Fluka kaolinte 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 & 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_{het} on Δa_w.

This all corroborates what was found earlier by, e.g., Koop & Zobrist (2009) and Knopf & 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.”

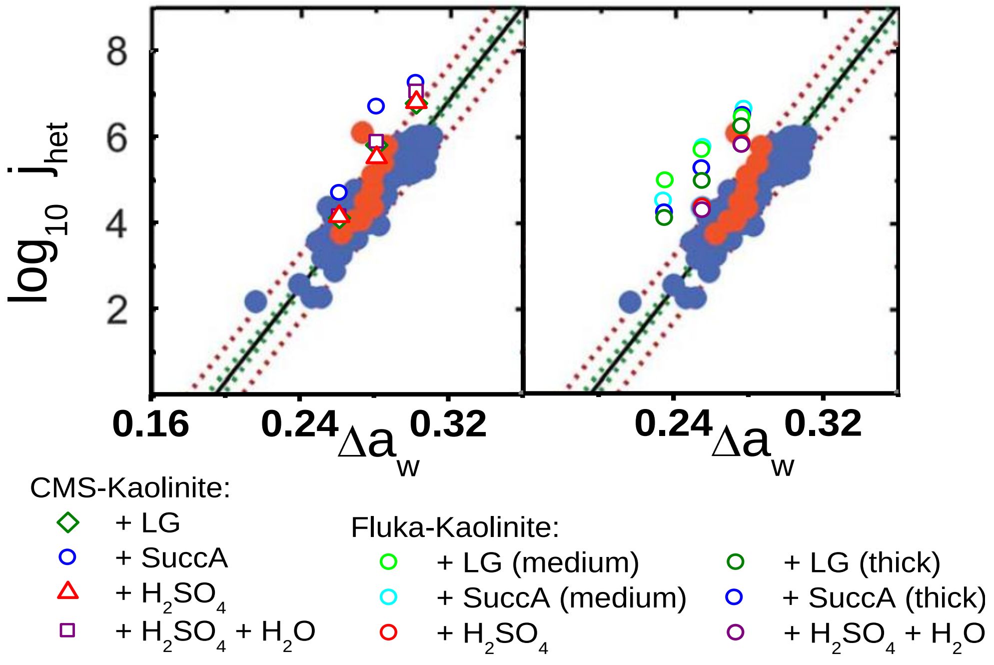

Fig. C1. This figure reproduces a part of Fig. 4 A from Knopf and Alpert (2013), showing data from Murray et al. (2011) (filled blue dots) and Pinti et al. (2012) (filled red dots). The solid black line is a linear fit through the data, the dashed green and red lines represent confidence intervals and 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.

Interactive comment on “Kaolinite particles as ice nuclei: learning from the use of different types of kaolinite and different coatings” by H. Wex, P. J. DeMott, Y. Tobo, S. Hartmann, M. Rösch, T. Clauss, L. Tomsche, D. Niedermeier, and F. Stratmann

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The paper by Wex et al. represents a nice experimental study on the immersion and deposition freezing ability of two different kinds of kaolinite purchased either by Fluka or the Clay Mineral Society (CMS) and with coatings of succinic acid, levoglucosan, and sulfuric acid with variable thickness. The authors find that the immersion freezing point depression for subsaturated conditions is explained by the solute effect analyzed using the λ-approach for all particle-coating systems, with one exception to Fluka kaolinite coated by sulfuric acid.

We would like to point out that the water activity based immersion freezing model (ABIMF) published by us (Knopf and Alpert, 2013) can also be applied to describe corresponding heterogeneous ice nucleation kinetics represented by J_{het} for a wide variety of ice nuclei (IN) and can be calculated from knowledge of only Δa_w, also known as the water activity criterion. We thank Dr. Murray for also referring the authors to our recent publication. As shown in Fig. 4 in Knopf and Alpert (2013), our model for kaolinite forms a compact distribution of J_{het} as a function of Δa_w and accounts for differences in IN surface area and nucleation time. The ABIFM is by definition independent of the aqueous inorganic or organic solution, therefore it should describe freezing temperatures and kinetics for kaolinite particles coated with succinic acid, sulfuric acid and levoglucosan measured by Wex et al.

There may or may not be limitations when applying the ABIFM to particles in which their surface is chemically or physically altered, e. g. by reactions of Fluka kaolinite with sulfuric acid. We can think of three scenarios to evaluate the performance of the ABIFM for potentially modified IN surfaces in general described below and depicted in Fig. 1. Note that Fig. 1 is for exemplary purposes only and do not represent actual data. A) Non-modified IN, i. e. the aqueous solution has no effect on the IN surface: If freezing temperatures are plotted as a function of water activity for a constant frozen droplet fraction and follow a predicted freezing curve described by Δa_w as shown in Fig. 1A, then the ABIFM should apply. This is surely the case for CMS kaolinte given that the solute effect can account for the freezing point depression. B) Continuous modification of the IN surface: If the degree of IN surface modification that results in changes of ice nucleation efficiency is dependent on the concentration of the aqueous solution and/or available IN modification time, then the ABIFM may not apply. That is to say, freezing temperatures may deviate from predicted freezing curves constructed by Δa_w as depicted in Fig. 1B. This type of behavior has been discussed, e. g. for a surfactant IN by Knopf and Forrester (2011). Even in this case, however, freezing kinetics may still be easily parameterized in the J_{het} versus Δa_w space. C) Modified and unmodified IN: If surface modifications are independent of the concentration of the aqueous solution and/or cease rapidly with no further change to the particle’s nucleation efficiency before the start of ice nucleation experiments, then it would be expected that freezing temperatures for these modified particles would also follow predicted freezing curves as a function of a_w (Fig. 1C). In this case ABIFM would apply to both modified and unmodified Fluka kaolinite, only that two different parameterizations would be required to describe the freezing kinetics of these two different particle types. In summary, the ABIFM should hold for scenario A) and C) in which IN do not undergo significant surface modification to alter ice nucleation efficiency as water activity changes or the modification is so fast that the ice nucleation ability does not significantly change during the experimental time period.

We tested the agreement of CMS kaolinite data by Wex et al. (2013) with the ABIFM in the following way. First, frozen fraction data for CMS kaolinite from Fig. 5 in Wex et al. (2013) and their Eq. 1 was used to calculate J_{het} assuming 300 nm diameter spheres to get surface area and using a CFDC residence time of 5 seconds. These data points were plotted as a function of Δa_w calculated from the given temperature and water vapor saturation (or water activity, a_w) also taken from Fig. 5 in Wex et al. (2013)

Figure 2 is similar to Fig. 4 of Knopf and Alpert (2013) including data by Pinti et al. (2012) and Murray et al. (2011). Here we added the data by Wex et al. (2013) without uncertainty analysis. Clearly, the figure demonstrates that ABIFM can be readily applied to describe and predict the immersion freezing by inorganic and organic coated CMS kaolinite particles acting as IN, as described by scenario A) above. It is important to note that the assumption of spherical particles will underestimate surface area, and thus, overestimate calculations of J_{het}. A more precise surface area measurement/estimate could be used in the actual analysis. Furthermore, uncertainties in temperature and humidity will propagate to an uncertainty in Δa_w which should also be discussed. It is worthwhile noting that ABIFM describes the freezing temperatures and kinetics of 5 different data sets obtained by 4 different experimental methods with little scatter in the data and little computational effort (i.e. a linear equation).

The experimental data for CMS kaolinite by Wex et al. (2013) and derived ice nucleation kinetics can be predicted by the ABIFM along with data from Pinti et al. (2012) and Murray et al. (2011). Those results for Fluka kaolinite in succinic acid and levoglucosan should also be in agreement with ABIFM following a different predicted $J_{het}(\Delta a_w)$ curve. If Fluka kaolinte coated with sulfuric acid behave as described by scenario C) above, then unmodified and modified Fluka kaolinte would represent two different IN both of which can be described by ABIFM. We would like to ask the authors to include in their paper application of the ABIFM in i) an analysis of their data and uncertainty for both Fluka and CMS kaolinite with different coatings and ii) a comparison with previous data sets by Pinti et al. (2012) and Murray et al. (2011).

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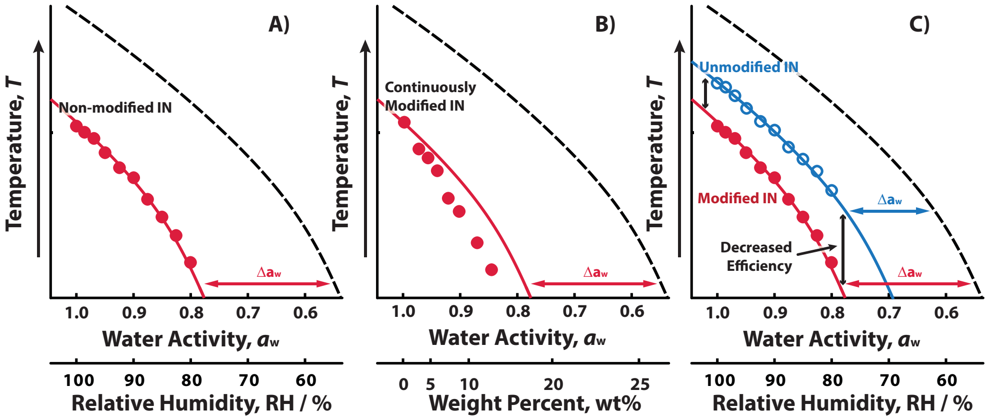

Fig. 1. Exemplary depiction of three scenarios representing the ability to predict immersion freezing temperatures as a function of a_w by construction using the water activity criterion, Δa_w. The IN in each scenario are A) non-modified IN for any aqueous solution, B) continuously changing IN surfaces due to concentration changes of aqueous solution, C) unmodified and modified by the presence of a particular aqueous solution. See text for further explanation.

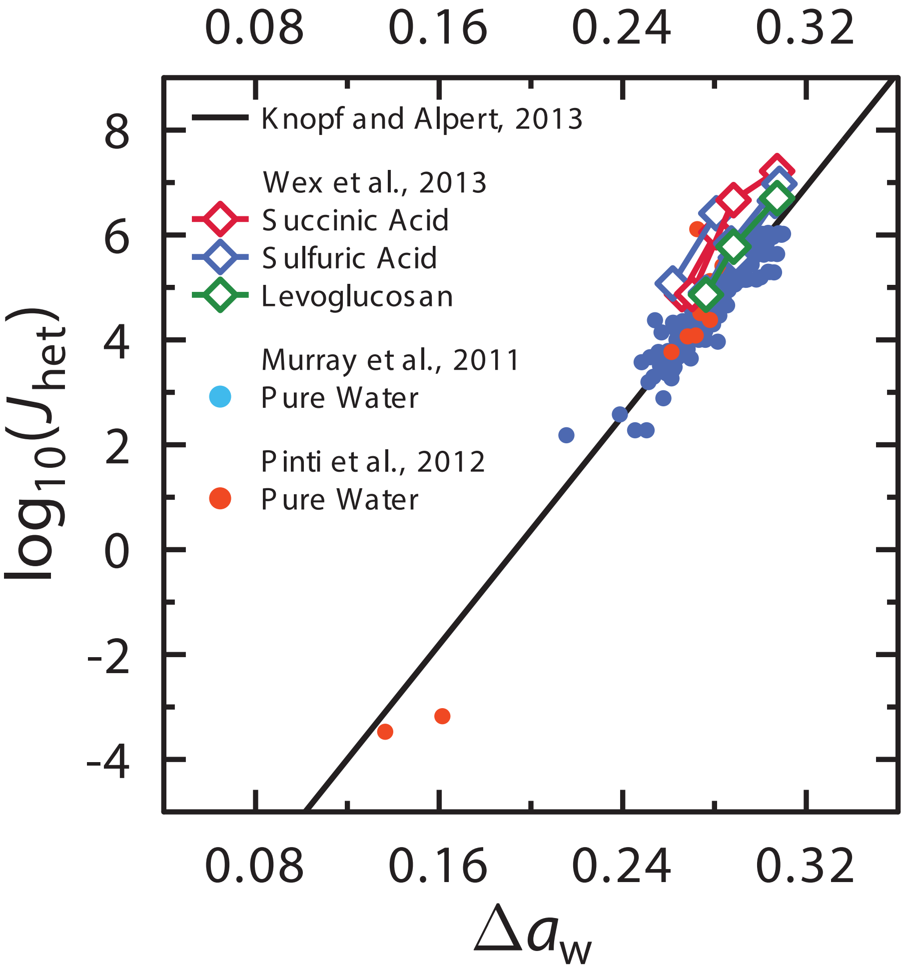

Fig. 2. The decadal log of heterogeneous ice nucleation rate coefficients, J_{het}, as a function of Δa_{w} for Kaolinite purchased by the Clay Mineral Society (KGa-1b) (Murray et al., 2011; Pinti et al., 2012; Wex et al., 2013) adapted from Fig. 4 in Knopf and Alpert (2013). The solid black line is a linear fit (Knopf and Alpert, 2013).

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 heterogenous 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 (Jhet = Aexp(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 (Jhet = Aexp(-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_{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)).“

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 or 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 (κ) was known from the CCNc measurements and had been derived to determine coating thicknesses. Using these κ 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 aw were roughly 0.6% lower than the respective Sw 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 Sw at which CFDC measurements had been done. This yielded the Kelvin term (K) and the corresponding aw (where Sw = K * aw). 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 Sw and aw 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 hererogenous 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:

$$f_\mathrm{ice} = 1 - \exp(-n_\mathrm{s} \cdot s) \tag{B1}$$

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 $n_\mathrm{s} = A' \cdot \exp(B' \cdot T)$. 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 ($A'_\mathrm{Fluka} = 5.07 \times 10^4\,\mathrm{m}^{-2}$, $B'_\mathrm{Fluka} = -0.44\,^\circ\mathrm{C}^{-1}$, $A'_\mathrm{CMS} = 0.00127\,\mathrm{m}^{-2}$ and $B'_\mathrm{CMS} = -0.91\,^\circ\mathrm{C}^{-1}$).

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:

$$f_\mathrm{ice}(a_\mathrm{w}) = 1 - \exp(-A' \cdot \exp(B' \cdot (T + \Delta T_\mathrm{het}(a_\mathrm{w}))) \cdot s) \tag{B2}$$

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

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 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 $\Delta\ a_\mathrm{w}$, where $\Delta\ a_\mathrm{w}$ 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 $\mathrm{H_2SO_4}$ (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 results obtained in our study: a parameterization describing coated CMS kaolinite also represents Fluka kaolinte particles well when they have been chemically altered due to a coating with $\mathrm{H_2SO_4}$. 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), 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 $\Delta\ a_\mathrm{w}$.

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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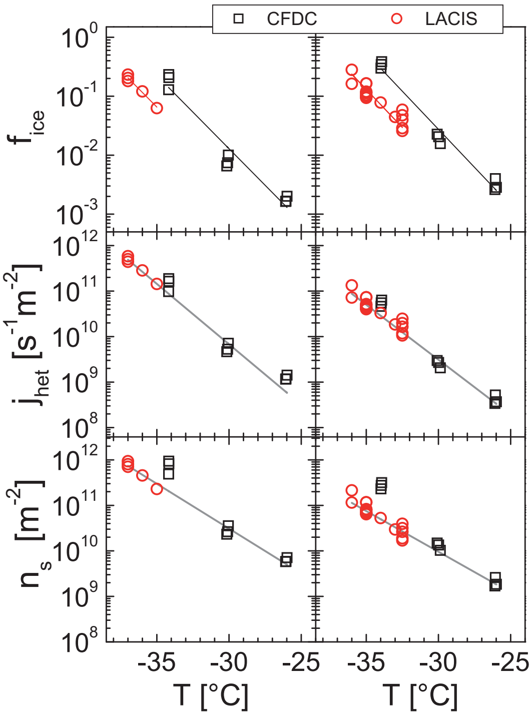

Fig. B.1. Measured f_{ice} and derived j_{het} for CFDC (at $104\% \leq \mathrm{RH_w} \leq 106\%$) and LACIS (i.e. for immersion freezing) for two particle types. Left panels: 300 nm Fluka kaolinite coated with LG at 80 °C; right panels: 700 nm Fluka kaolinite (no coating).

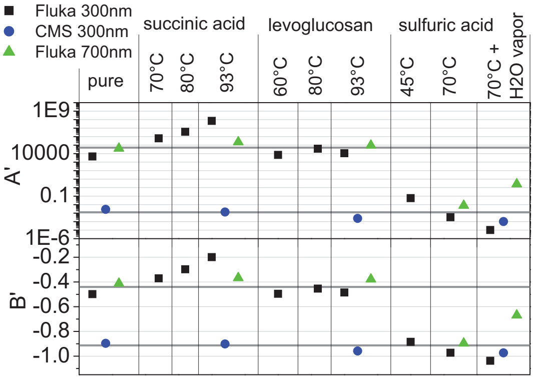

Fig. B.2. Similar to Fig. 4 in the main text, but values for A' and B' were obtained by fitting n_s obtained from measured f_{ice}. A separate fit was done for each of the 19 different particle types, each time accounting for all data available from both LACIS and the CFDC. Similar to the fit done for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

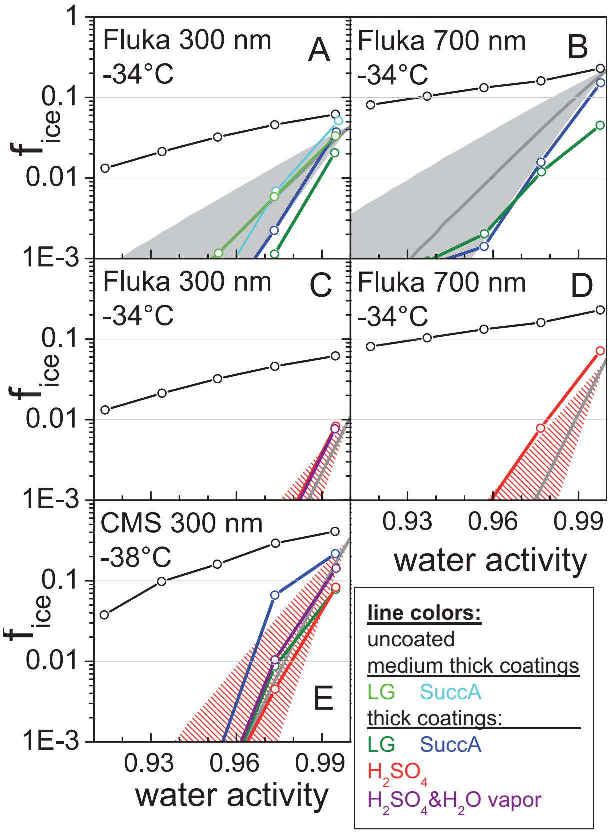

Fig. B.3. Similar to Fig. 7 in the main text, i.e. showing measured $f_{\rm ice}$ for deposition ice nucleation and expected ice nucleation behavior for particles which are completely coated by a solution. The difference to Fig. 7 is, that the calculations done to obtain the grey and red striped areas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

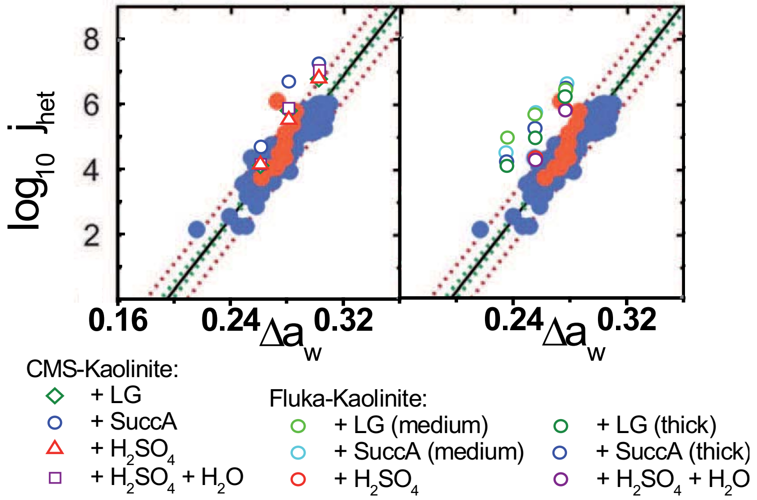

Fig. C.1. This figure reproduces a part of Fig. 4 A from Knopf and Alpert (2013), showing data from Murray et al. (2011) (filled blue dots) and Pinti et al. (2012) (filled red dots). The solid black line is a linear fit through the data, the dashed green and red lines represent confidence intervals and 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.