

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 In 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 In25. 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 In 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 In17. *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. In 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, In 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 up to 0.05 for the thickest coatings. Coatings $< 2\text{nm}$ 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, In 4: 1950's

done

2. P30315, In 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 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 \dot{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 \dot{j}_{het} . Grouping of the data is similar as observed for \dot{j}_{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 \dot{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
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 (\dot{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
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_{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. C.1 shows data for CMS kaolinite particles measured by Murray et al. (2011) and Pinti et al. (2012) and an additional linear fit through the data, as given in Knopf and Alpert (2013). Additionally included are CFDC data measured in our study for coated particles at water subsaturated conditions, separately for coated 300 nm CMS and Fluka kaolinite particles in the left and right panel of Fig. C.1.

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

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

References

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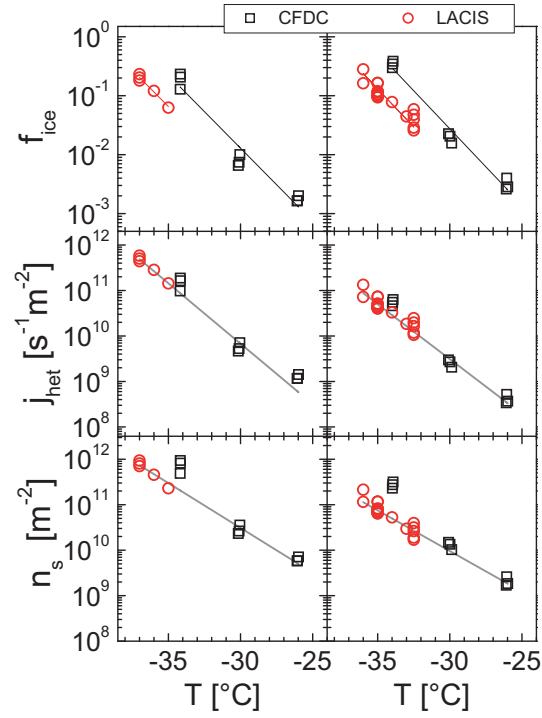


Fig. B.1. Measured f_{ice} and derived j_{het} for CFDC (at $104\% \leq RH_w \leq 106\%$) and LACIS (i.e. for immersion freezing) for two particle types. Left panels: 300 nm Fluka kaolinite coated with LG at 80 °C; right panels: 700 nm Fluka kaolinite (no coating).

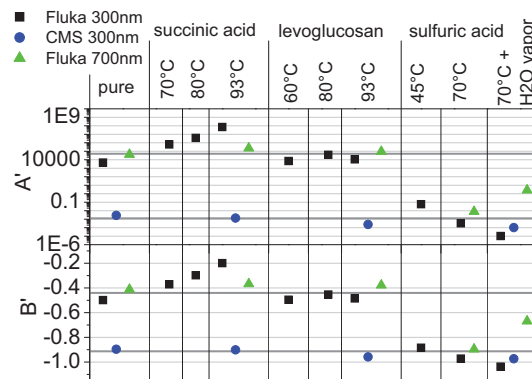


Fig. B.2. Similar to Fig. 4 in the main text, but values for A' and B' were obtained by fitting n_s obtained from measured f_{ice} . A separate fit was done for each of the 19 different particle types, each time accounting for all data available from both LACIS and the CFDC. Similar to the fit done for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

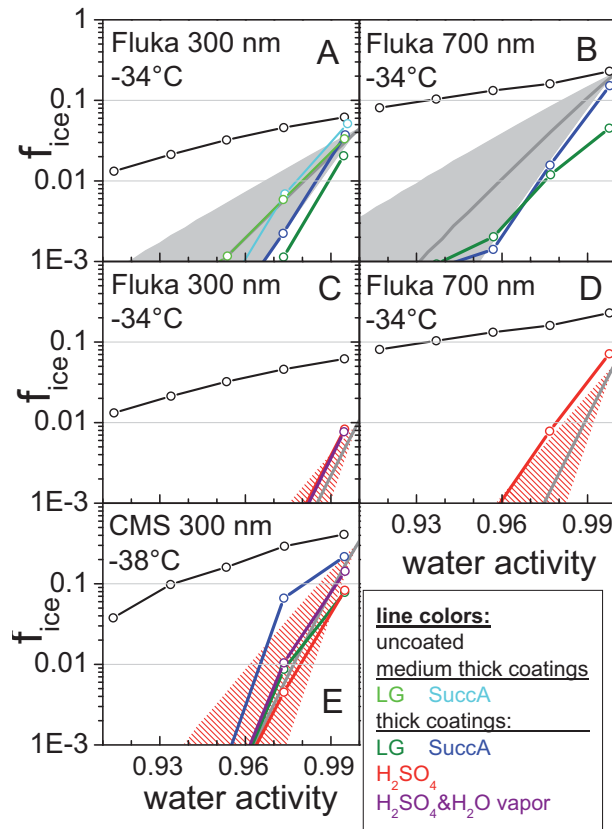


Fig. B.3. Similar to Fig. 7 in the main text, i.e. showing measured f_{ice} for deposition ice nucleation and expected ice nucleation behavior for particles which are completely coated by a solution. The difference to Fig. 7 is, that the calculations done to obtain the grey and red striped areas were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

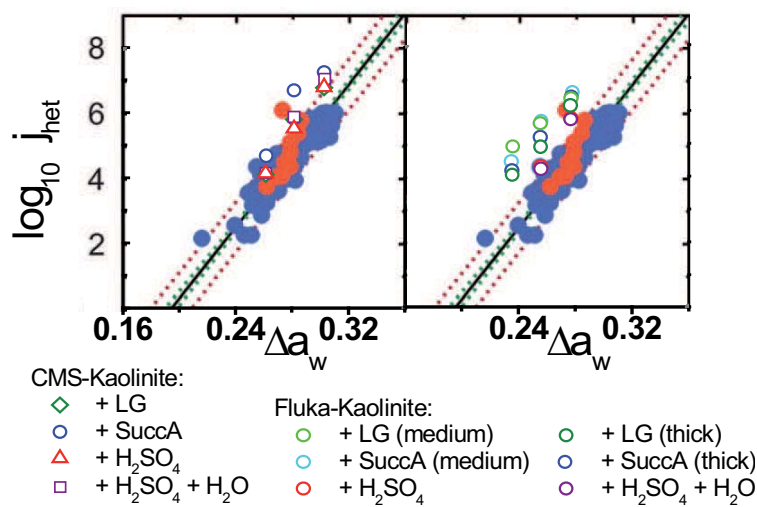


Fig. C.1. This figure reproduces a part of Fig. 4 A from Knopf and Alpert (2013), showing data from Murray et al. (2011) (filled blue dots) and Pinti et al. (2012) (filled red dots). The solid black line is a linear fit through the data, the dashed green and red lines represent confidence intervals and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