

## **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  $j_{\text{het}}$  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. 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 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 & 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  $\Delta a_w$ .

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.”

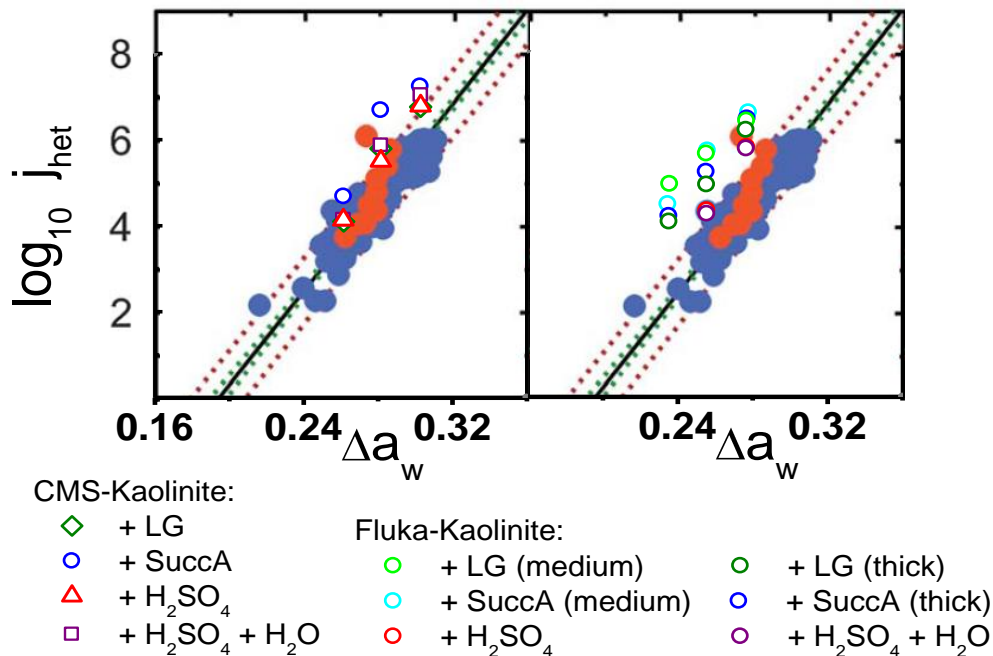


Fig. C1. This figure reproduces a part of Fig. 4 A from Knopf and Alpert (2013), showing data from Murray et al. (2011) (filled blue dots) and Pinti et al. (2012) (filled red dots). The solid black line is a linear fit through the data, the dashed green and red lines represent confidence intervals and 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  $\lambda$ -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 (ABIFM) 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  $\Delta a_w$ , 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  $\Delta a_w$  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  $\Delta a_w$  as shown in Fig. 1A, then the ABIFM should apply. This is surely the case for CMS kaolinite 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  $\Delta a_w$  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  $\Delta a_w$  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.

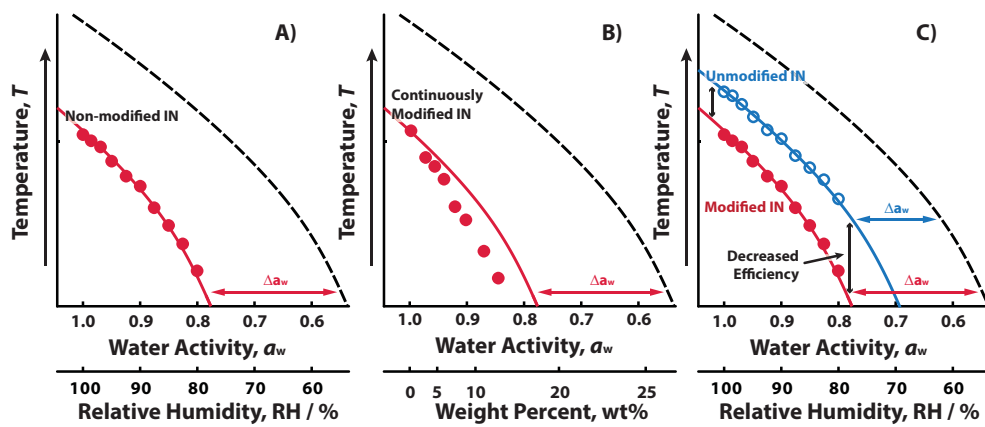
We tested the agreement of CMS kaolinite data by Wex et al. (2013) with the ABIFM in the following way. First, frozen fraction data for CMS kaolinite from Fig. 5 in Wex et al. (2013) and their Eq. 1 was used to calculate  $J_{het}$  assuming 300 nm diameter spheres to get surface area and using a CFDC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

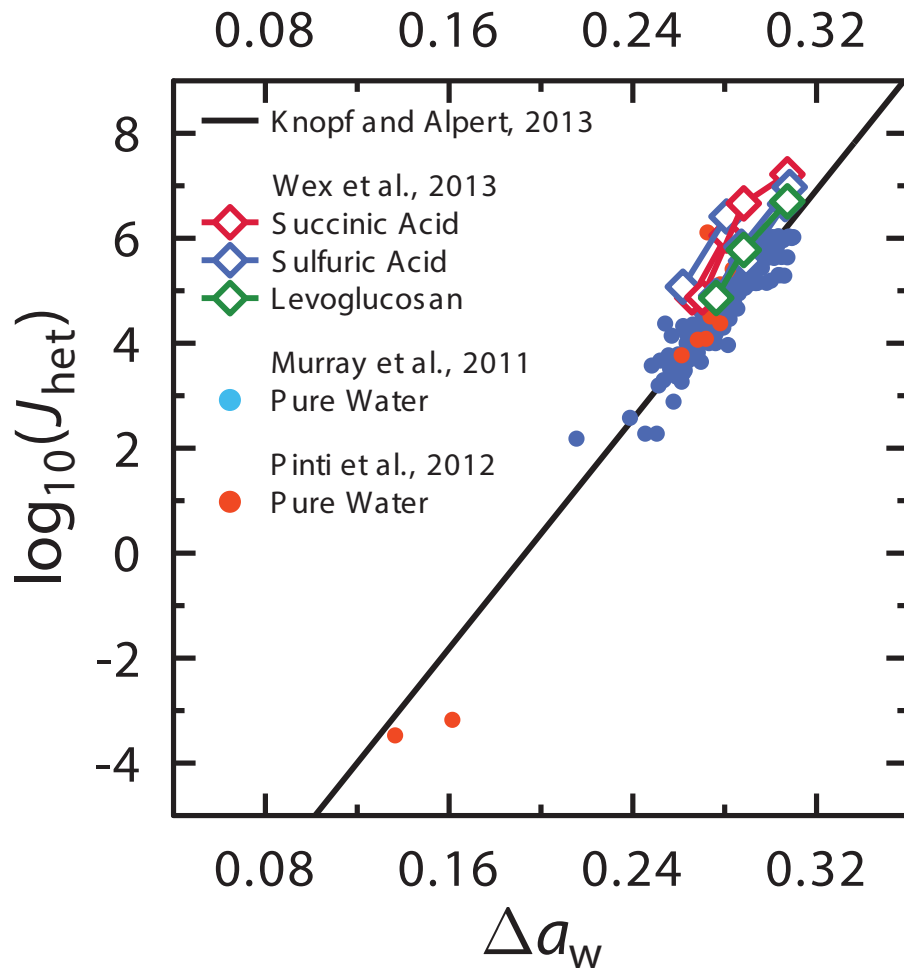
The experimental data for CMS kaolinite by Wex et al. (2013) and derived ice nucleation kinetics can be predicted by the ABIFM along with data from Pinti et al. (2012) and Murray et al. (2011). Those results for Fluka kaolinite in succinic acid and levoglucosan should also be in agreement with ABIFM following a different predicted  $J_{het}(\Delta a_w)$  curve. If Fluka kaolinite coated with sulfuric acid behave as described by scenario C) above, then unmodified and modified Fluka kaolinite 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).

## References

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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,  $\Delta a_w$ . 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,  $J_{\text{het}}$ , as a function of  $\Delta a_w$  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).