

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 (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 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 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 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 $J_{\text{het}}(\Delta a_w)$ 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

- Knopf, D. A. and Alpert, P. A.: A water activity based model of heterogeneous ice nucleation kinetics for freezing of water and aqueous solution droplets, *Farad. Discuss.*, 165, 513–534, doi:10.1039/c3fd00035d, 2013.
- Knopf, D. A. and Forrester, S.: Freezing of water and aqueous NaCl droplets coated by organic monolayers as a function of surfactant properties and water activity, *J. Phys. Chem. A*, 115, 5579–5591, doi:10.1021/jp2014644, 2011.
- 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, doi:10.5194/acp-11-4191-2011, 2011.
- 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, doi:10.5194/acp-12-5859-2012, 2012.
- Wex, H., DeMott, P. J., Tobo, Y., Hartmann, S., Rösch, M., Clauss, T., Tomsche, L., Niedermeier, D., and Stratmann, F.: Kaolinite particles as ice nuclei: learning from the use of different types of kaolinite and different coatings, *Atmos. Chem. Phys. Discuss.*, 13, 30311–30348, doi:10.5194/acpd-13-30311-2013, 2013.

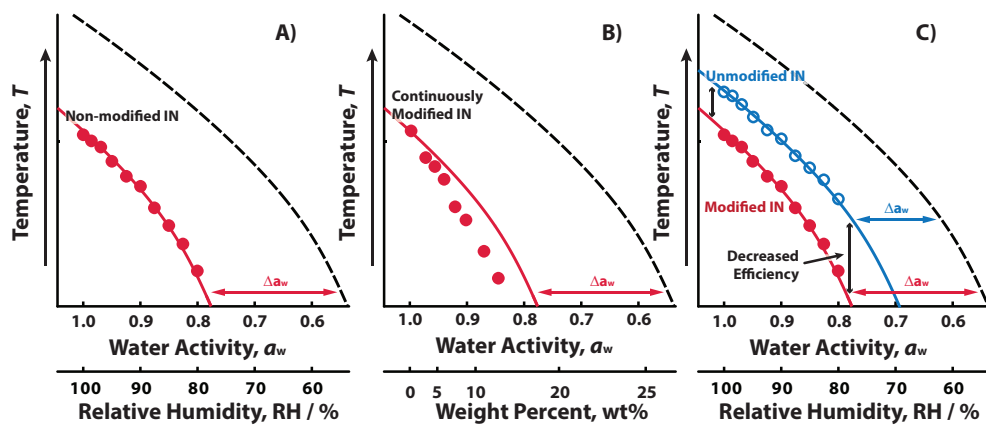


Fig. 1. Exemplary depiction of three scenarios representing the ability to predict immersion freezing temperatures as a function of a_w by construction using the water activity criterion, Δa_w . The IN in each scenario are A) non-modified IN for any aqueous solution, B) continuously changing IN surfaces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

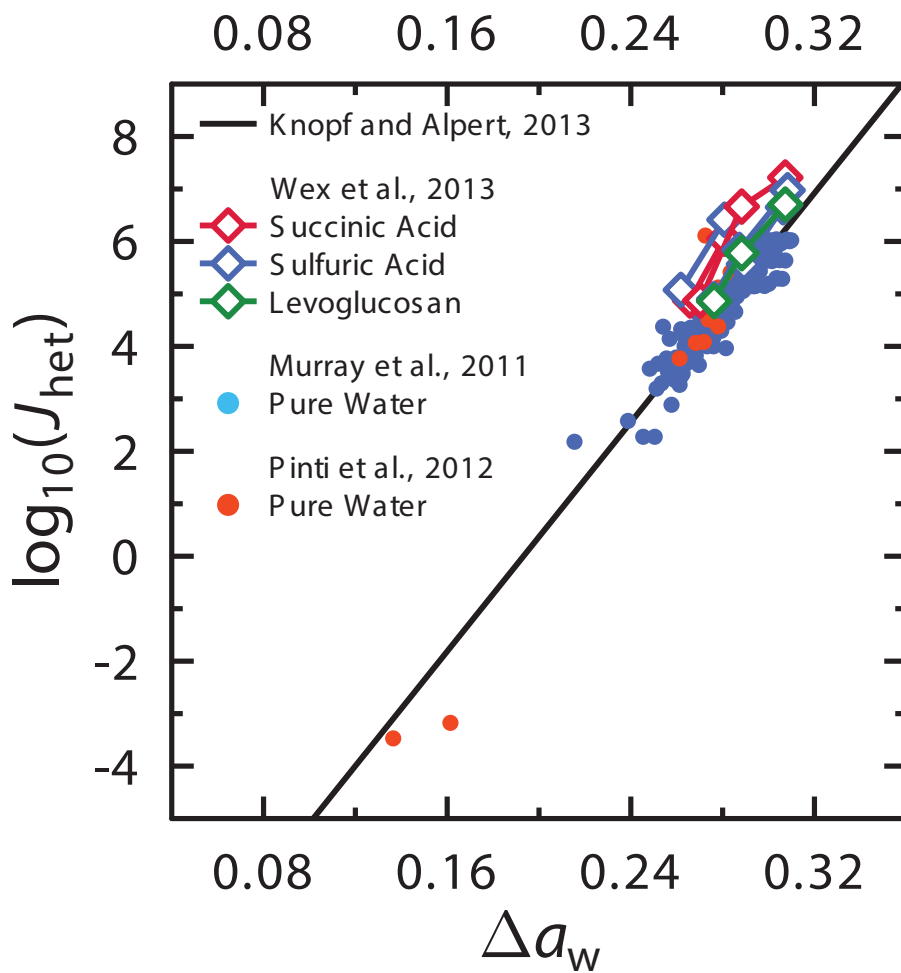


Fig. 2. The decadal log of heterogeneous ice nucleation rate coefficients, J_{het} , as a function of Δa_w for Kaolinite purchased by the Clay Mineral Society (KGa-1b) (Murray et al., 2011; Pinti et al., 2012; Wex et al., 2013) adapted from Fig. 4 in Knopf and Alpert (2013). The solid black line is a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