**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Deposition freezing on mineral dust particles: a case against classical nucleation theory with the assumption of a single contact angle" *by* M. J. Wheeler and A. K. Bertram

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Dear Editor,

Listed below are our responses to the comments from Niedermeier and referees #1 and #2. Niedermeier's and the referees' comments are in bold type and our responses are in normal text. We thank the referees and Niedermeier for carefully reading our manuscript and for their helpful comments. They have brought up several important points, and the revised manuscript will be much improved due to the points raised by the referees and Niedermeier.

Referee #1

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Particle size distributions should be analyzed and discussed in more detail. Welti et al. (2009) have published a size distribution of kaolinite from Fluka that peaks at ca. 500 nm with only a minor fraction of the particles larger than 1000 nm. This is in strong contrast to the determination performed in this study by static laser light scattering yielding an average particle size of 8000 nm for the same kaolinite. One reason for this discrepancy might be aggregation of kaolinite particles in the water suspension.

The referee raises an excellent point. We have gone back and determined size distributions using the images from the optical microscope, as we have done in previous publications (Chernoff and Bertram, 2010; Eastwood et al., 2008, 2009). In total, 383 particles were analyzed for kaolinite and 363 particles for illite to extract size information. Based on log-normal fits to the data, the mean geometric diameters were 10.7 μm and 7.3 μm for kaolinite and illite, respectively. In the final manuscript we will use the size distributions determined from the optical microscope since these are the size distributions used in the freezing measurements. This should eliminate the concern of the referee about the static laser light scattering measurements. Note that the particle size distribution used in our experiments for kaolinite is different from the size distribution reported by Welti et al. (2009) for kaolinite samples, since our method of impacting particles on the slide favours supermicron particles.

Particles that are smaller than 1000 nm cannot be discerned by optical microscopy. If a large fraction of such particles were present on the hydrophobic glass slide, the nucleated fraction would be much smaller. To see whether this was the case, a sample loaded with the clay minerals using the ultrasonic bath technique should be investigated by electron microscopy.

The referee raises another excellent point. As suggested by the referee, we have gone back and have used electron microscopy to determine if there is a large fraction of submicron particles on the slides in our experiments. From the electron microscope images, we conclude that the fraction of the total surface area that lies in the submi-

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cron range is <0.5% for both kaolinite and illite. This information will be added to the manuscript.

It would also be interesting to know whether nucleation always occurred on large (i.e. optically discernable) clay particles.

Experimental data shows that nucleation always occurs on paritcles with sizes greater than 1 μm. This confirms that submicron particles are not important in our experiments. This information will be added to the manuscript.

Also, the assumption of spherical particles leads to a considerable underestimation of surface area of supermicron clay mineral particles and should be refined using measured surface areas of kaolinites and illites.

The referee raises a good point. In the final manuscript we will carry out a series of sensitivity studies to determine if the conclusions or parameters determined from our fitting procedure are sensitive to the surface area.

Heterogeneous ice nucleation on kaolinite (Fluka) has recently been measured by Lüönd et al. (2010) in immersion mode and analyzed using the same nucleation models. They obtained contact angle values of ca. 90° compared to values between 3-14° in this study. Does this imply that kaolinite is a much better ice nucleus in deposition than in immersion mode? The authors might comment on this.

Contact angles alone should not be used to compare the ice nucleation ability for different modes. To compare the different modes, the ice nucleation rates or the ice nucleation rate coefficients should be compared at the same S_{ice} and temperature conditions.

Deposition freezing rates depend on supersaturation with respect to ice (Sice) and on temperature. In the present study, only trajectories reaching Sice = 1 at 242 K have been investigated and the dependence of nucleation onsets on

temperature is not discussed. Eastwood et al. (2008) have shown for kaolinite (Fluka) that there is little temperature dependence of Sice in the temperature range from 236 - 246 K. However, the temperature dependence might become more important for the smaller particle loadings used in this study. The authors should discuss this issue and state for what temperature range their parameterization is valid.

As mentioned, Eastwood et al. (2008) have shown for kaolinite that $S_{ice, onset}$ does not vary significantly over the temperature range of 236 - 246 K. Based on this, we assume that the parameters determined from our calculations should be valid over the temperature range of 239 - 242 K, which is the temperature range used in our studies. Further work is needed, however, to determine if the parameters determined in our study apply to a wider temperature range. This discussion will be added to the final manuscript.

The Bertram group presented immersion mode ice nucleation results of kaolinite (Fluka) already in Eastwood et al. (2008) yielding values that are at the upper end of the error bars of the values presented here. Some values in this study are at Sice <1 (including error bars). Do the results presented in this study have a bias to low Sice?

As mentioned, a few values reported in our study are at $S_{ice} < 1$ (including error bars). The results should not have a bias to low S_{ice}-values since the instrument is calibrated at $S_{ice} = 1$ (Dymarska et al., 2006). The few values at $S_{ice} < 1$ (including error bars) could be because the error in S_{ice} is slightly larger than reported. This discussion will be added to the manuscript to address the referee's comments.

Welti et al. (2009) also used kaolinite (Fluka) for their ice nucleation studies in immersion mode. The comparison with this study should therefore be more detailed.

Additional discussion will be added to the paper to compare the current results with the

work of Welti et al. (2009).

Specific comments

Page 21176, line 1: The authors should specify what exact quality of illite they purchased from Clay Minerals Society.

Illite was purchased from Clay Mineral Society (IMt-1). This information will be added to the manuscript.

Page 21181: how was equation 8 applied? By numerical integration or analytically?

All integrals presented in the manuscript were applied numerically. This information will be added to the manuscript.

Page 21182: exp is missing in equation 10.

We will fix Eq. 10 to include the correct formula for the normal distribution of contact angles.

Referee #2

My major concerns are related to the definition of the onset condition and the calculation of the ice-active particle fractions for comparison with the different formulations of heterogeneous ice nucleation. Heterogeneous nucleation rates and ice-active particle fractions are calculated for the so-called onset conditions defined as the time when the first ice crystal was detected in the humidity scans of the experiment. From a statistical point of view it is the worst case to calculate the rate of a stochastic process from just one event. I understand that the experiment was repeated a number of times, and an average was taken for the actual analyis, but would still like to know the accuracy of J_{het}.

This is an excellent point. Basically the referee is rightfully pointing out that we have not considered the uncertainty in the fraction nucleated in Figures 2c and 3c. There

are two ways to address this comment. (1) From Poisson statistics, one can determine the uncertainty when using one nucleation event (Garwood, 1936), or (2) the fraction frozen for each individual experiment can be determined, and from this information, the average fraction frozen and the uncertainty in the fraction frozen can be calculated. In the final manuscript we will use one of these two methods to determine the uncertainty in the fraction frozen.

It appears to me that Eq. 5 with one crystal nucleated only gives a lower limit for J_{het}. Only a few seconds later, more ice crystals could have been nucleated, or the one could have been nucleated in a shorter time interval which seems to be chosen somehow arbitrarily.

This is also an excellent comment. The referee is correct that at the onset S_{ice}, the number of nucleation events is ≥ 1 during the 20 second time window between images. This means that at the onset S_{ice} the rate of nucleation is ≥ 0.05 sec^{-1}. In the final version of the manuscript we will make this clear.

In addition, we will define a new variable that will be used in the calculations. The new variable will be the ice saturation ratio at which the nucleation rate = 0.05 sec^{-1} ($S_{ice,\,r=0.05}$). As mentioned, at the onset S_{ice} ($S_{ice,\,onset}$) the rate of nucleation is ≥ 0.05 sec^{-1}. In the image before $S_{ice,\,onset}$ there was no nucleation, i.e. the rate of nucleation = 0 sec^{-1}. Based on this, the nucleation rate = 0.05 sec^{-1} within the range $S_{ice,\,onset}$ and $S_{ice,\,previous}$ (where $S_{ice,\,previous}$ is the S_{ice} conditions when the previous image was recorded). $S_{ice,\,r=0.05}$ is calculated as $\left(\frac{S_{ice,\,onset} + S_{ice,\,previous}}{2} \right)$ with an uncertainty equal to $\pm (S_{ice,\,onset} - S_{ice,\,r=0.05})$. In the final version of the manuscript, $S_{ice,\,r=0.05}$ rather than $S_{ice,\,onset}$ will be used when testing the different ice nucleation parametrizations.

The experimental rate J_{het} is then compared to the single alpha model. Furthermore, an average particle diameter is used to calculate the total number of particles in the sample and from that the ice-active particle fraction at onset conditions as 1 over the total number of particles. This is an important approxima-

tion in the analysis and interpretation of the experimental results, because any of the formulations used in the manuscript rely, as far as I can see, on the assumption that all particles have the same freezing probability at a given set of contact angle, T and RHi. I think the analysis would only be accurate for monosdisperse particle samples. Therefore I would like to ask the authors to provide some more information about the range of particle sizes on the substrate, and to give at least an estimated uncertainty for the ice-active particle fraction and the mean particle diameter used e.g. in Eqs. 7, 8, 9 and 17.**

In the final version of the manuscript we will calculate size distributions from the optical images and use these size distributions when calculating the fraction of particles frozen. In other words, we will not use the assumption of monodisperse particles.

The approximations used in the fit equations should more clearly be mentioned and explained in the final manuscript, also at the end of the conclusion section.

As mentioned above, the approximation of a monodisperse aerosol population will not be used in the final version of the manuscript. We will try to state more clearly in the manuscript as well as at the end of the conclusions the remaining approximations used in the fit equations.

Minor points

Title and p. 21172, l. 24: I agree to the comment by Denis Niedermeier that the term "deposition freezing" should be replaced by "deposition nucleation", according to the definition by Vali, G. (1985).

The manuscript will be modified as suggested.

p.21176, l.20: How did the size from the laser scattering experiment compare to the projected area diameter determined with the optical microscope?

In the final version of the manuscript we will only use distributions determined with the optical microscope. The number geometric mean diameters from analysis of the

images recorded with the optical microscope are 10.7 μm and 7.3 μm for kaolinite and illite, respectively.

p.21178, l.8-12: I think, ice activity spectra as shown in Figs. 2c and 3c are only useful for predicting freezing in the atmosphere if measured or defined for at least size distributions of particles relevant for the atmosphere. This is e.g. discussed by Möhler et al. (2006).

To address the referee's comment, the sentence, "Plots like the ones shown in Figs. 2c and 3c (referred to as the activity spectrum) are often useful for predicting freezing in the atmosphere." will be changed to "Plots like the ones shown in Figs. 2c and 3c are often refereed to as the ice activity spectrum."

p.21187, l.4: I would recommend to state here, that the single alpha model seems not appropriate to accurately predict heterogeneous ice nucleation by mineral dust particles. The current statement implies that the single alpha model is accepted as the classical or "natural" formulation, which I think is not the case.

We agree with the referee, and the sentence will be modified as suggested.

Niedermeier comment

First of all, in the deposition mode water vapour deposits directly on the IN surface forming ice without the intermediate metastable liquid state. That means no liquid water is available which could freeze. Therefore I would suggest calling this process 'deposition nucleation' instead of 'deposition freezing'.

In the final version of the manuscript, deposition freezing will be changed to deposition nucleation.

Page 21174, line 5: Here, Niedermeier et al. (2010) is cited wrongly. In this paper, two parameterizations were used to fit the data. The first based on stochastic view on nucleation similar to the single-alpha model and the second based on the singular hypothesis according to Connolly et al. (2009). Therefore I would

suggest moving the citation to line 12. In our recent paper (Niedermeier et al., 2011) a multi component stochastic model is introduced which is related to the active site model of Marcolli et al. (2007).

As suggested, the reference to Niedermeier et al. (2010) will be moved to line 12. When discussing the active site model, we will also add a reference to Niedermeier et al. (2011).

Pages 21176-21177, chapter 2.3 and 3.1: Do I understand correctly that an individual sample consists of 1 to 1000 particles and the onset supersaturation is obtained for each single sample separately? In general, how is the onset defined? This question is especially important for cases where the sample consists only of a few particles. Were the measurements repeated for a specific sample or were samples just used once? Some more explanation would be helpful.

Yes, an individual sample consists of roughly 1 to 1000 particles and the onset saturation is obtained for each sample separately. The onset saturation for each sample was determined just once. This information will be added to the final manuscript for clarity.

Page 21179, Eq. (5): I suggest discussing the assumptions underlying Eq. 5 in more detail. In case available, a reference could be helpful, too.

The assumptions underlying Eq. 5 will be discussed in more detail in the final version of the manuscript to address the referee's comments.

Page 21180, line 8: Here it is stated that the measurements were made at 242.5K. However Fig. 1 indicates that the superaturation increases as the temperature decreases. Some explanation why a constant temperature was/could be used for calculation would be helpful.

Good point. For the calculations in the final version of the manuscript we will not assume a constant temperature. Rather, we will use the temperature at $S_{ice, r=0.05}$ which depends on the trajectory shown in Fig. 1

Page 21185, line 15: Why is constant temperature a reasonable approximation (see comment above)?

The wording in this sentence will be modified to the following to address the referee's comment:

"For deposition nucleation, we assumed that the particles have a surface density of active sites, n_S, that is a function of S_{ice}, but independent of T over the narrow range of temperatures investigated (239 - 242 K). Based on previous measurements of $S_{ice, onset}$ as a function of temperature for kaolinite particles (Eastwood et al., 2008), which show that $S_{ice, onset}$ is relatively insensitive to temperature over the range of 236 - 246 K, this should be a reasonable approximation. It is also assumed that the fraction of particles activated at a given S_{ice} is independent of time but related to $n_S(S_{ice})$ through the following equation:"

Page 21185, line 21: Here experiment temperature is given as 240K which differs from that used above (242.5K). An explanation would be useful here.

To address the referee's comment, this line will be changed to the following: "where $n_S(S_{ice})$ is the surface density of active sites over the temperature range of 239 - 242 K."

References

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