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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Immersion mode heterogeneous ice nucleation by an illite rich powder representative of atmospheric mineral dust" *by* S. L. Broadley et al.

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Response to referee 2

The referees' comments are italicised and our comments are in plain text.

While this is a thorough work I consider the amount and choice of material presented here as too broad for a single paper. In the end, I am missing a clear take home message because all model approaches discussed here have their weaknesses which however the authors correctly address. In summary, the amount of models/parameterizations seems a bit overwhelming to me while other approaches which have been shown to describe ice nucleation data well are not considered here.

I recommend the paper for publication but with revisions and possibly considering a re-organization of the manuscript or splitting it in two parts, one with a focus on measurements and material characterization and one which focuses on parameterizations and models.

We appreciate that this paper is rather substantial and have made efforts to make it as concise as possible. We did consider splitting the paper into one part containing experimental results and the second containing the detailed analysis, but felt that this would produce two unsatisfactory papers. We think that the results and interpretation need to be in the same paper. One way in which we have made the take-home message more clear is to split the abstract up into three paragraphs, one of each of the key points from the paper. The first is on our proposal that NX-illite is a much better proxy for natural dust than ATD. The second is reporting the basic results and the third highlights the complexity of ice nucleation and how this can be described.

Some detailed comments: Abstract: p. 22802, line 8: Please add a short not[e] about the usage of ATD as reference material for IN studies.

In the abstract we now state that 'Arizona Test Dust, which is used in other ice nucleation studies as a model atmospheric dust, has a significantly different mineralogical composition and we suggest that NX illite is a better surrogate of natural atmospheric dust.'

line 10: Heterogeneous nucleation in the immersion mode by NX illite...

Changed

line 14: . . . in terms of their ice . . .

Sentence rewritten: 'We show that NX illite exhibits strong particle to particle variability in terms of ice nucleating ability'.

line 16: . . . than assumed in a parameterisation . . .

Sentence rewritten: ‘In fact, this work suggests that the bulk of atmospheric mineral dust particles may be less efficient at nucleating ice than assumed in current model parameterisations.’

line 26: . . . is assumed that there . . .

Changed

1 Introduction: p. 22803, line 8: . . . of solid particles termed ice nuclei (IN). These IN are rare . . .

Changed

line 21: . . . about a third of all IN . . ..

Changed

p. 22804, line: 3: . . . condensation of liquid water . . .

Changed

line 18: . . ..was found to be . . ..

Changed

line 19: . . . found that there was . . .

Changed

2 Theoretical background: This section is very clear and a good summary of the concepts needed to understand the following data analysis. I only suggest to use A instead of S as a symbol for surface area in formulas 4, 6, 7, and 13, 14 because A is normally used for areas and S is often used in CNT for saturation ratios and can therefore be misinterpreted.

A is also used (it’s the pre-exponential in the classical theory equation). We’ve changed S to s throughout the paper.

3 Experimental p. 22811, line 25: It would be helpful to also give a typical size (mean and variance) of the droplets used. How does this and the wt% concentrations translate into a number concentration of particles/droplet? Are there experimental conditions met, where it is likely that on average less than one particle is present in a droplet? See also my comments on sections 4.1 and 4.3.

The median droplet size and width of the size bins are given in the tables. The reader is now directed to these tables for this information with an additional comment in the experimental section.

4 Results and discussion In general I have been confused many times with the experiment numbers. I recommend to re-name them to either numbers+letters (e.g.1a) or put at least a dash between roman number and extension (vi-a). But personally I think it is much easier to read a scheme like 1a or 1-a.

We agree, this is confusing. We have changed to a format ‘1a’ throughout.

4.1 heterogeneous freezing temperatures The fact that some droplets with low wt% concentrations of illite froze homogeneously brings up the question if in these experiments some of the droplets did not contain a particle at all. Please discuss this possibility as already suggested for section 3. Fact is that surface area is not distributed continuously but in discrete amounts (by adding particle by particle into a droplet). This is especially relevant if you come close to an average concentration of one particle per droplet (please consider a poisson statistical distribution here) Maybe this might explain some of the observations here (and in section 4.3). This is also a point to consider when the data is interpreted with atmospheric relevance in mind. In the atmosphere, normally exactly one particle is present in one droplet, here this can vary largely.

We addressed a similar comment by referee 1 and have inserted a discussion of the number of particles we predict to be in the droplets. Even for the smallest concentrations of dust there are 1000s of particles per droplet assuming they are evenly distributed.

The referee suggests there is exactly one particle per droplet in the atmosphere. This depends on how you define 'particle'. Most atmospheric dust particles will be agglomerates of many smaller particles.

4.3 High/low surface area regime. I am not so happy with this rather arbitrary distinction between low and high surface area regimes. If this is something real a possible scientific reason for this distinction should be discussed. One of them might be related to the points I made before regarding the statistical number concentration of particles within one droplet. On the other hand, it should be tested, that the change in median freezing temperature and its leveling at higher concentrations might not be explained and described by a continuous function in agreement with predictions made by the CNT based models in this study. In other words, are these two regimes really two different regimes or just different regions in a continuously changing function?

The exact boundary between the two regimes may not be clear and the referee may be correct that this behaviour may be related by some unknown continuous function. However, for practical purposes we can split the data into these two regimes and this allows us to analyse the lower surface area (and more atmospherically relevant data) in a quantitative manner. We thought about leaving the high surface area data out of the paper because it is perhaps not atmospherically relevant, but we feel it is important to document these effects because it will guide future experimental work in our group and others.

We have improved the pertinent section which now reads: 'As shown in sections 4.1 and 4.2, the freezing behaviour of droplets containing NX illite appears to depend on the total amount of material present in the droplets. Firstly, when low surface areas of NX illite were present in droplets freezing was cooling rate independent and the median freezing temperature clearly scaled with surface area. Secondly, when higher surface areas of NX illite were present freezing was cooling rate dependent and the median freezing temperature no longer depended on surface area in a simple way. For simplicity, in this study we split the data into two distinct regimes: a high and a low

surface area regime.'

p. 22818, lines 15-20. I am not sure if the data in Figure 4 supports the conclusion that only in the lower regime the data is surface area dependent. It may also be surface area dependent in the other regime just less pronounced, especially when considering the error bars.

We use the phrase 'approximately constant' and 'within uncertainties' in section 4.1. So, we agree with the reviewer.

4.4 model fits In figure 6: Do the error bars for surface area consider the statistical implications (poisson distribution of individual particles) discussed above?

No, as discussed above poisson stats are not required since we estimate that all droplets have many particles.

4.5 isothermal experiment no comments for this section. No response *4.6 multicomponent model Th[e] discussion in this section is very interesting and I see that this approach may be used to fit experimental data well. However, it comes without a good connection to the other approaches discussed earlier and without a connection to the theoretical section 3 as far as I can see. The question comes up because other authors have used approaches where a distribution of contact angles is assumed. Since this is a very lengthy part of the paper with alone 7 Figures – which are relevant and interesting indeed – I just question if this isn't too much material for one paper. If the authors intend to promote and characterize this model then I would make this more clear from the beginning or possibly put this material in a companion paper.*

As discussed above, we feel that the interpretation of the data and the actual data need to be in the same paper.

The multiple component stochastic model is discussed in the theoretical section and then it is applied to the data after showing that the single component stochastic model and the singular model can't represent all the features of the data. The referee mentions the contact angle based approach used by other authors – we have now added a brief paragraph on this at the end of section 4.

5 parameterization for models Given that so much effort in this paper is put into the previously described models I am surprised to see here again another approach to fit the data of the presented experiments.

In this section we wanted to provide the community with a parameterisation of the data in a form which is being used by others in the field. The parameterisation is based on Connolly's singular description which is being used increasingly as a means of comparing the ice nucleating ability of one material with another. We stress the limitations of this parameterisation in terms of time dependence.

p. 22826, line 4-6: I cannot follow the argument that the empirical multicomponent model of section 4.6 should be the most physically accurate one. If so the authors should describe more clearly how this model is related to the physics of nucleation which are described very clearly in the theory section of the paper. I hope I am not overseeing something obvious here.

We agree that 'physically accurate' is not the best term to use. We have replaced this phase with 'that can best describe'.

6 conclusions This sections highlights that each model discussed here seems to only fit well with a certain fraction of the data. Since the authors discuss some models used in other studies I cannot follow the motivation to selectively ignore those models which fit the data best in those studies (e.g. distribution of contact angles and active site model by e.g Marcolly et al. 2007 and Lüönd et al. 2010) while introducing the multicomponent model as a model with similar assumptions but without the physical basis (they are fully based on CNT). A comparison between these models and the multicomponent model presented here would have been much more interesting and could also be better motivated since the "simpler" models have already been shown to not fit well to experimental data sets in several studies.

As mentioned above and also in the response to referee 1, we initially attempted to use a contact angle based description of J in line with Marcolli's paper. We found that we were not able to reproduce the absence of cooling rate dependence using this model, which in itself is interesting. We have added the following paragraph at the end of section 4: 'Classical nucleation theory based model. This paragraph will briefly consider the implementation of CNT into the multiple component stochastic model. CNT based on Marcolli et al. (2007) (and all references therein) was used to describe J(T) (Eq. 15); the distribution of contact angles across the droplet population was determined as outlined above in Eq. (17) with ni = nPθ, where θ is the contact angle. Using this model resulted in a temperature shift of 0.6 K on a factor of 10 change in cooling rate, which is inconsistent with our measurements.'

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 22801, 2011.