

Interactive comment on “Heterogeneous freezing of water droplets containing kaolinite and montmorillonite particles” by B. J. Murray et al.

B. J. Murray et al.

b.j.murray@leeds.ac.uk

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We thank the reviewers' for their constructive comments.

The referees' comments are italicised and our response is in normal type.

Response to referee 1 (C2119)

This comment is a general one, Nevertheless, I believe that the authors should also give some consideration to what some past quantitative studies of condensation and immersion freezing have revealed about the nature of this process for other ice nuclei. For example, dominance of stochastic characteristics is inconsistent with the relative independence of ice nucleation on cooling rates in experiments for soot (DeMott, 1990) or soil-based particles (Vali, 2008) acting as immersion freezing nuclei.

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Gerber (1976) previously demonstrated dependencies on both size (surface area) and time for immersion freezing by AgI particles, but those studies also made clear that as the size increased, the time-dependent nature of nucleation faded strongly. This leads one to ask, what is the situation for mineral dust particles? Unless I am missing an obvious point, this paper does not answer the question directly, yet does select a stochastic model for framing the interpretations and for discussing implications of studies. This seems a critical issue facing the atmospheric ice nucleation community. There is no doubt that ice nucleation bears stochastic features, but deterministic features have been shown to dominate some regimes for heterogeneous populations of particles. It is unclear if and when either description of experimental data is most appropriate. Thus, I think the selection of the framework for analysis deserves some discussion in one of the introductory sections or within section 4.2 where data are first analyzed. Then, absent some compelling and comprehensive direct evidence, the extension of the method selected requires a caveat. In particular, it should be noted that in parameterising results, surface area dependencies were quantified experimentally, but cooling rate dependencies have not yet been validated.

We have now included new data to illustrate the time dependence of nucleation. Nucleation rate coefficients for kaolinite derived from experiments with variable cooling rates and also an isothermal experiment are in good agreement with the data in the initial version of the manuscript. This strongly supports the use of the stochastic model. We have explained this in more detail in the response to Vali's comments below. The specific articles cited by the referee are now discussed in the modified paper in the new section on evidence for the stochastic model (4.2).

1. Introduction

a. Discussion on page 9698-9699: A subtle point is absent from this discussion. Lack of knowledge of dust mass content or size was not the only inadequacy of previous data available for developing parameterisations of immersion freezing nucleation. Diehl and Wurzler (2004), the source reference for the freezing model used by Lohmann and

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Diehl (2006), made the assumption that they could ignore the content of dust or other ice nuclei by size, mass, or surface area in computing droplet freezing rates for cloud and climate modeling purposes. This was done to simplify matters for modeling and because they only had available for all categories of ice nuclei information on median freezing temperature.

We have added the following sentence: 'The parameterisation therefore did not include a surface area or time dependence partly because this information was not available and partly to simplify matters for the purpose of modelling.'

b. Last sentence of section: I would qualify this statement (e.g., "potentially"?), unless the authors can fully refute some of the comments to follow. The presentation and parameterisation of data are only useful to the extent that the model of ice nucleation assumed is correct, and that the extrapolation to conditions far outside the bounds of measurements is valid. Furthermore, if natural particles containing minerals are mixtures, there would seem to be additional assumptions needed in order to use the data for atmospheric prediction. Without such consideration, natural nuclei may be wrongly represented, with certain consequences in numerical cloud model simulations.

We have inserted the word 'potentially'.

2. Methods

It would be useful to add a statement regarding the number of drops used in populations monitored for experiments. I infer that it must be around 100. This has important implications for the valid experimental bounds for which the data should be used. Also, does the experimental apparatus allow for varied cooling rates in future studies?

The number of droplets in each experiment, as well as an estimate of the number of particles per median sized droplet, has been included in Table 2. We have also included an extra section on how experiments with slower cooling rates were performed.

3. Materials

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I can understand the authors' interest in focusing studies on individual minerals for the purpose of elucidating fundamental ice nucleation behaviors. Echoing my earlier comment, it is less clear how they envision using such data to describe the more varied composite behavior of natural dusts that they make note of here. Most have already understood and interpreted the noted observations to represent the fact that natural dusts probably possess a broad range of freezing activities. In fact, in light of other data, the data presented in this paper suggests that one cannot treat natural particles as unit-type dusts. So the question is how to plan to use the data presented in order to treat natural dusts? The need to suggest a future approach to this question is highlighted by the fact that a parameterisation is proposed later in this paper, which could be used inappropriately to represent natural ice nucleation by more varied mineral dusts.

We have extended section 4.6 in which we discuss how we envisage the community should use ice nucleation data on individual minerals. We suggest that knowledge of how each mineral (or nucleating species) behaves could be combined with information on the composition of natural and atmospheric dust/aerosol in order to predict the ice nucleating ability of any atmospheric aerosol.

4. Results and discussion

a. Given the analysis approach, it is vital to state what the total number of drops analyzed was in each cooling experiment. Based on Fig. 6, I have guessed that it is about 100 drops. It means that the freezing fraction assessment is only valid above about 1% of particles freezing. Based on results presented here, this limits the assessment mostly to temperatures below -28 C, consistent with a number of other recent studies that were more sensitive to freezing of smaller proportions of particles. Thus, the extrapolation of results to warmer temperatures is later done without any validation. This is the weakest aspect of the study, so far not well acknowledged, and a critical one as regards applying the developed parameterisations for the full range of relevant clouds.

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The number of droplets used to derive the rates in each run is now given in Table 2. In figure 11 we now clearly show the temperature range in which our parameterisation is extrapolated. We think that the extrapolations are reasonable given the evidence we present in support of the stochastic model.

b. Page 9702: "Pruppacher and Klett (1997) state. . ." I find this an extremely pedantic point, and one that takes the statements in the reference somewhat out of context. I think this should be rewritten. The application discussed in this reference is for a population of particles in volumes of impure distilled water, taken as a (possibly poor) surrogate of the situation of a real cloud particle having collected an array of different types of particles with different ice nucleation efficiencies. Statements are given there about the more complex situation expected for particles scavenged in real clouds, and about the more complex freezing spectra actually observed for cloud and precipitation water. In contrast, the observations in the present manuscript are for individual numbers or masses of one pure ice nucleating particle type. In this latter case one might expect to find dependence instead on surface area, if nucleation is a characteristic of the general surface or active sites are more likely to be found with greater surface area. In fact, a number of previous studies have assumed such for computing freezing rates for comparison to experiments (e.g., Hung et al. 2003). Vali (2008) clearly discusses the particular expected relation of nucleation rate and surface area for single species. Volume dependence of freezing of an undefined set of insoluble ice nuclei collected by drops has been shown. Application to single populations of nuclei that are explicitly treated for both capture and freezing in drops is the aspect that appears not to be valid. So although it may be valid to find fault with Diehl and Wurzler (2004) and subsequent articles that apply these concepts, I see no reason to fault Pruppacher and Klett (1997) in their general discussion of freezing of a population of natural cloud droplets. I suggest removing comments on this later in this section as well, and just emphasizing what is found.

We agree that this comes across as a rather pedantic point. We have modified the

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pertinent section as follows: 'We show that the mean T_f varies as a function of the surface area of kaolinite within the droplets (see Figure 3) for a constant cooling rate. In some parameterisations for use in models Diehl, 2006 406; Pruppacher, 1997 171; Bigg, 1953 105 ice nucleation is defined in terms of droplet volume. It is implicitly assumed in those studies that larger droplets will contain more particles, but nucleation probability is more correctly related to the surface area of the solid particles suspended within the droplets.'

We have also removed the reference to this in the abstract.

c. Page 9704: "We are therefore assuming that heterogeneous nucleation on kaolinite is a stochastic process, an assumption which is supported later in the paper." I find that this assumption is just that, and its validity should be left as a topic for further research. Again, unless I am missing an obvious point that needs explicit description, this assumption is not supported later in the paper. The data to support such would seem to require variation of cooling rate.

As mentioned above we have obtained and included new data which is consistent with the stochastic model.

d. Page 9705: The consequence of exclusion of data in the warmer temperature regime of "sporadic" freezing events means that most of the relevant freezing regime of mixed-phase clouds in the atmosphere is excluded. This should be acknowledged as a limitation of the present study (I do see a minor note in this regard at the end of section 4.3, but it is worth revisiting in conclusion, and it should give pause to any general recommendation for use of the parameterisation). Thus, regarding the observation that montmorillonite ice nucleation does not scale with surface area, I would also mention that this has not been validated over the full range of possible freezing conditions. Mineral dusts can and do freeze water drops at temperatures at least as warm as -15 C. It would be interesting still to know if surface area dependence exists for the less likely but more active surface sites that may nucleate ice at temperatures warmer than

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could be assessed in the reported experiments. This is especially a concern if one extrapolates this behavior to temperatures 10 or more degrees warmer, as done in Fig. 8.

We exclude 'sporadic' data at higher freezing temperatures from our determination of nucleation rates since the uncertainty associated with such values would be unreasonably large. All of the data is still included in the experimental fraction frozen curves in Figures 1, 2 and 9. We have modified the figures in which the parameterisation for kaolinite is used to either: only show the range over which our parameterisation is validated against experiment (Figures 9 and 10) or the extrapolated regime is shown as a dotted line (Figure 11). Having said this, we do feel that extrapolation of our parameterisation is reasonable given that it is based on a physically reasonable model which agrees with our experimental data (albeit at lower temperatures). In the future we plan to experimentally explore the high temperature region. Comments on montmorillonite have been removed since we have removed the parameterisation for montmorillonite (see response to Vali).

e. Page 9709: In the first paragraph of section 4.5, please make note that the impact of cooling rate assumed via a stochastic model has yet to be quantified. Furthermore, the entire proposal needs the caveat that the parameterisation should only be used to treat ice formation by pure minerals and that its application to real natural dust mixtures remains to be considered.

This is now clear in the modified section 4.6.

f. Page 9710: I do not believe it is valid (lines 18-20) to state that the parameterisations provide a reasonable approximation of nucleation rates over the temperature range of interest for mixed-phase clouds. I would go so far as to suggest that the authors consider lightly shading in the portions of Fig. 8a and b where observations were obtained (albeit at one cooling rate) and then extending the x-axes uniformly to at least 263K in order to get a feeling for the range of mixed-phase cloud for which results

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remain to be validated.

This comment has been deleted. We have also modified the figures to make it clear where the parameterisation is extrapolated (see previous comments above).

g. Page 9711: A comment similar in theme to previous ones. "A step function for freezing on clay minerals is inappropriate since nucleation has significant time dependence." In my opinion, it remains to be demonstrated under what circumstances it is inappropriate to assume a temperature and surface area dependent active fraction function for immersion freezing of mineral particles.

This comment has been deleted.

h. Page 9712, lines 22-24: Again, the statement here remains unproven.

This comment remains in the revised version and is justified by the new experimental data at variable cooling rates.

5. Summary and conclusions

a. Page 9712-13: Mirroring the above comments, the quantitative measurements presented are most accurately stated to be the freezing fraction of mineral particles in the immersion freezing mode (Fig. 1). The freezing rates are interpreted quantitatively in the context of the stochastic ice nucleation model in order to fashion a parameterisation. Can it be explained why the narrow range of freezing temperatures for a defined amount of material identifies heterogeneous nucleation as stochastic versus the result of specific characteristics of the material surface? In any case, it seems very likely that the situation of dust freezing in the natural atmosphere is more akin to the results of Marcolli et al. even if their surrogate dust was not necessarily representative. This work has justified the utility of more studies of individual minerals in addition to dust mixtures, but it remains unclear how the authors envision using the information ultimately to make reasonable atmospheric predictions. Using the parameterisations for single minerals, with the consequence that these can be described by a single contact

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angle for freezing, will poorly (and I would suggest wrongly) reflect the action of natural dust mixtures. I think what is recommended is to test both individual types and mixtures, to assess true dependencies on cooling rates, and to validate expectations over the full temperature regime of mixed-phase clouds. This may even require more than one methodology.

We agree that representing natural dusts with a single contact angle would be inappropriate and do not suggest anyone does this. We have rewritten section 4.6 (section 4.5 in the previous version) in order to clearly describe how we envisage our data being used. As discussed above, the ice nucleating properties of each mineral needs to be determined, in order to allow us to predict the ice nucleating spectrum of any natural dust. This is something that we would like to see tested in the future.

b. Page 9714: "The shape of the fraction frozen curves in Fig. 1 which are used to calculate a time dependent nucleation rate constant in Fig. 4 strongly suggest that the nucleation probability is time dependent, with an increasing rate of freezing as the temperature falls." Please explain why this is an obvious result.

This is the case because this is exactly the shape of curve one would expect to see with a temperature dependent nucleation rate coefficient in a stochastic model. Also, we have performed new experiments at variable cooling rates which provide more direct evidence in support of our choice of model. See response to Vali's comments below.

Editorial comment

Page 9704: As a practical suggestion, perhaps use the letter A for surface area, since the sigma symbol is commonly used for interfacial surface tension in nucleation studies.

Unfortunately, the letter A is often given to the pre-exponential factor in classical nucleation theory. There is also some precedent for using the symbol sigma for surface area so we have decided we should keep this as it is.

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Response to Vali's 1st comment (C2214).

With nucleation on a foreign surface, stochasticity would result either from having a uniform surface or from having a very large number of identical sites uniformly distributed on the surfaces of even the smallest particles of that material. Neither is a realistic assumption.

We disagree, the nucleation data for kaolinite suggest that this is the case. Further work is required for other substances. We discuss this in the paper and suggest that Vali and others observe a wide range of freezing temperatures because the samples studied are complex mixtures of minerals and other ice nucleating species. Natural soil samples, for example, should not be represented by a single contact angle.

Empirical manifestations of stochastic heterogeneous nucleation would be that the likelihood of nucleation would rise in proportion to the surface area of the foreign material in the sample, that all identical samples (drops) would have an equal chance to freeze at any moment, and that sooner or later any volume of water containing some of the material would undergo nucleation. The first of these manifestations is shared equally by the singular model, the second and third are not. Therefore, the first does not constitute proof in either sense. The other two afford possible ways to testing stochasticity. It is the negative outcome of such tests that constitutes powerful evidence against the stochastic model for heterogeneous nucleation, while the same kinds of test for homogeneous nucleation provide positive support. At the same time it should be emphasized that experiments in which temperature is decreased at a steady rate cannot provide any proof for stochasticity unless a large number of repetitions are performed with a large number of macroscopically identical samples. That is so, because time and temperature are loosely coupled and an increasing fraction of frozen drops, or other measures, can result from lapse of time or from activation on less active nuclei.

We have performed new experiments at variable cooling rates and an isothermal experiment. For kaolinite the results are very clear. Nucleation rate coefficients derived

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from these experiments (fully described in the revised document) are in good agreement with the data from the discussion paper. Also, in an experiment in which we held the temperature constant the number of liquid droplets decayed exponentially. This data is consistent with the stochastic model and inconsistent with the singular model.

These experiments were made possible by recent developments in our experimental approach. Previously, droplets were surrounded by N₂ gas and ice would grow on frozen droplets at the expense of remaining liquid droplets. To reduce this Bergeron-Findeison process we cooled at 10 K min⁻¹. We have now worked out how to encase these droplets with silicone oil which dramatically slows the mass transfer of water from liquid to ice particles. This has allowed us to perform experiments at slower cooling rates and under isothermal conditions. However, over longer timescales mass transfer still occurs, resulting in branches of ice growing out of frozen droplets and nucleating nearby water droplets. The effect of this process on experimental exponential decays has not been properly investigated yet. The isothermal experiment presented in the author comment (C2430) in the discussion unfortunately suffered from this issue (it took over 60 minutes) and is therefore not included in the revised paper. We are in the process of constructing a piezoelectric microdispenser to print droplets on demand in a more uniform and controlled manner than the nebuliser technique used here. This will allow droplets to be more widely spaced, reducing this problem. At present, generating a droplet distribution suitable for isothermal experiments is a matter of luck rather than skill. and we hope to systematically explore ice nucleation under isothermal conditions in the future using the microdispenser.

In summary, we have presented new data which confirms our choice of the stochastic model of nucleation. Also, our results for kaolinite do indeed suggest that all kaolinite particles possess a very similar ice nucleating 'potential' to each other, in contrast to Vali's comments.

The results summarized in the foregoing are not as simple as they are made to sound here, but their essence is as stated. The references cited complete the picture. How-

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ever, as the paper under discussion demonstrates, along with a number of other recent publications, those conclusions are not generally accepted, though it is fair to say that no contradictory evidence has been presented so far. It seems that the appeal of the stochastic description is hard to overshadow.

We disagree that no evidence for the stochastic model exists in the literature. In the revised version of the manuscript we refer to studies in which ice nucleation by AgI was examined by Heneghan et al (2002) and Gerber (1976). They clearly show that ice nucleation by this material is consistent with the stochastic model. It seems that at least some pure substances, including AgI and kaolinite, nucleate ice in a manner consistent with the stochastic model.

Specifically, on page 9704, lines 9-10, Murray et al. state that ". . . heterogeneous nucleation on kaolinite is a stochastic process . . . supported later in the paper." That support appears to be that the probability of freezing scales with surface area for kaolin. As pointed out earlier that is also consistent with the singular model.

The support now exists. We have created a new section specifically to discuss the stochastic nature of heterogeneous nucleation (section 4.2).

Differently from kaolinite, freezing temperatures didn't change with the mass of suspended montmorillonite. In the last paragraph of page 9713 the authors propose that the two minerals have to be described by the two different models. That is surprising as there is no reason to think that nucleation has some inherently different mechanism on one mineral or another. Only qualitative differences can reasonably be expected. The authors do not rationalize why different nucleation mechanism are at work for the two minerals. There is more than 6 C difference in the freezing temperatures reported for the two materials but both are well separated from the homogeneous freezing temperature for the higher particle concentrations. So, it is clear that nucleation is brought about by the impurities. How can then one material produce freezing depending on the amount of suspended particulate and the other not? According to Table 1, the amount

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of kaolinite had a ratio of 11.7 for the ratio of 20 in mass concentration (0.05 % to 1%), while the same ratio for montmorillonite is 22.2, close to what is expected. It is unclear what the 11.7 ratio means, but is consistent with having different size distributions for samples of different mass concentrations of kaolinite. Table 1 also reveals that there was roughly four times the surface area of montmorillonite (at 1% mass) than of kaolinite, i.e. particles on the average were smaller. None of this translates into a ready explanation of the different results for the two materials in terms of the density and quality of sites, i.e. the modified singular description, but it hints at the possibility that if the detailed size distributions of the particles were known perhaps clearer interpretations could be made of the results. Of course, just knowing the size distribution is not fully adequate since there is no assurance that the probability for a given type of site to occur will be the same, after generation of the powders by grinding or other means, for particles of all sizes.

The new data for montmorillonite has revealed that for the same concentration (1 wt%) at least, ice nucleation is consistent with the stochastic model. Only on changing the wt% do we see deviation from this model. We have suggested the montmorillonite crystallites may settle and stack upon one another in such a way that reduces the surface area available for nucleation. In light of the new data we have removed the parameterization of the nucleation rate coefficient for montmorillonite and state that the values in Fig 7 should be regarded as lower limits. More work is clearly needed for montmorillonite. The new data for montmorillonite was obtained by Mr J.D. Atkinson, who has been added to the author list.

While I clearly disagree with the interpretations of the measurements presented in this paper, those measurements reveal that the authors succeeded in developing a system that can produce important data on heterogeneous freezing nucleation.

Thank you.

Response to Hoose (C2261)

C6904

We agree that fundamental lab work on heterogeneous ice nucleation is needed for both pure mineral particles and more natural mixtures of mineral particles originating from major source areas. Experiments with more homogeneous particle samples of single minerals, may be more appropriate to shed light on the basic understanding of heterogeneous ice nucleation mechanisms and on the most important parameters controlling the ice nucleation rate. However, in order to translate those results into parameterizations for ice nucleation in atmospheric models, one still needs to know the relative abundance of respective minerals in the complex mixture of atmospheric dust particles. Experiments with mineral dust samples from desert source regions may be more appropriate to provide a link between fundamental lab work and atmospheric applications. In addition, artificially milled samples, as used here, might provide more active (rougher) surfaces than atmospheric dust (Möhler et al., 2006).

We agree that ice nucleation by natural desert dusts also needs to be characterized. Our approach is to measure the ice nucleating ability of each major mineral and this should then provide a method for predicting the ice nucleating ability of any natural dust made up of these minerals. In addition, after the long range transport of dust in the atmosphere the mineralogical make up of the dust is likely to change as larger size fractions sediment. Hence, the ice nucleating ability of transported dust will be different to the dust found at the source. Predicting this is certainly a challenge, but knowledge of how each mineral behaves will be an important part of the solution. We have discussed our strategy in more detail in section 4.6. This should help the reader appreciate why we have focused on individual minerals. In the longer term we plan to work with natural desert dusts. Contanzo (2001) makes the point that mineral samples from the Clay Mineral Society are processed in such a way as to minimize alterations to the clay properties, unlike the standard processes often employed when processing clay minerals and other dusts for industrial applications.

Specific surface area of the samples (Table 1). The values given in Table 1, mostly determined by BET, are for dry samples. In particular for montmorillonite, which easily

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takes up large amounts of water and has inner cavities (Karaboni et al., 1996), these values might not be valid for particles immersed in water.

We agree that this may be the case for montmorillonite. This is now discussed in section 4.4.

Information on the size distribution of the mineral particles and an estimate of the number of immersed particles per droplet (and their statistical distribution) would be helpful to interpret the data. Assuming monodisperse, spherical particles, back-of-the-envelope calculations yield montmorillonite number concentrations of > 1000/droplet, even for the lowest investigated wt%. This might give a clue on the peculiar behaviour of montmorillonite: If there is always a large number of particles in the droplets, and if they are sufficiently efficient at initiating freezing, freezing is always initiated immediately (saturation effect). On the other hand, for the lowest kaolinite concentration, estimated particle number concentrations per droplet are so small that it seems likely that many droplets did not contain any mineral particle at all. Such empty droplets would logically fall on the homogeneous freezing line. It should be mentioned whether it was technically possible to detect empty droplets and whether or not they were included in the data analysis. Cooling rate dependence. All experiments are conducted with a fast cooling rate of 10K/min, which is in the uppermost range of atmospherically relevant cooling rates. As classical nucleation theory is applied to the data, extrapolation to other cooling rates yields a strong dependence of the fraction of frozen droplets at a certain temperature on the cooling rate (Fig. 8). However, this is not supported by the experiment itself. We suggest that experiments with variable cooling rates need to be conducted to confirm or disprove this behaviour.

We have now given an estimate of the average number of clay particles per median droplet in Table 2. This was determined using the BET surface area and density of the clays. We do not have data for the size distributions. Even droplets made with the lowest concentration kaolinite suspension contained an average 21 particles (for the median sized droplets).

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Droplets which froze below 236.1 K were not included in the calculation of the nucleation rate since it was unclear if these droplets froze homogeneously or heterogeneously. This is discussed in section 4.2.

We have now conducted experiments over a range of cooling rates. This is discussed in more detail in the response to Vali's comments.

Although the kaolinite data are fitted well by classical nucleation theory, this is not a proof that a different model (e. g. a singular model with a certain surface density of active sites, as in Connolly et al. (2009)), would not fit the data equally well.

The variable cooling rate experiments provide strong support for the use of the stochastic model. See response to Vali.

Murray et al. provide a nice and clear direct proof of the surface area dependence of immersion freezing, but it should be noted that it is common knowledge in the community that the previously observed volume-dependence for freezing of suspensions is not due to the water volume, but to the fact that larger droplets contained more dust particles. The surface area dependence for immersion freezing has been experimentally demonstrated and discussed in previous publications by e. g. Zuberi et al. (2002); Hung et al. (2003); Archuleta et al. (2005); Marcolli et al. (2007).

We agree, our comments on this subject were inappropriate. This paragraph in section 4.1 has been revised to read: 'We show that the mean T_f varies as a function of the surface area of kaolinite within the droplets (see Figure 3) for a constant cooling rate. In some parameterisations for use in models Diehl, 2006 406; Pruppacher, 1997 171; Bigg, 1953 105 ice nucleation is defined in terms of droplet volume. It is implicitly assumed in those studies that larger droplets will contain more particles, but nucleation probability is more correctly related to the surface area of the solid particles suspended within the droplets.'

Note also that several parameterizations, also used in global and smaller-scale models,

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which are based on classical theory, include surface-area and time dependence (Liu and Penner, 2005; Khvorostyanov and Curry, 2005; Hoose et al., 2010). Pruppacher and Klett (1997) is cited as a reference for volume-dependent freezing; however, Pruppacher and Klett (1997) also amply discuss classical nucleation theory with surface area-dependent freezing rates.

The pertinent text in section 4.1 now reads: 'In some parameterisations used in models (Diehl et al., 2006; Pruppacher and Klett, 1997; Bigg, 1953) ice nucleation is defined in terms of droplet volume. It is implicitly assumed in those studies that larger droplets will contain more particles, but nucleation probability is more correctly related to the surface area of the solid particles suspended within the droplets. Parameterisations which account for surface area therefore more accurately describe heterogeneous nucleation (Hoose et al., 2010; Khvorostyanov and Curry, 2005, 2004).'

The total number of droplets examined should be given. An estimate of the number of particles per median sized droplet is now given in Table 2.

Response to Wex (C3783)

Recent work on the immersion freezing behavior of droplets containing single Arizona Test Dust (ATD) particles (Niedermeier et al. 2010), shows results (fraction of droplets frozen versus temperature) that are similar (within error bars) to the 0.005 wt% Kaolinite solution described in the current paper. The measurements were made with the Leipzig Cloud Aerosol Simulator (LACIS), where cloud droplets were activated and grown by vapor diffusion on monodisperse (size selected) ATD particles.

We have added a comment on this in section 4.3: 'Niedermeier et al. Niedermeier, 2010 462 recently reported nucleation rate coefficients for Arizona Test Dust immersed in water droplets. They find a J value of $107 \text{ cm}^{-2} \text{ s}^{-1}$ at 239 K, whereas we report a value of $105 \text{ cm}^{-2} \text{ s}^{-1}$ at the same temperature for kaolinite. This would appear to indicate that ATD, or at least the component of ATD which nucleates ice, is more active than the kaolinite used here.'

C6908

In our opinion, differences in results obtained for ATD in different studies are at least partly due to the use of polydisperse dust versus size segregated dust particles. As already stated by Marcolli et al. (2007): "For a stricter validation, freezing experiments of size-selected ATD samples are needed."

We have modified the discussion in the materials section. We now state: 'Later in the paper we suggest that the wide range of freezing temperatures observed in some immersion mode experiments Marcolli, 2007 386; Vali, 2008 455 is in part a result of the wide range of minerals present in natural and test dusts. Marcolli et al. (2007) also suggest there is dependence on the size distribution of mineral particles.'

We also note that a two-parameter parameterization of nucleation rates for immersion freezing based on classical nucleation theory (CNT) was introduced by Niedermeier et al. (2010), which is similar to the formulation given in your work. We suggest that these points should be discussed in your work in order to place the results in context with prior work.

This is now discussed in section 4.2.

Response to Vali's second comment (C2498)

Vali's main comment is on the preliminary isothermal data presented in our initial response (ACPD 10, C2430). We have since decided not to include this data because we need to further investigate the effects of mass transfer between droplets in experiments which take more than 20 minutes as nucleation of liquid droplets can occur from ice branches extending from frozen droplets (see above, in the reply to Vali's main comment). The preliminary isothermal experiment lasted longer than an hour and was unfortunately subject to this artefact. The isothermal experiment included in the final version took less than 15 minutes altogether, including the ramping sections, and so mass transfer was not an issue. We have argued above that the isothermal and also the variable cooling rate experiments lend strong support to the use of the stochastic model.

C6909

C6910