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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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General Comment

This manuscript provides an interesting and useful new data set on the ice nucleation properties of individual mineral dust species. This work could lead toward advances in parameterising ice formation by mineral dust particle populations in cloud model simulations, but I do not feel that the present extension has been given due consideration or explanation. To summarize my primary point for consideration, choice of a fully stochastic nucleation model is an assumption that has not been given definitive support by the measurements presented, and hence, a few caveats appear necessary regarding the quantitative limitations of the methods proposed for representing ice nucleation behavior in this manner across the full mixed-phase temperature regime of clouds for which data have been extrapolated. For the same reason, the paper should highlight not just the utility of additional studies of individual mineral particles, but the need for measurements fully documenting the time dependence of freezing and if, when and how this becomes expressed for natural populations of dust particle mixtures.

Specific Comments

Abstract

This comment is a general one, since I am not sure where in the paper it needs to be given discussion. The abstract and the paper support that these are the first "quantitative" experiments on immersion freezing of pure water drops by individual mineral particles, primarily due to carefully controlling the amount of material placed in drops, an important missing piece of some earlier studies that were used for proposing parameterisations. 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. 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

ACPD

10, C2119–C2126, 2010

Interactive Comment

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.

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 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.

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 parametrisation 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.

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?

ACPD

10, C2119–C2126, 2010

Interactive Comment

3. Materials

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.

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.

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.

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.

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

ACPD
10, C2119–C2126, 2010

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 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.

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.

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 remain to be validated.

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.

ACPD

10, C2119–C2126, 2010

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

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 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.

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.

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.

ACPD

10, C2119–C2126, 2010

Interactive Comment

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ACPD

10, C2119–C2126, 2010