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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 1

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

I recommend publication of the paper as it is well-written and well-argued. It would be a valuable addition to the literature were it to be published as-is. That said, I have a few comments, suggestions, and questions that the authors can consider.

First, I think the authors have buried the lede. While the analysis that they've performed is extensive, I think the data they mention but exclude from the analysis is the most in-

teresting aspect of the paper. On pg. 21, the authors discuss the fact that there seems to be a special type of particle present in some of their samples which dominates the freezing behavior if it is present in the droplet. Their estimate is that 1 in 10^5 particles of their powder is this type. They re-affirm this conclusion on pg. 30 (first paragraph, C9867 which starts on pg. 29.) The existence of these rare but highly effective IN is an important finding. The fact that 1 in 10^5 particles are of this type deserves to be in the Abstract.

We have inserted the following sentence into the abstract: 'We show that NX illite exhibits strong particle to particle variability in terms of ice nucleating ability, with 1 in 10^5 particles dominating ice nucleation when high surface areas were present.'

There's another point, which is potentially even more significant (in my opinion), which is not spelled out, but may be lurking in the data and the analysis. The authors show in Figure 3, for instance, that experiments in which they used a low concentration of dust (0.007 weight percent by mass) were consistent with homogeneous nucleation of water over a range of temperatures. Does that mean there were no particles in the droplet or that there were particles in the droplet, but they had no effect on the nucleation rate over the timescale of the experiment? (You could estimate this with a couple of assumptions. I calculate that a droplet with a diameter of 20 μm has a mass of 4.2 ng and an aerosol particle with a diameter of 1 μm has a mass of 1.4x10$-$12 g. (That assumes a spherical particle.) That works out to an average of about 1 particle per droplet for a weight percent of 0.007. That corresponds to (using Poisson statistics) the same probability of having 1 or zero particles in a droplet.) If there are particles in the drop but ice still nucleates homogeneously, that's more important than the existence of the rare, but effective, particles in the powder sample. I would say that the community assumes that if something like illite were present in a cloud droplet, the freezing temperature would be higher than homogeneous. If there are particles present in drops that are nucleating homogeneously, that should be stated in the Abstract.

Yes, it is interesting that homogeneous nucleation can compete with heterogeneous

ACPD
11, C12658–C12664, 2011

Interactive Comment

nucleation and we discussed this extensively in a previous article on heterogeneous nucleation by kaolinite (Murray, ACP, 2011). According to our calculations all droplets in the present study contain many dust particles because the mean size of NX illite particles is on the order of 20 nm. This is now discussed in an expanded discussion in the results section which now reads: ‘The number of particles per droplet can be estimated using the surface area of NX illite per droplet if the size of the NX illite particles is known. Based on the estimated size of individual NX illite particles (20nm, see section 3), calculations indicate that even for the lowest concentrations (0.006 wt %) there should be at least 1000 of these individual particles per droplet. We assume here that the individual 20 nm particles are evenly distributed throughout the droplets.’

In addition we have highlighted the fact that our parameterisation of ice nucleation allow the competition between homogeneous and heterogeneous nucleation. We have inserted the following into section 5: ‘Another important point is raised on inspection of Figures 15 and 16: homogeneous nucleation is predicted even though the droplets contain solid particles. This shows that homogeneous nucleation can be more effective than heterogeneous nucleation under certain conditions. This behaviour was also observed during experiments investigating immersion mode freezing by kaolinite and was discussed in some detail previously (Murray, 2011).’ and also inserted the following into the summary and conclusions section: ‘. In fact, we show that heterogeneous freezing on many NX-illite particles does not compete with homogeneous freezing.’

Pg 4, 1st paragraph: ”Atmospheric IN in mixed phase clouds are thought to be...” Not thought to be. The IN are mineral dust, soot, etc... And not just in mixed phase clouds, cirrus clouds too, though I suppose you could argue that the ice nuclei in cirrus could also include things like solid ammonium sulphate

Agreed, changed,.’thought to be’ to ‘are’.

Pg. 5, last line of the 1st paragraph: ”Additionally, this ’inside-out’ contact nucleation was observed to occur at higher temperatures than immersion freezing for the same

ACPD
11, C12658–C12664, 2011

Interactive Comment

IN." This has been observed for all kinds of contact nucleation, not just 'inside-out'. See, as one example, Fukuta, J. Atmos. Sci., 32, 1597-1603, 1975.

This has been rewritten and now more correctly reads: '. Generally, contact nucleation has been observed to occur at higher temperatures than immersion freezing for the same IN.'

Pg. 8, first full paragraph: The discussion of active sites here is incomplete. While it is true that ice has been observed to form over and over again on specific sites on a substrate, there are other cases in which ice did not exhibit a preference. There's a recent article by Gurganus et al. in J. Phys. Chem. Lett. which shows no preferred location for ice nucleation from supercooled water on a silicon wafer. You could argue that there's no preference in that case because there were no active sites on the surface of the silicon wafer (though I think that's stretching the concept of active site pretty thin). There is also work (e.g. Bryant, Hallett and Mason, J. Phys. Chem. Solid, 1960) which showed ice nucleation from the vapor where it did not seem to form preferentially at steps, cracks, edges, etc... (at least from the photos they show). I think the discussion of active sites in this paper is superfluous. You don't even need it for the discussion of the singular model. In my opinion, this discussion muddies the waters and leaving it out would improve the paper.

Yes, this is a complex topic and we agree that it is not central to this paper. We have removed the section in line with the referees' view that it is superfluous.

Page 8, last clause on the page: As a counter argument to the claim that the time dependence of ice nucleation by natural IN is negligible, I would offer a recent observation, documented in Crosier et al., ACP, 2011. Ice formation over such an extended time could be due to something that has a low nucleation rate at those temperatures, but which shows up over the time scales they document. (I realize that the authors are not claiming that time dependence in the atmosphere is negligible, but it wouldn't hurt to provide a counter example to the reference in Pruppacher and Klett.)

ACPD

11, C12658–C12664, 2011

Interactive Comment

At the end of section 2.1 (singular) we have added the following which leads into the discussion of the stochastic model: ‘ While the singular model is convenient and may be a good approximation under many atmospheric conditions, time dependence of nucleation may be important in some cloud types Crosier, 2011 87.’

Pg 10: acronym, IASSD. This is not used elsewhere in the paper and so no acronym needs to be defined here.

Changed

pg. 21: A few possibilities are cited in the second paragraph for the ”complex surface area dependence” of freezing in the ”high surface area regime”. I am not convinced by these explanations. Flocculation is agglomeration of particles in a colloidal suspension. Is the concentration of particles high enough in your droplets for this effect? (Estimate the number of particles in the 10 % by weight samples, perhaps.) In any case, I would expect that flocculation would change the surface area of the powder in the droplet by a little, but not by much. In any case, if there is a change due to flocculation (or settling out), there should be a time dependence since flocculation and settling out occur over a finite time scale. Was that observed?

We agree that this is not an entirely satisfactory explanation, but the key point is that we need to treat this very high concentration data with caution. We have adjusted the pertinent lines in order to make this more clear: ‘It may be possible these high wt % droplets were not stable; as the concentration of clay-in-water suspensions is increased, flocculation and settling out of material can occur; hence, results from concentrated clay-in-water suspensions should be treated with caution. This work highlights the need to use a range of cooling rates and IN concentrations when performing these types of experiments, in order to be able to quantify the ice-nucleating ability of a particular material in an atmospherically relevant manner.’

equation 15: a physical interpretation is given for b, but not for a. You state that a defines the slope of ln J, but what is that physically? If b is the distribution of nucleation

ACPD
11, C12658–C12664, 2011

sites, what is a? This is an interesting analysis, but you can fit a lot with two adjustable parameters. A physical meaning for b at least provides a toe-hold for eventually testing the idea, but unless a physical meaning for a is found, equation 15 is just an interesting mathematical exercise. (I would also advocate citing Niedermeier et al., (ACP, 11, 8767-8775, 2011) in this section of the paper. Their paper also attempts to reconcile the stochastic and singular descriptions of ice nucleation.)

The parameter a is simply how quickly the nucleation rate increases with temperature. We were driven to construct the model using just two adjustable parameters in this manner in order to be free of the assumptions made in classical theory. In fact, when we originally set out to build this model we tried using a distribution of contact angles, but found that we were not able to reproduce the independence of fice on experimental cooling rate. This showed that we needed a steeper ln J vs T curve than predicted by classical contact angle based theory. In a sense the referee is correct in saying it is a mathematical exercise, but this model allows us to explore what is needed and this challenges classical theory and we also intend to use this model in our cloud models. On hind sight we should have mentioned the classical theory and why we didn't use it. We have added a paragraph at the end of section 4 to describe this: '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 = nPθi, 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.'

In addition, we have added a few lines in the discussion of the stochastic models in section 4.6 and section 2 on the very new Soccer ball model. Section 2: 'A form of the multiple component stochastic model has also been discussed by Niedermeier et al. (2011), who presented a conceptual 'soccer ball' model in which a particle's surface

ACPD
11, C12658–C12664, 2011

was divided into separate patches whose properties were defined by a particular contact angle.' Section 4.6: 'Very recently, Niedermeier et al. (Niedermeier et al., 2011) presented a conceptual 'soccer ball' model with the aim of reconciling stochastic and singular behaviour in ice nucleation. Their model treats particles as having a surface containing a number of regions of varying ice nucleation ability. The nucleation efficiency on each surface region was described with a contact angle and the nucleation probability then determined using classical nucleation theory.'

Minor comments There are frequent references to Pruppacher and Klett, Microphysics of Clouds and Precipitation, 1997. That's a 954 page book. Please provide at least a pointer to the chapter you are referencing (section or pages would be better). Just referencing the book doesn't help much. Someone familiar enough with the field to know where to find the relevant material in PK probably doesn't need the reference, and someone who doesn't know the field that well, needs more than just a reference to the whole 954 pages. I commend the authors on their decision to use both color and symbol/line style to differentiate their data. There are folks out there who are red-green colorblind, for example.

There was perhaps an over reliance on Pruppacher and Klett in the paper. We have replaced a number of the citations with more focused and more recent journal articles.

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ACPD

11, C12658–C12664, 2011

Interactive Comment