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Discussions

Interactive comment on "Pre-activation of aeosol particles by pore condensation and freezing" *by* Claudia Marcolli

Anonymous Referee #1

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This manuscript puts forward a literature review-based concept of pre-activation by aerosol particles via the pore condensation and freezing (PCF) mechanism. Application of this mechanism suggests that pre-activation by PCF is constrained by the melting of ice in narrow pores and the sublimation of ice from wide pores. For these reasons, the author argues pre-activation for cylindrical pores is imposed by restrictions on the temperature and relative humidity range. In addition to reviewing previous experimental data sets with regard of finding indications of this concept, the author also puts forward atmospheric scenarios where pre-activation may play a significant role in atmospheric ice formation.

The topic of this manuscript fits within the scope of ACP. The author carefully reviewed the previous literature dealing with pre-activation phenomena. Although, I like the proposed concept and the effort to use previous data for interpretation, I feel some revi-

sions that deal with the general uncertainty of proposed concept and data, are necessary before this manuscript can be published. The author has my full support of publishing this manuscript, hopefully encouraging further experimental investigation of this effect.

As written, the manuscript often reads as if the novel concept is a "fact". One has to keep in mind that there is no experimental in situ proof of the suggested mechanisms for discussed and investigated particles. Considering this, some statements appear "too factual" and thus should be changed in a way to convey the suggestive nature of this discussion.

For example, the ice formation experiments from the second half of the last century are not well constrained in terms of particle and ice crystal numbers, relative humidity, etc. Often no control or calibration experiments were performed. Considering that even current ice nucleation experiments deviate significantly (see recent data reviews or intercomparison studies), the experimental data can very likely not be used as a definitive support of the proposed concept. This is also indicated by the values in the presented tables which do not include any uncertainties and in many cases the errors, I believe, cannot even be defined or are just very large. Keeping this all in mind, some statements should be more adequately formulated.

For this review, I read Marcolli (2014) that introduces PCF. It is argued that homogeneous freezing occurs in the nanometer-sized pores. From this, as far as I understand, the critical size of the ice embryo fitting inside a pore is derived. However, does homogeneous freezing not also depend on the volume and time? The homogeneous freezing line corresponds to about Jhom=1E10 cm-3 s-1 (Koop et al., 2000). Pores 4 – 20 nm wide and about 16-20 nm deep have a volume of about 1E-19 cm3, resulting in an ice nucleation rate of about 1E-9 s-1. Obviously, one would need to wait 1E9 s at those fixed conditions to observe 1 ice nucleation event in 1 second. The liquid in 1E18 pores would be needed to observe a freezing event in 1 second. Maybe Jhom in pores is different but then other aspects/assumptions break down. Very recently Koop and

Murray (2016) showed that Jhom is not continuously increasing with decreasing temperature, limiting the rate for nucleation to about 1E12 cm-3 s-1. Maybe I am missing here something? My point is that all reported or applied ice nucleation data sets inherently are based on different particle surface areas and experimental time scales and have different pore numbers (and sizes), all of which are mostly unknown or associated with large uncertainties. Thus, it is very unlikely that any of the stated experiments can be used to make a definitive case for pre-activation by PCF.

The same discussion/exercise can be done assuming immersion freezing in a pore by an active site. Immersion freezing and deposition ice nucleation are known to depend on particle surface area (e.g. Kanji et al., 2008). Looking at the literature (e.g. review article by Murray et al. 2012) it looks like "a lot of surface area" has to be provided to detect ice formation. For example, typical experimental particulate surface areas are larger than 1E14 nm2 to observe ice formation. Many pores are needed that contain an active site to be able to reproduce the data sets.

I am not stating this to cast doubt on the PCF mechanism, which I like and support, but at current stage I recommend to be more careful how to discuss this concept with regard to experimental data. Having said all that, I am not surprised to see some experiments somehow following the presented concept and some not, even if same or similar porous materials were applied. The data sets are just not sufficiently constrained. Statements that a particular approach, such as the cold stage experiment, as discussed in more detail below, is producing potentially erroneous data with respect to pre-activation is, however, unfounded and should be discarded. With present uncertainties and lack of experimental proof, those statements are unjustified. As a matter of fact, these statements detract from the overall nice manuscript.

Page 5-6, section 3: It would be interesting to know how long it takes for ice or water to evaporate from the different pores. This could be done as a function of difference of pore equilibrium RH and ambient RH (and exemplary pore size). This would give an idea if the transient state is important or not. In particular, in an actual cloud with

eddies (up/downdraft), the transient state may be a crucial parameter.

Page 7, line 10: "However, . . .". This sentence seems to be confusing.

Page 8, line 25: "A freeze concentrated. . .". How are the water activity values derived?

Page 9, line 28: I highly doubt that the freezing point in that type of experiment can be measured to this degree in 1949. This may not be even possible today.

Page 10, line 28: "Results of ball milled Iceland spar in the size range from 1 – 15 μm with large numbers from 1 – 3 μm were presented in most detail: 1 – 5 % of the particles showed pre-activation when kept for 1 min at 84 – 98 % RHi (see Table 3)." This sounds a bit confusing: Did you mean "Results of ball milled Iceland spar particles, in the size range from 1 – 15 μm with the largest particle numbers in the size from 1 – 3 μm, were discussed/investigated in most detailine In this case, 1 – 5 % of the particles showed pre-activation when kept for 1 min at 84 – 98 % RHi (see Table 3)."?

Page 11, line 22-24: Can it be shown quantitatively that equilibrium was not reached? This is related to my comment above regarding sublimating ice.

Page 12, line 33: "However, . . .". Please avoid this statement. There is no evidence for this and just speculation. Though the authors of this study did not use microscopic techniques, as far as I recall this work, this is just not a qualified statement. With better experiments in the future, time will tell. One cannot just say a technique is "wrong" when it does not "obey" a new concept.

Page 13, line 18: "Therefore,. . .". Again this is an unsubstantiated statement considering all uncertainties and should be omitted. In fact, Roberts and Hallet observed the particles and ice crystals with a microscope. Some general remarks for this study and following cold stage experiments below:

If ice forms between a particle and substrate, it will move the particle and the sample image would change. Any microscopist would observe and notice this effect and this would have been long established in the community. This is so significant that it would have not been missed. In particular, when looking at the particle multiple times for pre-activation. Furthermore, since mineral dust particles are not uniform, the gaps between particle and substrate are very likely much larger than a few nanometers. Having "accidently" a gap where the particle touches the substrate similar to a specific pore size active at that specific supersaturation is unlikely. Pores of a few nanometers, one finds almost only on apparently planar and smooth surfaces but not between a few hundred nanometer to micrometer sized particle touching a smooth substrate. Also, if this would be the case, one would, in principle have always some degree of pre-activation using deposited particles which is not the case. Depositing different mineral types, one measures different ice formation conditions. See e.g. Eastwood et al. (2008), where calcite deposited on a substrate shows vastly different ice formation than Kaolinite. The arguments put forward would also imply that deliquescence and efflorescence data are prone to artifacts as well which hasn't been substantiated. Lastly, even if one argues that there is a gap between particle and substrate in suggested pore size, it is a gap and not a pore and one side of the gap is chemically vastly different compared to the mineral dust particle. The case, that there are pores of specific properties due to having particles deposited is just completely unsubstantiated.

Page 13, line 30: "Edwards....". Please omit and see previous comment.

Page 17, section 5.1: This section should be completely omitted. This is way too speculative to be included. There are so many groups using this technique and an issue like this would have been communicated previously. See comments above.

Page 23, line 3: Statements can be changed in a way: "...indicating the presence of pores..." for "...suggesting the presence of pores...", etc. Again, it is a new concept only....

Page 25, line 17-18: Again, unsubstantiated claims that in all cold stage experiments water is present between particle and substrate causing pre-activation and in principle artifacts. This should be discarded. Bringing this point up over and over in this

manuscript is really detracting.

Technical Corrections:

Page 1, line 14: Maybe omit "severe". Not really a quantitative statement.

Page 1, line 19: Maybe "is" instead of "are".

Page 7, line 3: Maybe "decreases" instead "sinks".

Figure captions 1-3: Captions could be shortened in cases where same data are shown.

References:

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