

*I thank the reviewer for his/her thoughtful comments, which I address below in italic.*

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 revisions 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.

*This review is intended to have an explorative character by asking the question: assuming that pre-activation is due to ice persisting in pores, what pore properties would be needed to explain the experimental findings? Recent studies carried out with mesoporous silica materials permit to constrain the conditions needed for pre-activation due to pore ice. However, contributions of other mechanisms to the reported cases of pre-activation cannot be excluded. I added a new Section 5.4 (Alternative pre-activation mechanisms) to make clear that the analysis of the experimental data with respect to a mechanism involving pore ice does not preclude other mechanisms leading to pre-activation. In the revision process of the manuscript, I checked the statements for their factuality and emphasized more their suggestive nature.*

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.

*Some of the reviewed papers give detailed description of the experimental conditions including uncertainty ranges others are rather qualitative. Each study should be judged on its own and not be discarded just because of its age.*

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  $J_{\text{hom}}=10^{10} \text{ cm}^{-3}\text{s}^{-1}$  (Koop et al., 2000). Pores 4 – 20 nm wide and about 16-20 nm deep have a volume of about  $1\text{E-}19 \text{ cm}^3$ , resulting in an ice nucleation rate of about  $10^{-9} \text{ s}^{-1}$ . Obviously, one would need to wait  $10^9 \text{ s}$  at those fixed conditions to observe 1 ice nucleation event in 1 second. The liquid in  $10^{18}$  pores would be needed to observe a freezing event in 1 second. Maybe  $J_{\text{hom}}$  in pores is different but then other aspects/assumptions break down. Very recently Koop and Murray (2016) showed that  $J_{\text{hom}}$  is not continuously increasing with decreasing temperature, limiting the rate for nucleation to about  $10^{12} \text{ cm}^{-3}\text{s}^{-1}$ . 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.

*Thank you for bringing up this question which I in fact considered when I prepared Figure 3 of Marcolli (2014), but these consideration are not stated in the paper. So I do it here:*

*Figure 3 of Marcolli (2014) shows the freezing data of completely filled pores, most of them determined by differential scanning calorimetry (DSC) with cooling rates of 0.5 - 5 K/min and evaluating the onset of the freezing peak. This experimental data is compared with the freezing temperatures determined from the*

CNT parameterization by Zobrist et al. (2007) applied to the pore freezing conditions in the DSC and evaluated as a function of pore diameter. For the calculation of the freezing rate, it was assumed that the experiment was carried out at a cooling rate of 0.5 K/min and that the onset of the freezing peak is representative of a frozen pore fraction of 0.01. Since only for the cage-like pores homogeneous ice nucleation is expected (data from Kittaka, 2011; Janssen, 2004; Liu 2007), freezing was assumed to occur in spherical pores. It can be seen from Fig. 3 of Marcolli (2014) that the measured freezing temperatures of homogenous nucleation are in good agreement with the calculated ones. This justifies the assumption that homogeneous ice nucleation is still quite efficient in small volumes as long as the volume is larger than the critical nucleus size given by CNT.

With the parameterization by Zobrist et al. (2007) a nucleation rate coefficient of  $J_{hom} = 10^{10} \text{ cm}^{-3}\text{s}^{-1}$  is reached at a temperature of about 235 K. At 230 K, it is already  $J_{hom} = 10^{18} \text{ cm}^{-3}\text{s}^{-1}$ . These values are much larger than the ones from the new CNT parameterization by Koop and Murray (2016), which was derived using physically consistent parameterizations of the key parameters of CNT, namely, ice-liquid interfacial energy and the diffusion activation energy. However, this parameterization does not seem to be applicable to ice nucleation in pores. In fact, the uncertainties associated with homogeneous ice nucleation rates are notoriously high and even increase the lower the nucleation temperature is. This is due to experimental uncertainties and difficulties. To reach very low freezing temperatures, either the sample has to be cooled very fast or the sample volume has to be very small. To justify their parameterization, Koop and Murray (2016) refer to Laksmono et al. (2015) who applied very high cooling rates to their samples. They found nucleation rate coefficients below  $10^{13} \text{ cm}^{-3}\text{s}^{-1}$  between 226 - 232 K when they cooled micrometer-sized droplets by 1000 - 10000 K/s. Since cooling rates of  $10^7 \text{ K/s}$  lead to vitrification instead of freezing, the maximum nucleation rate coefficient that can be obtained from experiments with microdroplets is  $10^{16} \text{ cm}^{-3}\text{s}^{-1}$  (Laksmono et al., 2015). This restriction does not apply to nanodrops or nanopores, since here, high nucleation rate coefficients can be reached with lower cooling rates because the volume is smaller. Manka et al. (2012) and Huang and Bartell (1995) reached nucleation rate coefficients of  $> 10^{23} \text{ cm}^{-3}\text{s}^{-1}$  when they investigated nanometer-sized droplets in the temperature range from 202 K - 228 K. I think, that the relevant experiments to estimate freezing rates in nanopores are the ones that are carried out with small volumes rather than huge cooling rates. The best argument that homogeneous ice nucleation in nanopores indeed occurs is the freezing peak in the DSC experiments with SBA-16 with cage-like pores that are connected by too narrow pores for ice to propagate, so that water has to nucleate in each cage individually. From this it can be concluded that nucleation rates are high enough for pore freezing.

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  $1\text{E}14 \text{ nm}^2$  to observe ice formation. Many pores are needed that contain an active site to be able to reproduce the data sets.

*The probability of immersion freezing in pores has been estimated in Marcolli (2014; pages 2082 – 2083) for ATD using the parameterization by Marcolli et al. (2007). Indeed highly porous particles are needed to render the presence of an active site within a pore probable.*

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.

*Cold stage experiments are not discarded in the discussion of pre-activation. However, it is important to mention possible artifacts, even if further investigations might not substantiate them.*

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.

*The timescale of pore sublimation is indeed an important question, however, there is no simple answer to it. Recently, some experimental and modeling studies have been published that investigated the rates and processes of pore evaporation. These studies are now summarized in the revised manuscript in the new section 3.2 (Kinetics of pore ice sublimation).*

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

*Thank you for pointing this out. This sentence should read: “However, a cylindrical pore with 4 nm diameter should have a similar ability of pre-activation.”*

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

*The water activity is not derived. It is assumed to be 0.95 when the pore is completely filled as stated in the sentence above.*

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.

*This is a problem of converting from degree C to Kelvin. To be consistent within the manuscript, all temperatures are given in Kelvin. When the original paper states the temperature in degree C with one decimal place, I transformed to Kelvin by adding 273.15 K. This leads to two decimal places in the converted temperature.*

Page 10, line 28: "Results of ball milled Iceland spar in the size range from 1 – 15 $\mu\text{m}$  with large numbers from 1 – 3  $\mu\text{m}$  were presented in most detail: 1 – 5 % of the particles showed pre-activation when kept for 1 min at 84 – 98 % RH<sub>i</sub> (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  $\mu\text{m}$  with the largest particle numbers in the size from 1 – 3  $\mu\text{m}$ , were discussed/investigated in most detail. In this case, 1 – 5 % of the particles showed pre-activation when kept for 1 min at 84 – 98 % RH<sub>i</sub> (see Table 3)."?

*Yes, this was meant. I revised the manuscript accordingly.*

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.

*Recent studies indeed indicate that it takes minutes to reach equilibrium. I added the sentence: "Capillary evaporation within such timescales is in accordance with measurements performed with mesoporous silica materials (see Sect. 3.2)."*

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.

*I would like to keep the sentence but I will weaken it by stating: "However, as the particle were deposited on glass cover slips, the location of pore ice might also have been voids between the substrate and the particles instead of pores within the particles or between particle aggregates (see also Sect. 5.1)".*

Page 13, line 18: "Therefore, ...". Again this is an unsubstantiated statement considering all uncertainties and should be omitted. In fact, Roberts and Hallett 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 "accidentally" 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.

*To be susceptible to pre-activation, the voids need to be in the low nanometer range. The filling of such narrow pores is not discernable in a light microscope. It will also not lead to a detectable movement of the particle. The study by Eastwood et al. (2008) used a microscope with a 10x objective lens to detect ice crystals growing from mineral dust particles. Figure 3 of this paper shows that with this magnification even a micrometer movement of a particle is not detectable. The study by Eastwood et al. was not designed to detect pre-activation since the samples were only cooled once. This is the case for most studies that investigate deposition nucleation. To detect pre-activation, the same sample must be cooled at least twice without warming above 273 K between cycles.*

*Irregular shaped particles on a substrate may give rise to irregular shaped voids in which water can condense. Such irregularly structured voids might offer suitable geometries for persisting pre-activation.*

Moreover, they might be swelling. The voids do not need to have specific properties. Just a portion of them needs to be of the right size so that capillary water can condense in them.

Particles that deliquesce and effloresce consist of soluble material. Unlike mineral dusts, they dissolve when relative humidity is increased.

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

*I omit this sentence here.*

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.

*The difference in the fraction of successfully pre-activated materials observed by cloud chamber experiments compared with cold stage experiments is significant: In the cloud chamber experiments carried out by Fournier d'Albe (1949), Mossop (1956), Day (1958), and Mason and Maybank (1958) 8 – 34% of the tested materials were susceptible to pre-activation. In the cold stage studies by Higuchi and Fukuta (1966), Roberts and Hallett (1968), Edwards and Evans (1971) and Knopf and Koop (2006) 80 – 100 % of the tested materials were susceptible to pre-activation, and pre-activation persisted over long conditioning times at low RH. Capillary water and ice in voids between particles and substrates is an explanation that deserves consideration for this systematic discrepancy between the two techniques. Therefore, I would like to keep this section. It should be a caveat for future studies. The arguments given by the reviewer why such an effect cannot be present are not convincing. I improved in the revised manuscript the explanation why I think that water collected between substrate and particle can be responsible for persistent pre-activation in cold stage experiments.*

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....

*I have changed the manuscript accordingly.*

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.

*I agree that it is not more than a claim. But I think that this claim should not be discarded. There is indeed a significant difference in the persistence of pre-activation observed in cloud chamber experiments compared with cold stage experiments that deserves a better explanation than to declare old studies untrustworthy. I hope that keeping this statement in the conclusion can stimulate more careful consideration of this issue in future cold stage experiments.*

Technical Corrections:

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

*Omitted.*

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

*Corrected.*

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

*Changed.*

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

*I would like to keep the captions the way they are.*

References:

Marcolli, C.: Deposition nucleation viewed as homogeneous or immersion freezing in pores and cavities, Atmos. Chem. Phys., 14, 2071–2104, doi:10.5194/acp-14-2071-2014, 2014.

Koop, T., Luo, B. P., Tsias, A., and Peter, T.: Water activity as the determinant for homogeneous ice nucleation in aqueous solutions, Nature, 406, 611–614, doi:10.1038/35020537, 2000.

Koop, T. and Murray, B. J.: A physically constrained classical description of the homogeneous nucleation of ice in water, The Journal of Chemical Physics 145, 211915 (2016); doi: 10.1063/1.4962355

Kanji, Z. A., Florea, O., Abbatt, J. P. D.: Ice formation via deposition nucleation on mineral dust and organics: dependence of onset relative humidity on total particulate surface area, Environ. Res. Lett. 3 (2008) 025004.

Murray, B. J. O'Sullivan, D., Atkinson, J. D., and Webb, M. E.: Ice nucleation by particles immersed in supercooled cloud droplets, *Chem. Soc. Rev.*, 41, 6519–6554, doi:10.1039/c2cs35200a, 2012.

Eastwood, M. L., S. Cremel, C. Gehrke, E. Girard, and A. K. Bertram: Ice nucleation on mineral dust particles: Onset conditions, nucleation rates and contact angles, *J. Geophys. Res.*, 113, D22203, doi:10.1029/2008JD010639, 2008

*References:*

*J. Huang and L. S. Bartell, J. Phys. Chem. 99, 3924 (1995).*

*H. Laksmono, T. A. McQueen, J. A. Sellberg, N. D. Loh, C. Huang, D. Schlesinger, R. G. Sierra, C. Y. Hampton, D. Nordlund, M. Beye, A. V. Martin, A. Barty, M. M. Seibert, M. Messerschmidt, G. J. Williams, S. Boutet, K. Amann-Winkel, T. Loerting, L. G. M. Pettersson, M. J. Bogan, and A. Nilsson, J. Phys. Chem. Lett. 6, 2826 (2015).*

*A. Manka, H. Pathak, S. Tanimura, J. Wolk, R. Strey, and B. E. Wyslouzil, Phys. Chem. Chem. Phys. 14, 4505 (2012).*