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Interactive comment on “Deposition nucleation viewed as homogeneous or immersion freezing in pores and cavities” *by* C. Marcolli

Anonymous Referee #3

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General Comment

This manuscript provides comprehensive support for the idea that true “deposition” nucleation does not really exist for any known ice nucleating aerosol, but that instead there is overwhelming support for the concept of pore condensation freezing (homogeneous or heterogeneous) as an explanation for ice formation occurring below water saturation. The idea that “deposition” might involve a liquid phase process and hence that all ice nucleation on aerosols is freezing has been imagined for some time, although a thorough hypothetical explanation of such a phenomenon was never offered. The comprehensive nature of the support given in this paper is both a blessing and a curse. Much of the discussion is too extensive in repeating the results of literature in review form, and hence requires relegation of a great deal of material to the appen-

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Interactive Discussion

Discussion Paper

dices. I recommend publication after addressing a number of mostly minor comments, and after some consideration is given to removing some of the pure literature review from this paper and thereby getting more quickly to the point of each section dealing with the ice nucleating behavior of different aerosol types. I found that I did take issue with proven conclusions made about Snomax aerosols. I also gained the sense in reading through the paper that some qualifying statements could just as easily have explanations rooted in experimental artifacts, and I am not sure how one would tell the difference. For example, I am curious also to hear comments about the implications of the results for 1) whether surface supports might have some impact on ice nucleation studies since this automatically creates a crevice that would not otherwise exist, and 2) whether or not the treatment of aerosol samples prior to nucleation experiments is of concern toward what is observed, since aerosols are in some cases taken from high RH conditions at warm temperatures to low RH conditions at low temperatures.

Specific Comments

Page 16369, abstract: I suggest to spell out the complete conceptual description of nucleation mechanisms, and hence, contact-freezing, condensation-freezing and immersion-freezing. Also, rather than “supposedly,” more appropriate words might be hypothetically or conceptually. The latter might be most appropriate, since all IN mechanisms listed in Vali (1986) are conceptual.

Page 16370, line 14: IN may be ubiquitous in large volumes of water, but all evidence is most certainly that they are rather sparsely distributed in the atmosphere, where ice phase transitions are powerful via the Wegener-Bergeron-Findeisen proces. Thus, to avoid this statement being misconstrued, I simply suggest that it be reworded as “Because IN are ubiquitous in large volumes of water, it is hardly possible to cool large drops to temperatures. . .”

Page 16371, line 18: I believe that deposition nucleation was always intended to be called just that, to distinguish it from liquid “freezing,” and so the use of the term “deposition freezing" only adds ambiguity. I realize that this paper is not unique in using those words, but since such great care is taken otherwise in discussions, I suggest not using this term.

Page 16373, line 11: Please identify the literal meaning of all acronyms for materials such as KIT at their first mention.

Page 16394, line 28: suggest to use term "condensation-freezing" mode.

Page 16394, lines 29-30: To me it is always striking and important to note that ice nucleation often proceeds only in a small fraction of particles. Hence, I think it most accurate to say that "supermicron particles start to nucleate ice in small fractions. . ." This may be implied by the word "start" but I suggest being very clear about the meaning and what the results show so that the "onset" of ice formation from an aerosol population is understood to usually proceed on a small proportion of the population and only rarely involve a large portion of the particles in the "deposition" regime. Why this is so is not clear. Apparently, what is promoted here is that the pore be large enough and that there be an active site present along the pore wall.

Page 16394 and Fig. 5a: I note that Tobo et al. (2012) contains data at 0.1 and 1% activated fraction of CMS kaolinite compilation at sizes of 300 and 700 nm (and temperatures from 239 to 247K for comparison and contrast to the Zimmerman references for supermicron CMS.

Page 16396, line 4: Should "higher" in line 16 on page 25 be "colder" or do I misunderstand the discussion there?

Page 16396, line 11: "have" for has.

Page 16396, line 17: The particles nucleated ice or began to nucleate ice below water saturation?

Page 16397, lines 10-13: This statement may well be true regarding "slow" ice formation versus absence of pores, but what about the 99% or more of particles of 100 nm size that do not appear to nucleate ice at all? Is this just time? I think there is some doubt.

Page 16397 and beyond, discussion of Fig. 5c (6 also) data requiring water saturation: Reference is made to ice formation at water saturation. Some of the data shown are at well above water saturation, but it should be understood that in continuous flow chambers, this is partly an artifact of focusing the aerosols into a laminar region for which the RH still has some edge-to-edge variance, and for which an RH for CCN activation is first needed for relatively hydrophobic dust, and for which perfect encapsulation of all of the aerosol in the lamina may not always be achieved (see, e.g., DeMott et al. 2011; Petters et al. 2009). These data should not be interpreted as being firmly attached to these higher RH values, and only qualitatively to the CCN activation RH. If you retain plotting them as is, please adjust the interpretation of them as a sign of anything other than the experimental method of using any real-time IN instrument with flowing aerosols. Thus, a data point at 105% RH is not a problem or even “uncertain” as to the detection of IN, but rather it just needs to be understood as representing condensation or immersion-freezing of small fractions of the population at just above water saturation. A number of papers use this higher RH to emphasize such nucleation and it is now standard technique for CFDC measurements (Sullivan et al. 2010; Tobo et al. 2012). Resolution of RH sensitivity to activation above water saturation will remain as a difficult, if not impossible, measurement for any IN technique.

Page 16399-16400: This discussion does not represent proof that heterogeneous immersion freezing follows the same steady-state rate process as homogeneous freezing, and hence there is as yet little understanding of how much residence time matters.

Page 16400, lines 17-20: Monodisperse IN results from ICIS 2007 (e.g., Koehler et al. 2010) are mentioned here, but results for polydisperse particles with an upper limit of 1-2 micron (DeMott et al 2011; Koehler et al. 2010, others) were also collected and could perhaps be mentioned as support that ATD needs to be well in the supermicron range to show deposition nucleation at warmer than about 248K.

Page 16401, lines 17-19: Please be careful with speculation and presumptuousness such as made in this statement passing off CFDC data due to the higher RH required for observing ice crystals. I mentioned references to the source of this disconnect between detection of ice nucleation and the apparent conditions required in such instruments when ice formation is due to droplet freezing. This is not the indication of water droplet breakthrough, which most CFDC investigators have carefully characterized for their individual instruments and know well enough to recognize and stay firmly away from.

Page 16403, line 4: Canary Island.

Page 16404, first full paragraph: This is a beautiful conclusion paragraph. If verboseness is reduced in the rest of the article, excellent writing like this will stand out.

Page 16405, line 5: reverse word order – "shown though. . ."

Page 16406, line 27: Can "dry" be defined here? How dry can ice survive in such pores, or is this something unexplored? Are there trajectories of air parcels in the atmosphere that will frequently support this? What about the space at the interface of particles on a surface? Is this at all problematic experimentally for diffusion chambers?

Page 16407, line 17: What is meant by "specific interactions?" Do you mean reactions, such as discussed in studies of ATD by Sullivan et al. (2010) and Reitz et al. (2011), that lead to a reduction in ice nucleating ability of particle in excess of that expected based on simply freezing an ideal solute coating?

Page 16410, Snomax^{TM} section: P. syringae are most definitely not proteins. Please revise. Secondly, I wish to voice dissent that it is a proven fact as yet that ice nucleation by the IN within Snomax in previous studies that did not involve the purposeful application of soluble coatings clearly fits the assumption of an immersion freezing mechanism. And why repeat this again in Appendix B? A great deal of data was in fact collected in the ICIS-2007 studies reflected in a few of the references herein, and

I suggest that either some actual data be examined carefully on a water activity versus temperature plot before assuming that the data fit the Koop and Zobrist (2009) model, or this speculation is removed. Also, in generation in the laboratory, the pellets are usually greatly diluted in water prior to atomization.

I suggest that the Appendices should be published as supplemental material. For example, while great detail is present here, the description of different instruments is also present to some extent in DeMott et al. (2011). Also, Hoose and Möhler (2012) review crystalline ammonium sulfate.

Page 16425, lines 19-20: I am not sure which reference this statement is pointing to, but what direct evidence exists in any study ever published that the composition of "a small fraction (0.01–0.2%) of urban ambient particles formed from anthropogenic precursors" have the ability to nucleate ice heterogeneously. Is not this by inference based on the composition of "most" ambient particles rather than specific measurements of the composition of ice nuclei?

Page 16427, line 10: add "their" before "own"

Page 16428: "The maximum activated fraction at any temperature for this sample was approximately 10%, probably limited by the 12 s residence time in the instrument." Is this speculation even necessary here? One could also speculate that it is an incorrect assumption that all of the particles should freeze if given time at any temperature.

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