Answers to reviewers

I would like to thank the reviewers for their helpful and constructive comments, which are addressed in detail below (in italic):

Referee #1:

1 General Comments:

This paper puts forth an interesting hypothetical mechanism (PCF) for the phenomenon of droplet freezing at low relative humidities. The phenomenon is important in the atmosphere (although it is not clear that elucidation of this mechanism will have practical consequences there) and the idea is intriguing. However, the author's meticulous review of available measurements relevant to melting and freezing in confined spaces (a herculean task) makes the paper at the same time too focussed on technical details and too little focussed on assessment of the strength of evidence for the new hypothesis.

The paper should be accepted; it provides a basis for new understanding of a basic atmospheric phenomenon. My major comments have to do with suggestions for substantial editing. The major hypothesis and strongest evidence for it should be put forth in focused paragraphs; secondary observations, details and comments (in particular, in sections 2.4, 2.5 and 3.1) should be relegated to another (review) paper or to tables and appendices. Criteria for disregarding the old (" deposition nucleation") hypothesis in favor of the new ("PCF") hypothesis should be stated and evoked for each case study investigated.

Sections2.4, 2.5, and 3.1 have been moved to appendices according to the referee's suggestion. Criteria for disregarding the deposition nucleation hypothesis are now explicitly stated at the beginning of the "Deposition nucleation on clay minerals and mineral dusts" section (section 3.1 in the revised manuscript). The discussion of the case studies has been improved. Summarizing sentences that highlight the major arguments for PCF are added to the discussion of the different mineral types.

2 Specific Comments

1. Abstract:

Instead of immediately providing the detailed observations of freezing on certain classes of particles, it would be better to clearly identify (quantitatively) the signatures of "deposition" freezing, homogeneous freezing in pores and Immersion freezing in pores. Preactivation should be discussed in another paper.

The abstract has been improved according to the referee's suggestions. The preactivation section is removed from the manuscript.

2. Figures 2 and 3 compile observations made with a wide range of techniques. The scatter in the data is thus both due to the scatter in the freezing itself and due to differences among techniques. The melting observations (shown in Figure 2) seem to correspond to a single mechanism but freezing observations (Figure 3) show a great deal of scatter. This scatter should be discussed in light of the range of observational techniques, the range in characteristics of confined water, the possible distribution of pore sizes in the various samples, and possible solute effects. With what uncertainty can we identify (for each data set) one freezing mechanism? The overall message of this figure as it now stands is not clear.

The discussion of Figures 2 and 3 is improved in the revised manuscript. Homogeneous ice nucleation is observed in cage-like pores that are "isolated" from the external surfaces of the particles. If the cages are connected to other cages or to the external surface by channels that are wide enough so that ice can propagate through them, pore freezing occurs at a higher temperature initiated by the external ice. This explains much of the scatter of the freezing data.

3. Section 2.6:

Melting and freezing are different phenomena, but are discussed together here, which is a bit confusing. The relevance of classical, macroscopic thermodynamics to the first stages in freezing even in unconfined samples is always suspect. In Sections 2.3 - 2.5 the author has emphasized the anomalous character of water and ice in confined spaces, including suggestions that the freezing might not be first order, the ice formed has intermediate density, and the water surrounding ice embryos is 'bound'. This discussion renders surprising the return to classical thermodynamics and standard parameter values such as the so-called ice-water surface energy. There should be some link between these two discussions. Having chosen to refer to the classical theory it would be helpful to include a reminder primer on phase transitions involving the gas phase; i. e., the chemical potentials of water in all three phases should be written down so that we can understand statements about where and when (under what relative humidities and temperatures) phase transitions are expected. Conceivably, a schematic "phase diagram" for confined water might help in the presentation.

Completely filled pores contain free (bulk) water in the middle of the pores and bound water adjacent to the pore walls.CNT can therefore be applied to describe the freezing of the bulk water in the middle of the pores. The discussion of CNT is extended and improved in the revised manuscript. It is found that CNT is well applicable to freezing in pores.

Line 20: The argument that the surface properties do not impact freezing and melting temperatures in pores because the pore walls are covered by water is a bit surprising; one would expect a layer of bound water 0.6 nm thick at temperatures well below 0 degC to be very different from bulk water and to reflect the pore wall characteristics.

The presence of a quasi-liquid layer on the wall surface shows that ice does not directly nucleate on the pore walls. Only the water with bulk properties in the middle of the pores freezes. Therefore, the wall properties are only of minor importance for ice nucleation.

4. Figures 5 and 6:

The broad distributions of data points show that many different factors in technique as well as in physical processes affect the results. It is almost impossible to extract a coherent message here. As suggested above, it would be helpful to have a checklist showing the PCF hypothesis is consistent with the stated criteria for this mechanism and inconsistent with other freezing hypotheses, in those cases for which the argument is strongest. The large number of subsidiary caveats and speculations necessary to support the PCF hypothesis in weaker cases should be organized as part of the discussion of future work.

Criteria of PCF are now explicitly stated in section 3.1 (Deposition nucleation on clay minerals and mineral dusts). The discussion of the case studies has been improved. Summarizing sentences that highlight the major arguments for PCF are added to the discussion of the different mineral types.

5. There should be a more ample discussion of the impact on freezing of the distribution of pore and inter-particle gap sizes. Presumably, freezing occurs first in the tail of the distributions, and the average pore size is of less importance.

Illites have pores in the size range 2 – 5 nm. Freezing should therefore mainly occur in the wider pores. Montmorillonites have pores in the whole diameter range relevant for PCF. Kaolinites are characterized by larger pores (20 – 50 nm). For these, the tail of narrower pores should be responsible for the observed activated fractions of 1 % because they fill at lower RH with water. The discussion of pore size and freezing is improved in the revised manuscript.

6. The active site parameterization (Marcolli, 2007) was derived from observations on entire single particles, not cracks within or between particles. Is it obvious that the same parameterization should be relevant within the individual surface features?

This is indeed a caveat for the discussion of active site densities within pores of ATD. Nevertheless, application of the Marcolli et al. (2007) parameterization to pores permits to obtain a rough estimate whether pores of ATD particles offer enough surface area to contain active sites for immersion freezing.

7. Soluble and insoluble impurities in the cracks must be important. They are yet another source of possible scatter in the observations but receive little mention.

Soluble impurities should not be an issue for mesoporous silica materials. They should also be of minor importance for clay minerals and ATD because the DSC curves of these materials did not show any melting or homogeneous freezing point depression (Marcolli et al., 2007; Pinti et al., 2012). Soluble impurities might be more important for natural dusts. The consequences of soluble impurities and coatings are discussed in section 3.2 (Coatings).

8. Section 3.2: Preactivation is very interesting, as is the speculation about "ink-bottle" shaped pores, but these topics should be relegated to a second paper or to an appendix.

The preactivation section is removed from the manuscript.

9. Section 4: In this paper the data are assembled, but their quantitative analysis is preliminary. Future work should include analysis of results of each laboratory technique separately, with particular focus on the scatter of results within a given technique, which would provide estimates of the amount of scatter expected from "deposition" nucleation and from PCF (and, possibly, other mechanisms). When these are included, what is the degree of certainty with which "deposition" nucleation can be excluded?

I agree that a more quantitative relation of pore structure and freezing of aerosol particles would be desirable. However, a more quantitative discussion is limited by the lack of precise information on pore structures for aerosol particles.

An interesting paper in this respect was just published by Welti et al. (2013), who investigated the temperature and humidity conditions at which different ice nucleation mechanisms are active for size selected kaolinite particles using particle surface models within the framework of CNT. They found that assuming deposition nucleation to be the governing mechanism below water saturation to be inadequate to represent the experimental data in the whole temperature range that they investigated.

There is clear evidence that PCF occurs below water saturation and is likely the prevailing mechanism for ice crystal formation below water saturation in the atmosphere. To prove the total absence of deposition nucleation might be difficult or even impossible.

Incorporation of pore size parameters into atmospheric models seems fruitless; these already are overloaded with unknowable parameters. That is not the goal of this paper, which is instead to extend our understanding of freezing.

If pore size parameters could replace aerosol type specific ice nucleation parameters, parameterizations in models could indeed be simplified.

3 Technical Corrections/ Suggestions

1. line 23, Abstract: Liquid does not 'attract' vapor. The rest of the sentence is unclear.

This sentence has been removed in the revised abstract.

2. Eq (1) Relative humidities are used in the rest of the paper; add " $\equiv$ RHw". D; V_m are not used further on.

In the revised manuscript, the relationship between pressure ratio and relative humidity is now explicitly stated. The diameter D of the curved water surface is only used in Eq(1) and kept as is. V_m *is replaced by* v_l*, consistent with the rest of the manuscript.*

3. Section 2.6 The notation needs a bit of editing; (p in eq (1) is now p_l and μ in eq (2) is not the same (doesn't have the same dimensions) as μ in eq (6); r_{ps}; r_{pl} in eq (2) are not defined.)

The notation has been improved/corrected.

4. Figure 5a: On my computer screen brown and red segments of the water saturation curve are visible but not orange segments.

The orange segments are between 255 and 264 K.

Figures 5 and 6. The various lines need clarification. The axes are temperature and RHi (never defined).

The definition of RHi is now also given directly in the figure caption.

The dotted black lines are said to be from Koop (2000) for constant J (nucleation rate). However, Koop shows J as a function of temperature and water activity. The step from water activity to RHi needs to be made explicit.

This information is now given in the revised manuscript: "The dashed black line gives homogeneous ice nucleation (Koop et al., 2000) for a nucleation rate of 10^8 $cm^{-3}s^{-1}$ *given as a function of water activity. The water activity scale is transformed to RHi using the parameterization by Murphy and Koop and assuming equality between water activity and RHw."*

Similarly, the light blue lines are said to be calculated from Eq (1), but Eq (1) is written in terms of RHw, not RHi. The missing steps, easy enough to fill in, would aid the reader of an already complicated set of graphs.

This additional information is now given in the revised manuscript: "The light blue lines delimit the onset of pore filling with water for pores with diameters given on the lines calculated using the Kelvin equation (Eq. 1) and transforming from RHw to RHi using the parameterization by Murphy and Koop (2005)."

Referee #2

This paper contains so much material that a thorough review would take many months of work. Hence, the comments below focus on the core issues and on some selected portions of the paper. My rating on presentation quality is directed to the excessive length of the paper and the lack of focus.

The basic tenet of the paper is laudable. Porous materials undoubtedly present conditions where interaction with water in any of its phases is different from bulk or uniform surface situations. The idea of liquid or ice remaining in pores even below the thermodynamic equilibrium conditions has been around for a long time. This paper is a thorough examination of the consequences of that phenomenon, with special emphasis on ice in pores being responsible for what has been viewed as deposition nucleation in the atmosphere.

Homogeneous freezing in pores is the clearest example of the importance of water retained in pores. The support for this is the increased frequency of nucleation below 235 K in all experiments. The effect of the pore walls on homogeneous embryo formation within the water in the pores is assumed to be negligible. Similarly, the formation of cubic ice is assumed to have the same homogeneous nucleation threshold as hexagonal ice. These assumptions are not as fully justified in the paper as one would wish.

The discussion of freezing in pores has been extended in the revised manuscript. The parameterization of Murray et al. (2010a) for homogeneous nucleation of cubic ice is added to Figure 3and discussed in the text.

The paper overextends the importance assigned to pores by also claiming that many observations of heterogeneous nucleation via immersion freezing are in fact explained by the presence of pore ice. Much of that analysis is speculative and results in losing the focus on deposition nucleation and in making the paper too long. In fact, this paper is a curious mixture of a broad review of immersion freezing and a specific point of view from which to examine past work. The review is quite comprehensive and detailed but it ends up providing few definite insights on immersion freezing.

In the revised manuscript, review parts are moved to the appendix. Thus, the main text is considerably shortened which should improve readability. The review parts should remain in the appendix since this paper is also intended to provide information and a literature overview for freezing in confinement for the atmospheric ice nucleation community and at the same time give similar information concerning ice nucleation of aerosol particles for the "freezing in confinement" community.

To someone not specializing in the study of porous materials, the descriptions of pore configurations (section 2.1) appears too simplistic. To what extent is it realistic to consider pores as tubes with a fixed radius, or to think of cavities as ink bottles with a round opening? Since the main properties of pores that enter into the quantitative analyses are size and contact angle, it is important to understand to what extent these are idealized quantities or true representations of the pore structures. Many references are given about porous materials; a judicious summary of the key issues would be helpful.

Pore size and shape of these mesoporous silica materials are indeed very uniform, since they are synthesized around templates with specific size and shape. The uniform pore shapes are confirmed by the analysis of the materials e.g. by transmission electron microscope and XRD. In the revised manuscript a sentence is added to make this clearer.

Schaller and Fukuta (1979) and Roberts and Hallett (1968) found ice nucleation requiring water saturation for temperatures above thresholds in the range 250-260 K with a sharp change to nucleation taking place below water saturation at lower temperatures. The discussion of these types of results in the paper (page 32, lines 7-12) focuses on temperatures near 235 K and invoke homogeneous nucleation in pores. That is untenable for the observations of Schaller and Fukuta and other similar results. Yet, the transition in behavior is an important finding and should be discussed, because the reasons for the transition near 260 K may also apply near 235 K and make it unnecessary to invoke pore phenomena.

Schaller and Fukuta (1979) together with other studies which investigated micrometer-sized and larger kaolinite particles observed a transition from immersion to deposition nucleation at 251-256 K. However, this transition is not abrupt as the one at 235 K since RHi required for ice nucleation gradually decreases with decreasing temperature. Assuming a PCF mechanism, this gradual decrease can be explained by an increasing density of active sites with decreasing temperature.

Cooper (J Atmos. Sci., 31, 1832-1837, 1974) also used the idea of ice germs of subcritical size with respect to the bulk phase to interpret contact freezing. That idea is different from the PCF hypothesis but it does deserve to be recalled. There are possible extensions of Cooper’s idea with pores also considered.

The paper by Cooper discusses the possibility that subcritical ice embryos on the surface of ice nuclei in vapor are able to nucleate ice when they come in contact with a water droplet. This is a different situation from the one of deposition nucleation since it needs water saturation.

Comments below are referenced in the following manner: page number/line number

Abstract: Much too long. Overly detailed.

The abstract has been shortened.

5/5-6 Is it justified to claim that deposition is always(!) pore freezing? There are numerous laboratory experiments with presumedly smooth surfaces on which deposition nucleation could be observed.

The analysis presented in this paper shows that all studies that presented ice nucleation below water saturation can be explained without assuming ice nucleation by water vapor deposition on a surface. However, this alone does not exclude the occurrence of deposition nucleation. A direct argument against deposition nucleation is the increase of ice nucleation efficiency when temperatures fall below 235 K, i.e. the homogeneous ice nucleation threshold. To prove the total absence of deposition nucleation might be difficult or even impossible.

5/18 Suggest the use of "cavities" instead of "caves"

The manuscript was changed accordingly.

8/15; Fig 1 It would make Fig. 1 more meaningful if the range of pore diameters were indicated with error bars instead of single points for each material.

Pore diameters of the mesoporous silica materials are very uniform and no uncertainties are given for them in the original literature. However, there is some uncertainty in determining the onset of capillary condensation. Error bars are therefore added to the y-axis of Fig 1 that reflect the uncertainty in reading off the onset of capillary condensation from the adsorption isotherms.

8/27 How was freezing initiated for the data shown in Fig. 3, i.e. how was an equilibrium freezing temperature determined?

Most studies that investigate freezing in mesoporous silica materials use DSC to observe freezing. Experiments are performed on wet powders so that freezing most probably starts at the surface of the particles. Only for materials with pores that are isolated from the external particle surfaces, homogeneous ice nucleation can be observed. The following sentence is added to the manuscript to make this clearer: "This external water nucleates first when temperature is decreased and can initiate freezing in pores."

10/1 What is the justification for using 1 min for this calculation?

This calculation is removed in the revised manuscript and replaced by a more detailed discussion of homogeneous ice nucleation within pores in section 2.3 of the revised manuscript.

17/13 It requires some justification that CNT parameters for hexagonal ice can be used for cubic ice.

The parameterization for cubic ice by Murray et al.(2010a) is now also shown in Fig. 3 and discussed in the text.

26/7-20 Is there an explanation for 'slow freezing'? Limited by heat transfer? What else?

Limitation by heat transfer can be excluded. Slow freezing occurs in pores with diameters between 2.5 and 3.5 nm. This is in the size range of the critical nucleus. As a consequence, ice nucleation rates seem to be lowered. This is now discussed in more detail in the revised manuscript.

29/8-9 On what basis does the author rule out the possibility that other than pore structures provided the nucleation sites in these experiments? Pits? Steps? Dislocations? Etc.

Pits, steps and dislocations cannot hold water with bulk properties below water saturation. Such water is however needed for homogeneous ice nucleation at conditions comparable to the ones in water droplets (as can be seen from the discussion of freezing in confinement presented in this study).

29/13-14 Why is it taken for certain that pores are involved?

See explanation to the question above.

29//21 Would be clearer to say "All studies except that performed on 50 nm particles. . ."

The manuscript was changed accordingly.

29/20 What type of solution is assumed for the black lines in Fig. 6.?

The meaning of the black lines is now given in the text to Figure 6. The black dashed lines represent the homogeneous ice nucleation curves based on the Koop et al. (2000) parameterization for solution droplets.

33/13-17 If pores do not offer a clear explanation, should perhaps other ideas be considered? Didn't the authors of the cited works offer some possible explanations of the observations?

This paragraph just summarizes the observations from different studies. These observations indeed can be explained by pores as is discussed in the following text of the manuscript.

Referee #3:

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 appendices. 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.

Most of the review parts are moved to the appendix in the revised manuscript as suggested by the reviewer.

I agree with the reviewer that surface supports might have impact on ice nucleation studies and address this point explicitly in the revised manuscript when investigations of particles on substrates yielded onsets of ice nucleation for $RH_i \geq 100\,\%$.

Treatment of particles at high RH might indeed lead to water retained in pores and influence the outcome of experiments.

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.

"Supposedly" is replaced by conceptually in the revised manuscript. The different heterogeneous nucleation mechanisms are mentioned in the abstract but not explained, because the abstract is already long, as criticized by referee 2.However, the explanation of deposition nucleation, homogeneous nucleation in pores and immersion nucleation in pores in the abstract has been improved.

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. . ."

This sentence is corrected in the revised manuscript.

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.

"Deposition freezing" is replaced by "deposition nucleation" in the revised manuscript.

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

These abbreviations are normally used in the original literature without referring to a meaning for the acronym. I could not find what KIT stands for. For SBA and MCM the meaning of the abbreviation is stated in the text.

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

This is changed according to the reviewer suggestion in the revised manuscript.

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.

The text has been changed according to the reviewer suggestion.

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.

The data from Tobo et al. (2012) is added to Fig. 5a in the revised manuscript.

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

A higher RHi is meant. This is made clear in the revised manuscript.

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

Corrected.

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

"began to nucleate ice" is more correct.

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.

It is indeed likely that not all of these very small particles contain pores in the right size range. This is now explicitly stated in the revised manuscript. Figure 5b shows the onset condition for 1 % activated *fraction. Welti et al. (2009) reach activated fractions of ca. 10 % for these experiments. Also with other IN the maximum activated fraction is typically ca. 10 %.*

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.

Thank you for these further explanations. The comments in the manuscript regarding potential artifacts due to breakthrough of water droplets were intended to reflect the opinions of the authors of the source literatures. Also, the presentation of the data points in the figures should be the same. Some of the points are indeed classified by the authors as possibly influenced by breakthrough.

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.

I agree with this comment. The Marcolli et al. (2007) parameterization nevertheless offers the possibility to check the consistency of ice nucleation measurements performed under different conditions. To apply the parameterization, a residence time has to be assumed.

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.

These measurements are now mentioned in the revised manuscript.

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.

Lines 17-19 are removed from the revised manuscript.

Page 16403, line 4: Canary Island.

Corrected.

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.

Thanks.

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

Corrected.

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?

It is assumed that the entrances of the pores are filled with a liquid plug that is thermodynamically stable due to the Kelvin effect. The ice in the cavity is thus protected from evaporation by the narrow opening of the pore. Such preactivation should occur when air parcels go through several ice cloud cycles. It should also be important for particles on a surface, when ice nucleation is performed several times with the same sample. It is not important for CFDC setups where the same IN is only sampled once. However, the discussion of preactivation is removed in the revised manuscript following the suggestion of referee #1 and possibly a subject for a second paper.

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?

Specific interactions are meant to be irreversible chemical reactions but also (reversible) surface adsorption. This is stated more clearly in the revised manuscript.

Page 16410, SnomaxTM 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.

The idea to assume an immersion freezing mechanism for ice nucleation below water saturation of Snomax particles arose from inspection of Fig. 5a of Hoose and Möhler (2012), which indeed gives the solution data from Koop and Zobrist (2009) in terms of temperature and ice saturation S_i*. (In the revised manuscript, direct reference to this Figure is given). It is striking that most data of other studies align with this solution freezing data. Snomax pellets contain proteins (30 – 50 %) and soluble components (25 % carbohydrates and nucleic acids) in similar amounts. When suspensions of Snomax pellets are sprayed, this ratio is preserved in the residues of the evaporated droplets. There is therefore enough soluble material available for a thick coating of the proteins. Since carbohydrates* *and nucleic acids are hygroscopic, the Snomax particles will be immersed in an aqueous solution. This should indeed be taken into account when discussing ice nucleation data from Snomax. These points are made clearer in the revised manuscript.*

The description of the experimental setups is rather intended for potential readers from the "freezing in confinement" community, who are not acquainted with these instruments. I would therefore like to keep them easily accessible in the appendix rather than moving them to supplementary material.

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?

This sentence refers to Knopf et al. (2010). The reference was missing and is now added to the revised manuscript.

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

Corrected.

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.

This sentence is removed from the revised manuscript.

References:

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