

Review to “Laboratory study of heterogeneous ice nucleation on black carbon containing aerosol” by Nichman et al. ACPD, 2018

The manuscript by Nichman et al. presents a laboratory investigation of the ice nucleation ability of black carbon (BC) particles of different type, an important topic, which fits within the scope of ACP.

The authors used two different sizes of BC particles (100 nm, 800 nm) in order to investigate the effects of particle physicochemical properties on their ice nucleation ability (morphology, surface oxidation, coating). The main conclusion from the presented manuscript is the attribution of a pore condensation and freezing (PCF) mechanism for the ice nucleation ability of BC particles.

The manuscript in its current state is incomplete (investigation of the effect of coating) and seems speculative for some of the effects investigated (surface oxidation). Besides, the manuscript lacks a proper in-depth analysis and discussion of some of the results presented (e.g. comment P8L25-27) and stays superficial at many places (e.g. effect of particle generation).

In general the description of observed “heterogeneous ice nucleation of BC particles” (P8L28) and the suggested PCF mechanism, where the pore water freezes *homogeneously*, is misleading and/or not stated with sufficient care: While a PCF mechanism as such could not take place without the presence of a pore, i.e. the particle, forming the site for the water vapor to condense (“heterogeneous freezing process”), the actual ice formation takes place through homogeneous *nucleation* of this pore water.

Many flaws could have been prevented by a more critical read by some of the more senior authors prior to submission. I suggest major revisions of the manuscript in its current form and reevaluating it after the points listed below have been carefully addressed and incorporated.

General comments:

- How do the industrial BC particles investigated in this study compare to atmospheric soot particles, for instance those emitted by aircrafts or fly ash particles (Grawe et al. 2018; Umo et al. 2015)? The particles tested might not be atmospherically relevant due to different physicochemical properties. This limitation should be explained and discussed in more detail in Sect. 4. Also, why do you refer to your particles as “BC-containing particles” in the abstract and Sect. 1? What else is in these particles?
- I suggest to reduce the discussion on field study results (P2L16-27) and put the focus on results of laboratory studies, comparable to the presented manuscript.
- **Investigation of surface oxidation:** P10L24-P11L15: Even though, I agree that surface oxidation state might play an important role for the ice nucleation ability of (soot) aerosol particles, your data are insufficient to make a clear statement here, as there is no systematic experiments provided, showing a clear effect of surface oxidation on the ice nucleation ability of soot. In the framework of PCF, a surface oxidation should lower the soot-water contact angle and thus enhance the ice nucleation ability of a soot by PCF. Next, the observation, that the surface oxidized soot (Regal 400R) freezes homogeneously is lacking a proper discussion. The pH-values of this soot is measured at 4.9, indicating that soluble material was washed off the particle surface in solution. This indicates the presence of soluble material, which agrees well with the observed freezing along the homogeneous freezing line. I therefore suggest to completely revising the discussion on surface oxidation and its influence on ice nucleation presented in the manuscript.
- **Investigation of coating:** P11L16-27: The coating is insufficiently characterized and SEM or PALMS measurements should be provided to do so. On P6L18-26 the authors make it sound like an effect of coating on the ice nucleation ability of soots is systematically investigated using different soots and different coatings. The results presented in Fig. 8 and discussed on P11L16-27 read like a contingent selection of data, which is insufficiently discussed and interpreted, with the majority of P11L16-27 presenting a repetition of information that had already been given in the introduction. Why was R2500U only coated by cis-pionic acid and stearic acid, but not with oxalic acid? Please provide all coating measurements performed for each soot type, so that an effect can be systematically investigated and discussed. Otherwise the promises made on P5L12 about providing “some clarification on the effect of organics on the IN activity of BC particles” is obsolete. In case this data is not available, I suggest removing all data and discussion on organic coating of BC particles from the manuscript.
- **Stochastic vs. deterministic description of ice nucleation data:** Sect. 3.2: The ns-based interpretation of the data is inconsistent with the interpretation of the authors, that PCF is the mechanism with which soot nucleates ice. While for the ns concept, the ice nucleation is

triggered by so-called active sites, describing a *heterogeneous* ice nucleation process, the PCF mechanism can purely be described with CNT: Capillary condensation taking place in pores and subsequent *homogeneous* freezing of this pore water. In other words, the ns-based approach is invalid for homogeneous freezing. The whole discussion about the two concepts of stochastic vs. deterministic description of ice nucleation as presented in the manuscript (P3L7-15, P11L28-P12L11) is superficial and does not fit the framework of the paper. Since the authors claim a PCF mechanism, I suggest to remove any discussion of ns from the manuscript for consistency. At the same time, this avoids discussion of any uncertainties introduced through the estimation of BC effective surface area (P7L6), which lacks a proper discussion of assumptions made.

Specific comments:

- P1L1: The title should be revised as it is misleading and inconsistent with the major finding of the authors on P13L12-14. The freezing of pore water is homogeneous and not heterogeneous as implied by the title.
- P1L18: I suggest to move the sentence “The current study focusses on laboratory measurements...” at the end of p.1 l.23 to improve the flow of the reading, first discussing field study observations, then laboratory studies and finally say that your current study focusses on laboratory measurements.
- P1L22: add “... can be highly active IN under certain conditions.”
- P1L24: the addition “... commonly understood to be deposition mode ice nucleation.” is not true. Other ice formation mechanisms, e.g. homogeneous freezing, can also take place within the cirrus temperature regime. You should delete that part of the sentence, or specify that you refer to RHw conditions below homogeneous freezing conditions.
- P1L25: Why are you using “carbon black” and not “black carbon (BC)”? I suggest being consistent throughout the manuscript.
- P1L34: change dependence to depends
- P2L2: Please specify: “low ice supersaturations”.
- P2L5: Your usage of “INP” differs from your definition on P1L21, where you describe ice nucleation particles as “IN”, which in turn is inconsistent with your usage of “IN” on P2L7. I suggest to stick to the terminology presented in Vali et al. (2015) and consistently use INP throughout the text.
- P2L7: Do you consider “soot” and “BC” to be the same? You should clarify this and give a definition on how you use the term soot in your manuscript and then stick to this for consistency.
- P2L15 Change “ice nucleation particles” to INP.
- P2L19: Please specify what samples were studied in Pratt et al. (2009) and Eriksen-Hammer et al. (2018). Did they probe samples similar to Chen et al. (2018)?
- P2L20-22: Please specify for which cloud types soot is considered an important INP for the different studies. All clouds or just cirrus clouds?
- P2L22-27: “While in these...” I suggest removing this paragraph from the manuscript to improve readability and streamline the introduction. It does not contribute to the general understanding of ice nucleation ability of soot particles and thus to the scope of the presented manuscript, which is not on ice-multiplication processes.
- P2L29: I suggest to remove the reference to China et al. (2015)a. This study does not investigate ice nucleation activity of soot particles, but quantifies a morphological change of these particles upon ice formation (and cloud droplet formation) on the soot particles and the consequences for the radiative impacts of the soot particles.
- P2L30: Kärcher and Lohmann (2013) is not a laboratory study. This reference is miss placed here and thus should be deleted.
- P2L32: Change to aircrafts.
- P2L36: Your usage of the Kärcher et al. (2007) study to motivate the absence of a contribution of soot to ice nucleation is delusive, as you use the same study on P2L33 to say the opposite. Please clarify.
- P2L3: Your citation does not support your statement that “numerous soot types have shown high IN activity” when coated. Crawford et al. (2011) investigated soot derived from a propane burner (miniCAST and CAST). In this case the burning conditions (air to fuel ratio) can be

changed to mimic soots with different organic carbon content, also all soots are from the same source. Is that what you refer to as “numerous soot types”? Please clarify.

- P2L4: Add this reference: Möhler et al. (2005)
- P2L7: What do you mean with “quantitative relationships”? Relating physicochemical properties of soot particles to their ice nucleation activity? Please clarify.
- P2L10: This statement is only true for activated fractions less than 0.1 as shown in e.g. Niemand et al. (2012), Hiranuma et al. (2014). Please change your statement accordingly.
- P2L12: Do you want to compare measurements to modelling results or do you want to use no parametrizations derived from measurements for modelling purposes.
- P2L13: None of the given references preliminary discusses the limitations of the deterministic description of ice nucleation. I suggest deleting these here. In case you like to give an example for time dependent ice nucleation, e.g. use: Welti et al. (2012).
- P3L18-21: “Porous materials...” I suggest moving these sentences after the explanation of the PCF mechanism given in the next paragraph.
- P3L20: Please add the following references: Alstadt et al. (2017), Mahrt et al. (2018) that are very relevant to the work discussed in the current manuscript.
- P3L22: Change to: “... fill with water due to capillary condensation at relative humidities (RH_w) below water saturation, which freezes homogeneously (Marcolli 2014).”.
- P3L22: You might want to give a more well rounded list of references describing the PCF mechanism, including e.g. Christenson (2013); Higuchi and Fukuta (1966).
- P3L23: PCF is not only determined by the pore diameter, but also by the contact angle, see for instance Marcolli (2016).
- P3L23 delete “(< 100% RH_w)” it is sufficient to say below water saturation.
- P3L22-29: The discussion about “suitable” pore sizes for PCF stays superficial. What does suitable mean? Is it pores with diameters in the range of μm or nm ? I suggest taking a contact angle typical for (atmospheric) soot and calculating some critical pore diameters, i.e. diameters at which a pore would fill with water (at a typical cirrus temperature), in order to support your argument and then relate these pore sizes to those typically observed in soot aggregates.
- P3L29-31: Please specify how the PCF mechanism predicts the observed decrease in ice nucleation activity with increasing temperature between 210-240 K.
- P3L30: Change to “... (typical of cirrus clouds, Hoose and Möhler 2012).”
- P3L36: Marcolli et al. (2014): I cannot find this citation in your reference list.
- P4L2: Change “spheres” to “spherules” to be consistent with terminology on P4L1.
- P4L4: “In the image...” Delete this sentence here and put it to the caption of the figure.
- P4L6: I disagree with this statement. There can be slit-like pores formed in between sintered primary spherules. Since your “external branch” in Fig. 1c) consist of multiple primary spherules, it can have pores and thus contribute to PCF.
- P4L17-18: This statement is not consistent with your statement on P4L7, where you define a pore as an “empty space between aggregates”. Please clarify.
- P4L27: The way you use the reference of China et al. (2015a) is misleading, as it is not about the impact of aerosol generation method on the soot morphology. Please rephrase.
- P3L34: Is only the number density of pores changed between the large BC agglomerates and the small BC agglomerates or also the pore size distribution? At a similar pore size distribution, the ice nucleation ability, when caused by PCF, should be identical between the large and small agglomerates, as the pore filling is just a function of pore diameter (and contact angle). Please clarify.
- P5L16-19: The numbering of the soot types in the main text is confusing. I suggest indicating the supplier directly within the table and referring to the sample names throughout the text to be consistent.
- P5L17: The statement about the Raven 2500 Ultra seems weird, as the Monarch 880 and Monarch 900 have very comparable BET surface areas.
- P5L20: Delete “... in the deposition mode regime.” This is confusing with the point the authors try to convey, that soot nucleates ice via PCF.
- P5L27: Delete comma after Table 1.
- P5L27: Move explanation for OAN from L30 to here.
- P5L35: Please specify what this oxidation process encompassed.

- P5L13: I suggest removing the references to “issue xy in the Introduction” here and at the other location sued. This seems unnecessary and repetitive. If you want to keep these please use proper Section numbering when referring to different parts of your manuscript, e.g. “as outlined in Sect. 1”, consistent with the style of ACP (“Manuscript composition”): https://www.atmospheric-chemistry-and-physics.net/for_authors/manuscript_preparation.html
- P6L18-20: Why did you choose these acids for coating? Please briefly discuss their atmospheric abundance and relevance.
- P6L20: Do you want to investigate the effect of coating of the effect or organic carbon content?
- P6L20: Add comma after heated
- P6L24: Change to “... coatings consisting of super-cooled aqueous solutions can become crystalline or glassy solids (references).”
- P6L26: Add: Murray (2008); Zobrist et al. (2008)
- P6L34: Delete “and mixtures”
- P7L1: Change to: “...single particle mass spectrometry instruments”
- P7L1: Change to : “Therefore, hundreds of...”
- P7L1: Please clarify whether PALMS was operated on DMA size selected particles in the text. This should also be clarified in the caption of Fig. A1. From Fig. 2 it looks like PALMS was operated on size selected aerosol. Please comment whether there is a chemical difference between your 100 nm and 800 nm aerosol particles.
- P7L3: From your Fig. 2 this looks like lacey carbon copper grids. Please specify and give manufacturer details.
- P7L4: Please be quantitative: How many SEM images were taken for each BC type? What fraction out of all images taken showed a “clustered, spheroidal structure”? This should also be indicated in the caption of Fig. A2.
- P7L9: For discussion of eq. (1), please see my comments P2L10.
- P7L6: Please clarify how the SEM images were used to estimate the effective surface area. I suggest putting the equations used for your calculation into a supplementary information, which should also discuss the assumptions made by you. For instance, from your SEM images in Fig. 1 and A2 it looks like a strong overlap of the individual spherules/monomers, which would lead to an underestimation of the total number of spherules making up an aggregate and with that to an underestimation of the effective surface area.
- P7L7: Replace “frozen fraction” by “activated fraction”
- P7L10: Is Lf a SPIN specific correction factor?
- P7L11: Why do you only consider the “outer shell” of the aggregate? This seems inconsistent with suggesting a PCF mechanism for ice nucleation. Pores are clearly formed also within the clustered structure.
- P7L14: It is not clear to me where the factor 3 results from.
- P7L16: Please change to: “(see Sect. 3).”
- P7L20: Delete “i.e.”
- P7L24-26: This statement is incorrect. I assume you are just describing the cirrus temperature ($T < 235$ K) regime. Homogeneous freezing of solutes takes place at water subsaturated conditions. Please phrase your statement more carefully.
- P7L29: Several micrometer in diameter?
- P7L32: This statement is inconsistent with the suggestion of the authors that BC particles nucleate ice via a PCF mechanism for cirrus temperatures. In case PCF takes place the water is taken up into pores at water subsaturated conditions due to capillary condensation. This pore water subsequently freezes homogeneously and not heterogeneously, at $T < 235$ K.
- P7L31-33: This statement should be followed by a reference.
- P7L36: Change “centerline” to “lamina”
- P8L17-19: Why is this “time dependent”? This is purely a matter of how you interpret your results... This statement should be deleted.
- P8L16: Abbreviate “Figure” with “Fig.” throughout the manuscript; see ACP guidelines (“Manuscript composition”): https://www.atmospheric-chemistry-and-physics.net/for_authors/manuscript_preparation.html
- P8L23: Change “IN agent” to “INP”.

- P8L25-27: “Both types demonstrated temperature dependence of ice onset similar to ..., associated with the PCF mechanism, that is, increasing ice onset point with increasing temperature in the range 217-235 K”.
 - o Please clarify how you arrive at this conclusion and justify why the observed increase leads you to the conclusion that PCF must be responsible for ice formation.
 - o Assuming that PCF in fact causes the ice nucleation of your BC particles, the freezing is purely determined by the pore size and the soot-water contact angle. Thus for a given/fixed pore size and contact angle, your ice formation is purely deterministic and should take place, as soon as the critical RH_w for pore filling is reached during your RH_w scan. In other words, the freezing should take place at the same RH_w throughout all temperatures $T < 235$ K, i.e. along an RH_w-isoline. This is inconsistent with your results and your argumentation. I do believe that PCF indeed takes place for your samples, but I think that the increase in onset RH towards 235 K, is due to a lower homogeneous freezing rate at this T compared to $T \ll 235$ K.
 - o This could be easily proofed by running some more experiments for R2500U and Regal 330R at $T < 225$ K. In case of PCF, you should observe a similar levelling-off in onset RH_w as observed for the ethylene combustion soot. I suggest adding some more experiments at these very low temperatures, to support your argument.
- P8L28: See my general comment. In case of PCF, the freezing of the water is homogeneous.
- P8L32: I suggest to tune down “significant”
- P8L32: Please reference “in the Introduction” as “in Sect. 1”.
- P9L2: I suggest to just using the abbreviation “R2500U” within the text, to be consistent with the legend and improve readability.
- P9L8: Can you quantify “high RH”? Also, please use “RH_w” for consistency.
- P9L10: The whole discussion is qualitative and seems speculative. Can the authors provide information about pore sizes and pore size distribution associated with the individual soot types?
- P9L16: Change to: “... a weaker inverse Kelvin effect and therefore can only fill with water at higher RH_w.”
- P9L13-19: Is the higher degree of branching of the Monarch 880 soot (higher OAN number) supported by your SEM analysis? Please comment and provide images to support your argument.
- P9L17-20: Most of your Monarch 880 data points lie within uncertainty of the homogeneous freezing curve indicated in your figure, which makes a statement about PCF speculative. At the same time, your Monarch 880 experiments are constrained to $T > 230$ K. This makes it almost impossible to infer a clear trend, which you try to impose with your colored lines, and compare the ice nucleation trends of the individual soot types. I suggest to extend your measurements for Monarch 880, 900, Regal 330R and R2500U to 217 K, similar to the ethylene soot, to allow for a more complete comparison among the different soot types.
- P9L22: Can you quantify the variability observed in the measured effective density? I assume the values reported in Tab. 1 are mean values. Please indicate the number of particles measured and give the standard deviation, so that the reader can access the degree of variability within each BC type, which then allows to intercompare the different types.
- P9L24: The statement about the aerodynamic diameter and its relation to mass and shape factor are confusing. Do you not derive the effective density from the vacuum aerodynamic diameter and the mobility diameter? Please clarify.
- P9L27: Add “... can likely be explained”
- P9L28-31: This statement is not supported by your data, or I am misinterpreting it. For instance, ethylene soot has the lowest effective density, but around 225 K shows a similar ice nucleation ability to R2500U, which has the second highest effective density. Please explain. In addition, your argumentation is inconsistent with the effective density given for Regal 400R, which you argue is not PCF active at all. This should be clarified. Alternatively, are you trying to argue that within one soot type, aggregates with higher effective density nucleate ice more readily by PCF compared to aggregates of the same soot type, but which have a lower effective density and that this can for instance explain the variability of your R2500U data points around 230 K? If the latter is the case, this is an interpretation of your data and should be clearly stated as such, as you do not show any measurements comparing compact, high effective density soot particles

- of a given diameter against low effective density soot particles of the same diameter and soot type, which would support your argument.
- P9L31-37: The statement made in this paragraph about deriving soot particle compaction from the OPC signal needs to be elaborated further.
 - o The authors state that "... the most active INP (e.g. R2500U, Monarch 900) showed lower polarization shift signature, which suggest a more optically spherical shape." How can this be read out from the two values $\log(S1)$ and $\log(P1)$ listed in your Tab. 1? Please specify and/or give appropriate references.
 - o Besides, the $\log(S1)$ and $\log(P1)$ values for Monrach 880 and 900 are identical, but at the same time these soot types show differences in ice nucleation. Please comment.
 - o Next, on P8L5: You state that your OPC starts seeing particles, which are *optically* larger than 500 nm in diameter. How does the optical particle size compare to the mobility size of 800 nm? Is there any clear relationship between these two sizes? Can it be that some of your 800 nm mobility diameter soot particles are aligned in such a way in the OPC, that they scatter only little light, thus cannot be detected and bias your results?
 - P10L1-7: "The results showed no visible sign of compaction effects on the IN activity..." Is this supported by your SEM analysis, i.e. do wet and dry aerosolized particles look identical? If SEM images are not available, I encourage to include another table, where you display similar to Tab. 1, the $\log(S1)$ and $\log(P1)$ data of the wet and the dry generated aerosol, which should be available. From these values it should, according to the authors, directly be visible whether a compaction of the particles took place or not.
 - P10L7: "... of initial compactness of the particles was provided by the low values measured in the OPC (Tab. 1), which are associated with the sphericity of the particles."
 - o In the last paragraph (P9L31-37) the authors try to make a case, that the OPC data can be used do estimate particle sphericity. Moreover, the authors claim that more spherical (compact) soot types are better INPs for PCF compared to less spherical soots and that the differences in the OPC values listed in Tab. 1 can be used to support this hypothesis. The statement made here (P10L7) now says that in general the soot types are all very spherical already, supported by the OPC values in Tab. 1. In my eyes, this is directly contradictory to earlier statements in the manuscript (P9L31-37). Please explain.
 - o Following your argumentation from P9L31-37, the soot types presented in Fig. 5 have different sphericities, based on the OPC data. Even if the R2500U soot was already perfectly spherical and compact for the dry generation method, the Regal 400R is not (see your OPC values in Tab. 1) and thus should show a difference in compactness (and ice nucleation) upon wet generation. Please explain.
 - P10L14-15: Change to "... the probability of active sites will be higher for larger particles, increasing their probability to nucleate ice."
 - o One assumption for the active site concept is that active sites are homogeneously distributed over the particle surface and thus n_s is constant with particle size. So what changes when going from 100 nm to 800 nm particles is just the probability of having an active site.
 - P10L19-20: Please explain why the 100 nm aggregates without suitable pores would nucleate ice homogeneously? This is only possible if there is any soluble material on these soots, which can cause homogeneous freezing. Is this the case?
 - P10L21: Change "ice heterogeneously" to "ice below homogeneous freezing conditions".
 - P10L21-23: Are your ice nucleation data corrected for multiply charged particles? If not, how does the 1% AF chosen as appropriate ice nucleation onset threshold compare to the amount of multiple charged particles and to the maximum AF reached within one RH scan? What is the size distribution of the soot samples? Can you give a particle size distribution from your SEM images, or from the measured vacuum aerodynamic diameter in PALMS? Furthermore, I suggest putting the complete AF curves of your measurements into a supplementary information. These AF curves contain very useful information and could support your arguments about a PCF mechanism, which should result in very steep activated fraction curves, due to the homogeneous freezing of the water in the pores.
 - P10L8-24: Did you measure the other soot types also for both 100 and 800 nm? Why is this data not presented here? The selection of data points seems a bit random: Why do you only

show one data point for 800 nm particles of Monarch 800 around 227 K? Is this statistically significant to compare one RH scan here to two RH scans performed on 100 nm particles at similar temperatures?

- P10L30: Change to "... while the non-oxidized sample showed ice nucleation activity, well below homogeneous freezing conditions."
- P11L1: This statement is incorrect and should be revised. The PCF mechanism is in fact very sensitive to the pore wall hydrophilicity, usually considered in terms of contact angle, see e.g. Eq. (1) in Marcolli (2016). You can use the indicated equation to calculate the RHw for pore filling at a fixed pore diameter and check its sensitivity to the contact angle. In other words, a porous particle will not be able to nucleate ice via PCF, i.e. at conditions well below water saturation, if the contact angle is too high, even though if pores of suitable diameters are present. For instance, a pore of 6 nm diameter and a contact angle of 0° requires a RHw of 57% to be filled at -50°C, whereas the same pore would require a RHw of 91% in case the contact angle was 80 °.
- P11L6-8: I disagree with this statement and I believe this conclusion cannot be drawn from your data. The Regal 400R as presented in Figs. 1 and 7 nucleates ice at homogeneous freezing conditions and does not nucleate ice via PCF, as you correctly argue throughout the manuscript. The absence of PCF freezing for Regal 400R can have various reasons, such as absence of suitable pores, too high contact angle or soluble material on the soot filling the pores and thus preventing pore condensation due to the inverse Kelvin effect etc. Your argument that surface oxidation leads to inhibition of pore filling and freezing (PCF) due to surface polarity would only be true if you were to take a soot (e.g. Monarch 900), which clearly shows PCF (Fig. 4) but has a non-oxidized surface (Tab. 1), and that this PCF freezing disappears upon oxidation of this soot. Finally, from your Fig. A1 it looks like the ethylene soot also shows a tendency to have relatively high O-peaks. This, along with the slightly acidic ph listed in Tab. 1 suggests an oxidized surface to me (see also your description P6L1-5). Nevertheless, the ethylene soot clearly reveals a PCF freezing mechanism, which contradicts your statement.
- P11L14: This argument about ice lattice seems out of place here and should be removed.
- P11L16-20: This is a repetition from P5L6-7 and P3L4-6 and should be removed here.
- P11L23: "The cis-pionic and stearic acid when atomized, nucleate ice homogeneously." I suggest adding these data points to your Fig. 8.
- P11L25: Do you mean "ice supersaturation" of 10%?
- P11L24: If your coating of cis-pionic and stearic acid fills all the pores of your BC agglomerates, the ice nucleation onset should be shifted towards homogeneous freezing conditions, as the pores are blocked and can thus not trigger ice nucleation via PCF. The results in your Fig. 8c seem not very robust, with one blue data point lying at the homogeneous freezing curve and the other one lies within uncertainty of the uncoated (grey) data point.
- P12L1-2: In Fig. 9 you compare your ice onset nucleation in terms of an activated fraction threshold to a ns parametrization by Ullrich et al. (2017). This does not make any sense. Please revise this figure and convert your AF based onset data points to ns. I feel you can omit this figure and plot the Ullrich et al. parametrization directly in your Fig. 9 for better comparison. Also, your Fig. 9 should include all your soot data.
- P12L3-6: This is a repetition from the methods described on P7L6-16 and should be deleted here.
- P12L9-11: How do the authors arrive at this conclusion? If I look at your non-oxidized data point around -54 °C in Fig. 9, the error bars cross the isolines of both 10^{11} and 10^{10} m⁻². But again, the comparison of AF based thresholds and ns is misleading, see my comment on P12L1-2.
- P12L13-16: This is a repetition of P2L28-30 and should be removed here.
- P12L18: Replace "hindering" by "limiting"
- P12L24: "For comparable..."; see my comment P12L1-2.
- P12L27: The sentence "Hence, the ..." should be moved in front of the last sentence to finish the discussion about oxidation, before starting to talk about coating effects.
- P12L32: I suggest to tune this down and say "... can partly be explained"
- P12L21: Change to "... dominates, coverage of high clouds..."
- P12L23: contributes

- P12L29: Rephrase to: "... our results of BC ice formation below homogeneous freezing conditions..."
- P13L2: Delete "which is sensitive to coating"
- P13L2-4: How do the authors derive at this conclusion? Why would such a droplet splintering inside the pore only lead to an underestimation of BC in ice residuals? Such an effect should be similar for other porous materials, such as volcanic ash particles and also porous mineral dust, to name a few... (Marcolli 2016; Wagner et al. 2014).
- P13L8: Delete: "the in situ type"
- P13L9: Delete "simulated"
- P13L10-11: the "strong dependence on temperature" is inconsistent with a PCF mechanism, but likely an instrument limitation, see my comment P8L25-27.
- P13L16: The discussion of the compaction of 200 nm BC particles should be followed by a reference.
- P13L23: Change to: "... can take place well below homogeneous freezing conditions."
- P13L26-27: This has systematically been done in a recent study by Mahrt et al. (2018).
- P13L33: Who is "MF"? Do you mean "MW"?

Fig. 3:

- I suggest to have the error bars in the same color as the dots to increase readability.
- Your caption should be changed to: "Ice nucleation onset conditions defined as 1% of the total aerosol to nucleate ice for 800 nm BC particles." If you claim PCF to be responsible, the freezing process is not heterogeneous, but homogeneous, see my comment P7L36. Also, there is no need to repeat the temperature range in the caption, as it is indicated by the x-axis.
- I assume each dot represents an individual RH scan in SPIN, correct? What do the error bars represent?

Fig. 4:

- The solid colored lines should be removed or the parametrizations for the fits should be given and justified.

Fig. 5:

- Include grid lines and boxes around the graph to be consistent with your Figs. 3, 4.

Fig. 8:

- Add grid lines and boxes.
- Unit on x axis should read °C not °C
- Why do only a few data points have error bars and why are these of different size for the data points?

Fig. 9:

- Why do you constrain yourself to 3 of your soot types measured?
- Also, it is not clear how you decide to just plot 1 data point for the three soot types shown? How do you derive this from your data presented in Fig. 3? You should include all your data in this summary plot.
- Constrain legend to: "Kanji et al. (2017)"

Fig. A1:

- Delete "800 nm" in the legend and write into figure caption that this data corresponds to 800 nm particles.
- I suggest to plot the mean/center for each cluster/soot type into the plot at the same color, but larger symbol size to guide the eye.

Tab.1:

- Please add uncertainties to measurements of ph, O:C ratio and OPC values.
- subscript of "m" after D.

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