

Review to “The effects of morphology, mobility size and SOA material coating on the ice nucleation activity of black carbon in the cirrus regime” by Zhang et al.

The work by Zhang et al. presents laboratory data of the ice nucleation ability of different types of black carbon, along with a characterization of the physical and chemical particle properties. The study extends previous laboratory measurements on the ice nucleation ability of soot. This topic fits well within the scope of ACP, and the results are novel and of great interest for the ice nucleation community.

Overall, I find the manuscript is well written and structured and the results are presented in a clear way and put into context of previous literature. However, from my point of view there are some aspects, in particular in the discussion of the ice nucleation results, that should be revised. Once the points outlined below are sufficiently addressed, I support publication of the manuscript in ACP.

Overall comments and general concerns:

- The authors do not seem to provide a consistent view of the ice nucleation mechanism of the investigated soot types, which I find in part hard to follow. At various instances throughout the manuscript the authors describe the observed ice nucleation activity to result from deposition nucleation (e.g. L25, 27, 68, 90, 284). At other instances, the authors describe how earlier studies by Nichman et al. (2019; including authors from the present study) and Mahrt et al. 2018 (L80-84) have identified soot to form ice via the pore condensation and freezing (PCF) mechanism at cirrus cloud temperatures, the temperature range studied here. The PCF mechanism is then suggested to explain the observed ice nucleation results (e.g. L228-332) and also used to argue how the coating of the soot particles with secondary organic aerosol (SOA) leads to filling of the pore, which renders these pores unable to contribute to ice formation via PCF (e.g. L396-397). This seems to be in stark contradiction to the suggested ice formation via deposition nucleation for some of the bare soot particles. In their discussion (L438-439 and L460) the authors then vaguely talk about “verifying the PCF” mechanism in future studies but it does not become fully clear if the ice nucleation observed in the present study is attributed to PCF or to “classical” deposition nucleation.

I assume that the authors interpret the observed ice formation as PCF and whenever the authors refer to “deposition nucleation”, they refer to ice formation at cirrus temperatures below water saturation (and below homogeneous freezing conditions, to be specific). However, this terminology is confusing for the reader, and suggests a flip-flop between both mechanisms, i.e. classical deposition nucleation and PCF. I would appreciate if the authors could provide a clearer description of the ice nucleation mechanism of the observed ice formation on the investigated soot particles. A relatively simple solution to reduce the in part confusing back and forth would be to use just “IN activity” rather than “deposition IN activity” to describe the ice formation below homogeneous freezing conditions and then provide a comprehensive discussion of both “classical” deposition nucleation and PCF in the results section.

- The title of the presented manuscript suggests that an effect of particle size, morphology and coating on the ice nucleation ability of BC is investigated in this study. While I appreciate the efforts in comprehensively and carefully characterizing the physical and chemical properties of the investigated soot types the associated uncertainties are not sufficiently discussed, which I find problematic. For example, the goodness of the size selection and hence the difference between a 300 nm and a 400 nm R2500U particle are not discussed. Upon revision of the manuscript, the uncertainties of the various measurements of these variables on the dependent variable (ice nucleation activity), should be more clearly emphasized and discussed. As another example, I am not clear whether the O:C ratio of the COJ300 and the R2500U samples are really different.

Specific comments:

- L22: Delete “aerosolized”
- L25: Delete “(-24 to -46°C)”
- L25,27: “Deposition IN”; please see my general comment above.
- L31: “We attribute the inhibition of IN ability to the filling of pores on the BC surface by the SOA material coating.” In other words, the IN ability of the uncoated particles results from the pores, i.e. takes place by PCF. This is in contradiction to the “deposition IN” mentioned above and at various other instances in the manuscript. Please see my general comment above.

- L33: Delete first “days”
- L37: Delete “terrestrial”
- L39,41: I suggest replacing the given references by primary reference, e.g. the classical textbook by Pruppacher and Klett (1997).
- L43: Why are you only introducing “deposition IN” here and not also PCF?
- L45: Rephrase as: “BC from aircraft emissions may be an ...”
- L53: Delete “simulate the atmospheric environment”
- L59: Hoose and Möhler (2012) is not a primary reference and I suggest deleting it here.
- L63-64: Similarly, the probability of a BC aggregate to contain a pore with the right properties (e.g. pore size and contact angle) increases with increasing aggregate diameter, which would favor PCF for larger particles (Mahrt et al., 2018). This could be added.
- L68: “deposition mode”; see my general comment above.
- L70: Rephrase to “...during atmospheric aging, leading...”
- L71: Add Bhandari et al. (2019) and Khalizov et al. (2009)
- L80: Delete Kumfer and Kennedy (2009)
- L80-81: This statement is not true and needs to be revised. E.g. see Table 1 and Fig. 3 in Mahrt et al. (2018). The investigated “FS” soot has the second highest surface area, but “LB_RC” shows a similar or higher IN activity.
- L82: Delete Koop (2017) and Marcolli (2017). Add David et al. (2020).
- L83: Rephrase to: “...in which IN of BC is considered as homogeneous freezing of...”
- L84: Replace references by Fisher et al. (1981).
- L90, 100: “deposition nucleation”; please see my general comment above
- L102: “-38°C”
- L128: Add: “... in particles of aircraft engine exhaust...”
- L131: Please specify “light” aromatic species
- L133: How representative is β -caryophyllene for biogenic SOA? How does it compare to other major biogenic SOA types such as α -pinene SOA? For the Sect. 2.1.2. more discussion on the atmospheric abundance and relevance of the chosen SOA precursors should be given.
- L146: Can the authors comment on how the wet dispersion in the atomizer affects the BC particle morphology?
- L150: The flow reported here (1.5 SLPM) and on L215 (2.2 SLPM) are different. How does this change your flow rate through the DMA and possibly affect your size selection. Please comment in the main text.
- L152-153: Have the TSI and BMI DMA been compared? Can the authors provide a size distribution of the soot types investigated that was size-selected with both DMAs to ensure that there is no difference in the uncoated and coated particles due to the instrumentation used? Please also add the aerosol-to-sheath flow ratios used in the DMAs for aerosol size selection.
- L155: An RH value of 16% seems extremely high. Please comment how this affects your IN measurements that are performed using this air stream (conserving specific humidity) but exposing it to $T < -40$ °C.
- L160: Please specify “MOUDI” acronym
- L170: Rephrase as “... by the PALMS.”
- Table 1:
 - o da of R2500: Why is the projected area diameter for $d_m = 300$ nm larger than for $d_m = 400$ nm?
 - o da: Please comment in the text why the da values for $d_m = 400$ nm particles for COJ300 and R330R are significantly larger than for R2500U.
 - o Roundness: The roundness values for all soot types and mobility sizes are very similar and comparable. Can this be a result of the wet dispersion? Do the authors have data for dry aerosolized BC particles for comparison?
 - o Please add the standard deviation values for the reported fractal dimension.
 - o Please add the standard deviation for the reported O:C. Why is the median used here and not the mean? Is the difference between 0 (400 nm R2500U) and 0.02 (400 nm COJ300) significant?
- L178-179: From Figs. A2 and A3 it remains ambiguous how d_{pp} was determined. More information should be added.
- L196: Fig. A5 shows a very broad size distribution, even though $d_m = 400$ nm have been sampled. How does d_{va} and d_m relate? Please discuss in the manuscript how the broad, not monodisperse size distribution affect your conclusions for the IN measurements. A similar question arises when looking at Fig. 2.

- Please also specify what size threshold was used for the analysis of the SPIN OPC data and discuss this in context of the shown BC size distributions. E.g. Fig. A5 suggest presence of supermicron particles, which could have been miscounted as ice crystals.
- L203: Please add references
- L211: Are these number concentrations after size selection? They seem very high.
- L222: O₃ concentrations of 110 ppm seem very high. Please put this in context of typical tropospheric O₃ concentrations. Can this be used to then report estimates for “Equivalent atmospheric exposure days” of O₃ in your Table 2?
- L225: Replace “pyrolysis” by “photolysis”
- L228: Please specify how the reported “atmospheric aging time” of 10-15 days was calculated.
- L232: What causes the increase in RH from 16% to 25%?
- L236: Please add what the CPC number concentration was after flushing the PAM.
- L259: Delete references to Nichman et al. (2019) and Wolf et al. (2019).
- L263: Specify “centerline” of what?
- L276: Specify OPC size threshold used for AF analysis.
- L277: Please elaborate why different correction factors were applied for R2500U and R330 R and comment in the manuscript.
- Section 3.1: Please add the fraction of multiple charged particles in your population of size-selected particles to your Table 1 and discuss a potential impact on your reported IN onsets, using AF = 1% as threshold.
- L284: “deposition IN”; please see my general comment above.
- L286-287: Are the error bars based on theoretical calculations presented in the cited reference or based on measurements; please specify.
- L288: I suggest tuning down “substantially” here. Looking at your morphological parameters in Table 1 (AR, roundness, circularity), the values of the different soot types are within uncertainty of each other. Please see also my general comment above.
- L289: Please use the same precision for the given D_f values as in Table 1, i.e. D_f = 1.92.
- L292: Can this also simply result from uncertainty in the d_{pp} measurements? Please see Anderson et al. (2017).
- Fig. 3:
 - Panel A: Why does the temperature uncertainty change between the subpanels (a), (b) and (c)?
 - Panel B: Please specify if the scale bar is valid for all images. The SEM image of COJ300 suggest that this soot type is the most spherical. However, the roundness values reported in Table 1 are similar to e.g. d_m = 200 nm R2500U. Can the authors provide more SEM images for the Appendix to evaluate the representativeness of the shown images?
 - Panel B: Considering the values of the roundness of the various soot types and d_m = 400 nm, suggest that the morphology is the same within experimental uncertainty. In this context, the conclusion drawn that no clear dependence of IN on the particle morphology was found (e.g. L324, 451) is not surprising. However, the COJ300 soot type seems clearly more spherical on the (typical) images depicted in Fig. 3. Interestingly, at the same time this soot type reveals the largest ice nucleation activity. This trend is in-line with recent results of Mahrt et al. (2020), showing that more compacted, round soot aggregates are better ice nucleation particles (INPs) via PCF compared to more fractal soot particles. This provides further evidence that the observed ice nucleation activity in the present study is caused by PCF and might be worthwhile to consider for the discussion of the results. Do the authors have an explanation why the COJ300 aggregates look almost spherical?
 - Panel C: It looks like there is also some O (m/z = 16) for R2500U, also this is hard to see from the scale. This figure could be improved by moving the PALMS spectra to the SI (they are only mentioned once in the manuscript) and increase the size of the panels showing the IN results, which is the major focus of this work.
- L308: Add: “... relevant to the particle...”
- L309: “Representative uncertainty” of what?
- L310: “deposition IN”; please see my general comment above.
- L315: Add: “... R330R along the expected homogeneous freezing threshold in Fig...”
- L316: “...where the IN mode transitions from heterogeneous IN ability to homogeneous freezing...” Please consider revising this statement. During PCF, the formation of ice takes place by homogeneous freezing, i.e. PCF should not be viewed as heterogeneous ice nucleation process (Marcolli, 2020).

- L318: “higher” not “warmer” temperature
- L324-326: You might want to revisit these lines: The number of surface defects and pores for soot particles to form ice via PCF does not necessarily scale with the degree of branching of a soot aggregate. For instance, Mahrt et al. (2020) reported that cloud processes, more compacted (less fractal, even though associated with a higher fractal dimension) soot aggregates were more potent INPs to form ice via PCF. In these more compacted, round soot aggregates the probability of having a pore suitable for PCF is higher. In fact, your results are in-line with these previous findings and further support these. Your Fig. 3 reveals that COJ300 soot is most ice active and also most round based on the SEM image, with the latter being further supported by the roundness and fractal dimension values reported for COJ300.
- L331-332: Please expand your explanation on this aspect. What you show in Fig. C1 is not the saturation ratio required for pore filling (or onset of PCF), but the negative pressure resulting from keeping water within the cavity; this needs to be revised. Please also comment on how relevant the pore geometries investigated in Marcolli (2020), i.e. cylindrical and wedge-shaped pores are for the BC agglomerates in your study.
- Figs. 3 (and 5): Does each dot correspond to a single RH-scan?
- Sect. 3.2: Can you determine the coating thickness from your measurements. Adding an estimate of the coating thickness to this section would be helpful, in order to estimate for what coating thickness ice nucleation by PCF becomes inhibited.
- L337: “deposition IN”; please see my general comment above
- L346-347: It looks like the onset of toluene SOA-coated BC particles and bare BC particles is still within uncertainty.
- L349: 10-15 days is longer than the average tropospheric lifetime of soot particles. This should be reflected in your discussion.
- Fig. 6: Showing difference spectra between each panel and the bare soot shown in Fig. 6d would facilitate showing the differences between the coatings.
- L369: Rephrase to: “The IN onset...” ... “... in Fig. 5b show that these particles nucleate ice ...”
- L373: Can you provide a difference AMS spectra of the OH and the O₃ oxidized β-caryophyllene coated BC particles?
- L384: “form” instead of “forms”
- Fig. 7:
 - o It would be helpful to add the H/C and the O/C values of the O₃ oxidized β-caryophyllene soot here as well.
 - o Please verify that the suggested slope for the toluene coated SOA is correct. From your legend it looks like you should connect the white star in the lower left. corner to the blue star in the middle right. If that is the case, you need to revise your statement in L378-380.
- L392: Add: “In these studies shifts from...”
- L394-396: I do not think that it is the volatility that changes and allows a SOA particle to become glassy, but the phase state (here viscosity). Please reformulate.
- L396-398: If the suppression of the ice nucleation results from filling of the pores, the ice nucleation mechanism of the bare/uncoated particles would likely be best described by PCF, not? Please see my general comment above.
- L401: Please give details about the mass loadings used in the PAM and briefly comment on typical tropospheric SOA mass loadings.
- L412-415: This discussion should be expanded and more specific examples are needed to make the claim that the characteristics of the investigated BC types is similar to ambient soot.
- L419: The reported threshold of “ $d_m < 200$ nm” seems rather high and is misleading. For instance, Moore et al. (2017) report mode sizes of around 30 nm. While Kittelson (1998) report soot aggregates up to 200 nm (see their Fig. 11) a more profound literature search should be done here to support the given threshold.
- L223: Change to: “However, IN ability of small BC particles... may collapse forming PCF favoring...”
- L224-225: Why do you mention “surfaces” here and then talk about the “mesopores” in the next sentence.
- L225: The connection between the primary particle size and the mesopores is unclear and should be further elaborated.
- L226: I suggest tuning down: “This suggest that long-lived...INPs.”
- L433: Specify as: “... growth, SOA-coated soot particles...”
- L441: Delete “monodisperse”, your Fig. 2 indicates a more polydisperse sample.

- L444: Why is the R330R sample “atmospheric compacted”? The COJ300 is the most round according to your Fig. 3B and Table 1.
- L449: “deposition nucleation”; please see my general comment above. I think that in particular in the summary section you need to be careful on how to describe the ice nucleation mechanism, as in the same section (L456 and L461), you imply some ice formation via PCF.
- L451-452: See my earlier comment. The study by Mahrt et al. (2020) found more compacted soot particles to be better INP (via the PCF mechanism) compared to less compacted soot.

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