Response to 2nd Reviewer minor revisions for Nichman et al. ACPD, 2018.

We thank the editor and reviewers to their efforts. Reviewer's comments are in black. Our responses are in blue.

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 and sizes in the cirrus regime. The topic of BC ice nucleation is of high relevance for atmospheric science and climate, and as such for ACP.

General comment:
The manuscript is well structured and written. I would like to congratulate the authors, who have significantly improved the quality of the manuscript, compared to the previous discussion paper. The five aspects influencing BC ice formation identified by the authors (see P5) are discussed in fair detail, even though I found the introduction quite long and partly hard to read. However, the discussion of the measurement uncertainties in terms of RH and T is poor. This makes it hard to follow parts of the comparisons between the different soot types and the argumentation for some of the figures.

We thank the Reviewers' for their efforts reviewing our manuscript.
We added error bars in Fig.6. The uncertainties only briefly discussed here but more detailed description of RH,T uncertainties of this exact SPIN instrument can be found in the cited papers (Garimella et al., 2016; Garimella et al., 2017; Wolf et al., 2019).

**Garimella, S., Bjerring Kristensen, T., Ignatius, K., Welti, A., Voigtländer, J., Kulkarni, G. R., Sagan, F., Lee Kok, G., Dorsey, J., Nichman, L., Alexander Rothenberg, D., Roesch, M., Kirchgäßner, A. C. R., Ladkin, R., Wex, H., Wilson, T. W., Antonio Ladino, L., Abbatt, J. P. D., Stetzer, O., Lohmann, U., Stratmann, F. and James Cziczo, D.: The SPectrometer for Ice Nuclei (SPIN): An instrument to investigate ice nucleation, Atmos. Meas. Tech., 9(7), 2781–2795, doi:10.5194/amt-9-2781-2016, 2016.
**Garimella, S., Rothenberg, D. A., Wolf, M. J., David, R. O., Kanji, Z. A., Wang, C., Rösch, M., and Cziczo, D. J.: Uncertainty in counting ice nucleating particles with continuous flow diffusion chambers, Atmos. Chem. Phys., 17, 10855-10864, https://doi.org/10.5194/acp-17-10855-2017, 2017.
**Wolf, M.J., Coe, A., Dove, L.A., Zawadowicz, M.A., Dooley, K., Biller, S.J., Zhang, Y., Chisholm, S.W., Cziczo, D.J.: Investigating the Heterogeneous Ice Nucleation of Sea Spray Aerosols Using Prochlorococcus as a Model Source of Marine Organic Matter, Env. Sci. Tech. 53 (3), 1139-1149, 2019.

Overall, I recommend the manuscript for publications, after some minor and specific comments, which I list below, have been addressed:

Specific comments:

- P1L23: Change to "…that govern the ice nucleation activity of BC."

Changed.

- P1L31: Delete "lamina".

Changed.

- P2L16: Do you mean cloud types?

Changed to "... homogeneous and heterogeneous freezing mechanisms."

- P2L18: "While field…". This statement should be followed by references. I suggest deleting this sentence here, as you have a detailed discussion of both aspects further down.

Sentence has been deleted, as suggested.

- P2L34: Kanji et al. (2017) and Hoose and Möhler (2012) are review-type articles, sourcing data from other studies. Please delete these here and cite primary studies instead. Also, add: Häusler et al. (2018)

Several primary studies are already listed in the brackets, we removed the review-type articles and added Hausler et al. 2018.

- P3L7: "…(PCF) mechanism." Should be followed by a reference.

Added (Macolli, 2014)

- P3L11: delete "heterogeneous", this is clear since you say below homogeneous freezing.

Deleted

- P3L36: Change to "can be expressed"

Changed.

- P4L1: None of the given references makes sense to me. Are you just trying to cite studies that have used ns? Consider deletion.

References deleted as suggested.

- P4L11: Check formatting: “2014” of Marcolli is not in parenthesis, while other studies are. Add David et al. (2019).

Done

- P4L13: Delete “diameter”

Done.

- P4L20: Add reference after “diameter range”.

Added (Vali, 2014)

- P4L24: Add Umo et al. (2019)

Done

- P5L3: I suggest tuning this down and saying: “… have not fully been established.”

Changed.

- P5L29: Check formatting/indent.

Done.

- P6L14: Define “BET”

Removed “(high BET) value” here, as we use and define BET below.

- P6L17: “Submicron”

Done.

- P6L17: Delete “burner”

Changed “burner” to “flame”.

- P6L22: Replace “test” by “method”

Done.

- P7L17: “organic molecules.” Should be followed by a reference.

Added: Goldstein and Galbally, 2007.
**Goldstein, A.H. and Galbally, I.E.: Known and Unexplored Organic Constituents in the Earth's Atmosphere, Environ. Sci. Technol. 41 (5), 1514-1521, DOI: 10.1021/es072476p, 2007.

- P8L35: This is not completely true, ice supersaturation can/is also be achieved when water-saturation conditions are created in SPIN. Please rephrase and formulate more carefully.

Changed to “Because of the nonlinear relationship between saturation vapor pressure and temperature, supersaturation with respect to ice, in water-subsaturated conditions up to and including water-saturation, is achieved along the center of the chamber, allowing for ice nucleation.”

- P9L16: Are your ice nucleation data corrected for multiple charged particles? Please specify the sizes of double charged particles for the mobility diameters used by you. Could it be that the OPC detects a large, double-charged BC particle as ice?

This was answered in detail to comment **P10L21-23** of Reviewer2.
The data is not corrected for doubly charged particles; however, the 800 nm mobility diameter particles are essentially on the larger-diameter edge of the size distribution of BC particles. Soot’s main mode is on the order of several hundreds of nanometers as was shown in the figure attached in that comment in previous reply..
The doubly charged particles, of the 800 nm singly charged particles, would need to be approximately 1.48 micron in diameter (fractal dimension of 3 assumed due to sphericity) and literally in negligible concentration, and have higher losses in the lines. Moreover, the OPC detected particles only in the first 2 bins (associated with the 800 nm mobility diameter) but not in any other higher size bins.
In any case, if there were doubly charged particles (1.48 micron) present, the OPC would not detect them as ice since the OPC classification is based on several scattering and polarization

parameters rather than size alone. These parameters have thresholds for aerosol, water, and ice (see Garimella et al., 2016).
In regard to 100 nm ethylene soot particles, we expected all the 100 nm BC INP to freeze at the homogeneous line (see Mahrt et al. 2018). One possible explanation that it did not reach homogeneous nucleation, i.e. nucleate at a higher SS% but still below Koops line, is the presence of doubly charged particles (~151 nm) or triply charged (~195 nm), which are bigger agglomerates and nucleate better than the single aggregates, therefore improving the observed IN activity of the selected mobility diameter. However, they are not as active as if these were solely big particles. The broader PSD of flame generated soot is expected to have more multiply charged particles in comparison to commercial well defined batches of pigments.
Therefore, we state in the text of Sect 3.1, point (3), last few sentences: “Despite the reduction in activity, the 100 nm soot has nucleated ice below homogeneous freezing conditions. It is possible that a bias introduced by multiply charged particles, passed at the same DMA voltage, maintained the high IN activity of 100 nm mobility diameter soot”.

*Garimella, S., Kristensen, T. B., Ignatius, K., Welti, A., Voigtländer, J., Kulkarni, G. R., Sagan, F., Kok, G. L., Dorsey, J., Nichman, L., Rothenberg, D. A., Rösch, M., Kirchgäßner, A. C. R., Ladkin, R., Wex, H., Wilson, T. W., Ladino, L. A., Abbatt, J. P. D., Stetzer, O., Lohmann, U., Stratmann, F., and Cziczo, D. J.: The SPectrometer for Ice Nuclei (SPIN): an instrument to investigate ice nucleation, Atmos. Meas. Tech., 9, 2781-2795, https://doi.org/10.5194/amt-9-2781-2016, 2016.

- P9L24: Can you set this 1% threshold into context of the maximal activate fraction observed during your RH-scans. Please comment on this in the manuscript.

At highest supersaturation, we reached RH above homogeneous nucleation. In this case, depositional activation percentage is not defined because of the homogeneous freezing conditions. Above homogeneous freezing we reached 100% activation. In other cases, when the scan was stopped below homogeneous freezing the maximal percentage varied 30 - 80 %.
New sentences:
“This figure shows a plot of water vapor supersaturation ratio with respect to ice versus temperature at which (1 %) ice onset occurs. As the scan continues, activated fraction increases. Finally, full (100 %) activation is observed if water saturation has been reached”.

- P9L34: I could not find the definition for “SSi”.

Changed to read, “The relationship between the supersaturation with respect to ice at the ice nucleation onset, SSi, and temperature…

- P10L4: Add Mahrt et al. (2018)

“...similar to some of the earlier observations of soot (e.g.,...”
Here we refer to earlier experimental observations of soot. Mahrt et al. 2018 was conducted in parallel with this study, and it is already mentioned in several places in this manuscript.

- P10L7: Why do you write “Heterogeneous ice nucleation”. On P4L10 you state that water in pores freezes “homogenously”. Please clarify in manuscript.

P4L10 currently reads, “The PCF mechanism proposes that empty spaces between aggregated primary particles fill with water due to capillary condensation at relative humidities (RHw) below water saturation, which freezes homogeneously (Marcolli, 2014; Christenson (2013); Higuchi and Fukuta (1966)).”

We have added the following sentence to the manuscript on P4L11 (following the above sentence):

“The PCF mechanism, which models ice formation inside small pores using homogeneous freezing theory, describes the heterogeneous formation of ice on solid particles, such as soot particles, due to the presence of the porous structure. Therefore, we refer to PCF as a heterogenous ice freezing mechanism (Vali et al., 2015).”

- P10L13: “The displayed…” This statement is not supported by your data shown in Fig. 4, in particular by the data points around T = 228 K. Please clarify. This would become even clearer if you were to include error bars in your data points, similar to your Fig. 3.

This one scan when taken out of context doesn’t represent well the observed trend described here. We tuned down the sentence to be more accurate.
Previous:
“The displayed onset supersaturation difference shows that the IN activity of R2500U is significantly higher than that of Regal 330R”
New:
“The displayed onset supersaturation difference shows that the IN activity of R2500U is higher than that of Regal 330R for the majority of runs in the temperature range 228 – 233 K”.

All the error bars and the compared data are shown already in Fig. 3. An addition of error bars in Fig.4 will overcrowd the figure, essentially in the same way as seen in Fig.3.
We added references to both Figs 3,4 in the text for reference to error bars:
“The most notable feature in Figs. 3, 4 is the gradient between the data sets for BC particles R2500U (red squares) and Regal 330R (yellow squares), including the BC types in between”.

- P10L29: Again, it is very hard to justify and/or follow this statement without error bars in Fig. 4.

This was answered in detail to comment P9L28-31 of Reviewer2, It is clear to the authors that there are some overlaps in data points of the experimental results; however, least squares fitted curves, suggested in the previous version of the manuscript show a clearer difference between the datasets of each compound.

All the error bars needed and the compared data are shown in Fig. 3. An addition of error bars in Fig.4 will overcrowd the figure essentially in the same way as seen in Fig.3.
We added references to both Figs 3,4 in the text for reference to error bars:
"Therefore, in accord with the PCF mechanism, one would expect Monarch 880 to display lower IN activity in comparison to Monarch 900 and R2500U, as is observed (Figs. 3, 4)".

- P11L33: The reported size dependence seems consistent with that observed in studies by Friedman et al. (2011), Mahrt et al. (2018) and Crawford et al. (2011) that you cite above. You might want to refer back to these studies.

"To test the extremes of the aerosol diameters used in previous studies we selected 100 nm and 800 nm BC particles".
We have included references of previous studies. Mahrt et al. 2018 was conducted in parallel with this study.

- P11L36: Replace "," by "."

Done.

- P12L2: "Hence, the…": I assume that every data point in your Fig. 6 represents a single run. Please comment on how reproducible these are within the manuscript. Also, if I consider the error bars reported in your Fig. 3 I am not sure how different your 100 and 800 nm ethylene soot in Fig. 6 are. Please include error bars in Figs. and in discussion of data.

Yes this is correct, each data point represents a single run (P9L20). The blue squares are single experiments and thus the two runs at the same temperature represent a (crude) measure of reproducibility. The error bars in Fig.3 represent the variability of the laminar conditions based on CFD simulations by Kulkarni and Kok (2012) (P9L27) and are estimates of accuracy (based on T and RH uncertainties), whereas multiple measurements per temperature gives idea of precision (reproducibility) of the measurements.
Fig.3 doesn't include 100 nm data points with error bars, therefore we agree that these should be presented in Fig. 6.
Text changed:
"The error bars of Monarch 880 data points partially overlap in some of the 100 and 800 nm runs. Nonetheless, some runs don't have an overlap in uncertainty at the same temperature and the trend of lower IN activity, in 100 nm particles, repeats itself. Similarly, the IN activity of 100 nm ethylene flame soot is reduced in comparison to the 800 nm soot. Despite the reduction in

activity, the 100 nm soot has nucleated ice below homogeneous freezing conditions. It is possible that a bias introduced by multiply charged particles of flame soot's broad size distribution, passed at the same DMA voltage, maintained the high IN activity of 100 nm mobility diameter soot.

- P13L7: Delete space between "sample" and "."

Done.

- P13L10: Include space before "However"

Done.

- P13L27: Delete space before "The"

Done.

- P14L10: Please define "channel process"

We have added: "..., utilizing natural gas impingement on iron channels to produce carbon black..."
More information can be found in the cited papers and references therein.

- P14L17: Please change to "INP"

Done.

- P14L32: Consider to replace "down" with "along"

Done.

- P16L3: Who is "MF"?

Thank you. Changed to "MW".

- Figs. 3, 4, 6, 7, 8: The y-axis should be labeled as "Supersaturation ratio with respect to ice", or simply "Sice", to be consistent with your terminology. "Supersaturation over ice" as used is wrong. I recommend to be consistent through out all figures within the manuscript.

Y axes changed.

Crawford, I., et al. (2011), 'Studies of propane flame soot acting as heterogeneous ice nuclei in conjunction with single particle soot photometer measurements', Atmospheric Chemistry and Physics, 11 (18), 9549-61.
David, R. O., et al. (2019), 'Pore condensation and freezing is responsible for ice formation below water saturation for porous particles', Proceedings of the National Academy of Sciences of the United States of America, 116 (17), 8184-89.
Friedman, B., et al. (2011), 'Ice nucleation and droplet formation by bare and coated soot particles', Journal of Geophysical Research-Atmospheres, 116.
Häusler, T., et al. (2018), 'Ice Nucleation Activity of Graphene and Graphene Oxides', Journal of Physical Chemistry C, 122 (15), 8182-90.
Mahrt, F., et al. (2018), 'Ice nucleation abilities of soot particles determined with the Horizontal Ice Nucleation Chamber', Atmospheric Chemistry and Physics, 18 (18), 13363-92.
Umo, N. S., et al. (2019), 'Enhanced ice nucleation activity of coal fly ash aerosol particles initiated by ice-filled pores', Atmos. Chem. Phys., 19 (13), 8783-800.