Review of "Enhanced ice nucleation activity of coal fly ash aerosol particles initiated by ice-filled pores" by N. S. Umo et al. for Atmospheric Chemistry and Physics

General comments:

In the present study, N. S. Umo and co-workers show and discuss the results of temperature cycling experiments with coal fly ash (CFA) particles at the AIDA cloud chamber. The aim of these experiments was to clarify whether the ice nucleation activity of CFA is increased by the pore condensation and freezing (PCF) mechanism under certain conditions. The authors achieve to convincingly demonstrate that this is the case for some of the used samples. The question of why some samples are more prone to PCF than others is not convincingly answered, but this cannot be expected in the case of CFA, which is a very complex and heterogeneous substance. From my point of view, the study is an interesting addition to recent findings concerning the ice nucleation behavior of CFA particles (Umo et al., 2015; Grawe et al., 2016; Garimella, 2016; Grawe et al., 2018; Losey et al., 2018). However, there are some content-related issues which need more discussion or clarification from my point of view. These are listed below (specific comments).
Parts of the manuscript could benefit from editing with respect to wording and presentation of the results but this can be easily resolved (see technical corrections). The figures are mostly clear, but I was wondering why a significant part of the results are not shown anywhere. The authors should consider including an Appendix for presenting the missing figures.
Generally, I feel that the topic fits the scope of ACP and that the study is worth publishing. To improve the overall significance and readability of the manuscript, I suggest the following minor points.

Specific comments:

1) Effect of size-dependent specific surface area and pore properties:

The investigation of PCF on CFA particles is a daunting task, since CFA is such a heterogeneous substance. I appreciate the authors' attempt at finding possible reasons for differences in the behavior of the different samples, but I also think that their approach lacks the discussion of an important point, i.e., the size-dependence of the particles' specific surface area, pore volume, and pore size. This type of information is probably very hard to come by and I do not expect the authors to perform further analyses. But it should at least be mentioned that the specific surface area and pore volume are very likely dependent of the particle size and that some particles might not even feature pores (Seames, 2003). Hence, the properties of the sieved bulk sample (0-20 µm) might not be representative for the properties of the particles that actually enter the AIDA chamber (< 2.5 µm). This should be made clear in the discussion (P9L37-P10L30).

2) Comparison to Wagner et al. (2016)

When viewing the results, I was wondering how CFA particles compare to other the substances which have already been investigated with the same instrumental setup and measurement routine by Wagner et al. (2016), i.e., zeolite, diatomaceous earth, mineral dust, volcanic ash, and soot. Concerning CFA_UK, it is mentioned very briefly (P6L19-20) that "a similar increase in the heterogeneous ice nucleation ability has been previously observed for zeolite and illite" but nothing is said about the other CFA samples and other substances tested by Wagner et al. (2016). This comparison could be expanded to put the CFA results into perspective.

3) Atmospheric implications

Although the authors discuss the atmospheric implications of their findings, they are missing one major point. How large is the probability that CFA particles reach such high altitudes where they experience 228 K? I understand that CFA particles can influence atmospheric ice nucleation close to the point of emission, but the number concentration of these particles at cirrus level is probably close to zero. Indeed, it is difficult to identify CFA particles in the atmosphere due to their similarities to mineral dust which is why there is a lack of information concerning atmospheric number concentrations of CFA particles. But despite this lack of information, the authors should not leave this issue completely unattended. A remark concerning this should be included in Sec. 3.3.

4) Explanation of the PCF mechanism

- Even though PCF has become an accepted concept in recent years, the process itself should be explained in more detail. The negative Kelvin effect, which is the reason why there is capillary condensation of water vapor at a relative humidity (RH) below water saturation, is not even mentioned. I suggest to include an explanation of the mechanism (capillary condensation of water vapor at RH below water saturation → formation of ice in pores at very low temperatures → pore ice persists as site for ice nucleation at warmer temperatures and ice-supersaturated conditions) where it is first mentioned (P2L14).
- At this point, it should also be mentioned, why PCF is restricted to certain pore sizes (P2L29). Furthermore, I expected a remark concerning the effect of the pore geometry (cylindrical pore, ink-bottle-shaped pore) on PCF. Which types of pores might be present in CFA? All of this needs to be explained in the introduction.
- Instead of Fig. 2, the authors could describe the temperature cycling process in a similar manner as Marcolli (2017; see Fig. 1-4), i.e., showing RH with respect to temperature. The time scales of the different steps could be mentioned in the caption.

5) Methodology

- The AIDA chamber is a well-established instrument but the authors should consider describing the measurement and data evaluation techniques in more detail. For example, there is no mention of the uncertainty of the f_{ice} determination. How does the large error of ±20 % of the ice particle number concentration affect the f_{ice} error?
- The explanation of how f_{ice} is calculated should be included in Sec. 2.6, not in Sec. 3.
- I do not understand how droplets can form in an environment which is slightly subsaturated with respect to liquid water (see Fig. 3, panels A and B). It looks like the black line (RH with respect to water) is below 100 % throughout the duration of the experiments. Is this due to the measurement uncertainty? Please clarify.
- P5L17-18: How can the air in the AIDA chamber be subsaturated with respect to ice when there is an ice layer on the inner chamber walls? Shouldn't it be saturated? Please explain.

6) Presentation of the results

- I was wondering why ice nucleation surface site densities are not included in the discussion of the results. The authors state that "Further analyses on the distribution of the ice nucleation active sites densities of these CFA particles is outside the scope of the current report and will be presented in a separate communication." (P6L32-34). An inclusion of these data in the current paper would make more sense to me, especially for a comparison of the intrinsic ice nucleation behavior of the CFA samples to the results other studies (P6L35-P7L21). Besides, which new information would this other report contain?
- The mentioning of T_{start} instead of the actual temperature at which $f_{ice,max}$ values were derived is not intuitive (see P6L27-28, Sec. 3.2, …). Please include both T_{start} and the actual T in your discussion.
- As stated above, parts of Sec. 3.2 are hard to follow. In the cases of CFA_Mi, CFA_Ja, and CFA_Wh, the authors describe specific features observed in the experiments, but they do not show the corresponding 3-panel plots. Some results are not even included in Fig. 7. I suggest to include the described examples in an Appendix so that the reader can follow the discussion.
- I find the amount of arrows, overlapping shapes, and different colors in Fig. 8 very confusing. What is the difference between the blue, red, light gray and dark gray arrows? What is the difference between the black, light gray, and dark gray particles? A legend, or at least an explanation in the caption, would be helpful. Also, it looks like the sublimation of ice particles directly leads to cloud formation. The authors should revise and thin out this figure to make it more intuitively understandable.
- Why is the CFA_UK sample discussed separately from the U.S. American samples? Fig. 6 and 7 should be combined. I also suggest to change from a bar graph to a scatter plot for more clarity. A change to a logarithmic y-axis should be considered for both Fig. 6 and 7.

Technical corrections:

I generally feel that the authors need to be more precise with their formulations. Sentences and paragraphs are sometimes lengthy due to unnecessary fillers and repetitions. Transition words are partly misleading. There are grammatical errors. Below, I list the issues that caught my eye but I advise the authors to recheck their manuscript carefully to improve readability and understandability.

P1L26	At which RH was this strong increase observed?
P1L27	Change to either "undergoing PCF" or "undergoing **the** PCF mechanism".
P1L31-35	This sentence would benefit from being split into two.
P1L36-39	It is a bit unfortunate that you refer to PCF in general in the first sentence and specifically to PCF on CFA particles in the second. At least this is how I understood it. Please reword.
P1L36	I suggest to introduce "intrinsic" as relating to unprocessed or not pre-activated particles.
P1L37	Change to "on the other **hand**".
P1L41	Change to "highly relevant to **our understanding/knowledge/ comprehension… of** cloud formation".
P2L3	Omit "primary". Heterogeneous ice nucleation is always a primary process. Also, define the terms "homogeneous" and "heterogeneous" before using them.
P2L8	Change to "with **the surface of** a …".
P2L11	Omit "however" at the start of the new paragraph.
P2L12-13	Change to either "such **a** particle" or "such particles".
P2L19	Change to "before ice nucleation **takes place**".
P2L20	Change to "Here, we define…".

P2L21	There are references to Wagner et al. (2016a), Wagner et al. (2016b), and Wagner et al. (2016). Yet, there's only one Wagner et al. paper from 2016 in the reference list. Please correct.
P2L27	"zeolite" and "illite" should not be capitalized.
P2L34-36	This sentence does not say anything else than the one on P2L16-18. I suggest to remove it (also the following sentence).
P2L39	Change to "global **cloud** ice budget".
P2L41	A "significant amount" is not very precise. Are there really no estimates of the emitted CFA mass?
P3L4	There is no question that immersion freezing was investigated by Grawe et al. (2016, 2018) and Umo et al. (2015). Hence, differences in the freezing behavior of the investigated samples are not due to differences in the freezing mechanism. Please remove this part of the sentence. Furthermore, Grawe et al. (2018) showed that the immersion freezing behavior of CFA can be strongly dependent on the amount of time that the particles spend immersed in the droplet prior to the initiation of freezing. This issue is worth mentioning here because it can also affect the immersion mode AIDA measurements.
P3L6	"various atmospheric conditions". Be more precise.
P3L7	Change to "different CFA **samples**". Also on P3L14.
P3L15-17	"The results from these new laboratory measurements are presented in this report." This sentence is unnecessary and should be deleted.
P3L23-25	How representative is material from the EPs in comparison to material that is emitted into the atmosphere. Please include a statement concerning this matter.
P3L25	Omit "However".
P3L25-29	I am aware that the authors do not focus on the effect of chemical composition of the samples on their ice nucleation behavior. However, it would be interesting to include some more information, e.g., are the samples of class C (high Ca) or class F (low Ca), since it has been shown that the composition affects the ice nucleation measurements. This information is easily obtainable from Garimella (2016) and should be mentioned here.
P3L29	Please note that Losey et al. (2018) investigated the same sample set. This publication should be referenced here as well.
P3L30	Change "name" to "operators/owners". The name itself cannot prefer anonymity.
P3L31-33	Were the other samples not sieved? Why not?
P4L3	Please combine the instrument abbreviation and the manufacturer in one set of parentheses to avoid "(…) (…)". Check throughout the manuscript.
P4L20	Which types of cyclones were used? What is their cut-off diameter?
P4L26	Change "Min" to min".
P4L27	Change "mins" to "min".
P4L27	How does this coating affect the morphology of the particles? Could pores potentially be covered? Please include a short statement.
P4L36	"argon" and "nitrogen" should not be capitalized in running text.
P5L21	"inherent" and "intrinsic" seem to be used synonymously throughout the manuscript. I suggest to avoid the use of both terms and stick to one.
P5L31,33	Make sure that the empty squares are replaced by the Greek letters in the new version of the manuscript.
P5L35	Since you list all experiments in Table 2, you could also include the used size thresholds there.
P6L11	Change "t =~ 300 s" to "t ~ 300 s". Also in all other occurring instances.
P6L25	Insert "–" behind "CFA_Wh".
P6L26	Insert "mode" behind "immersion freezing".
P6L35-P7L21	I agree that a comparison to previous ice nucleation studies with CFA is interesting. However, by only reporting onset ice nucleation temperatures, the reader does not get an idea how the here investigated samples compare to

	those from previous studies. This could be resolved by including a figure showing $n_s(T)$.
P7L3-4	"Both studies can access warmer freezing temperatures for INPs than the dry generation method that our system is designed for.". Please explain shortly why this is the case.
P7L5	The Schnell et al. (1976) reference is not a good choice here. Actually, in this study "no detectable effects from a coal-fired powerplant plume" (see title) on atmospheric ice nucleation were found. Better cite Parungo et al. (1978), who conducted a similar experiment and found an enhanced ice nucleation efficiency of the plume aerosol in comparison to the background aerosol.
P7L10	Which of the two studies are you referring to?
P7L10	Actually, Grawe et al. (2018) state that the amount of hydratable components is important and that quartz only contributes in those samples which contain a small concentration of hydratable components. But this could also be included in the introduction (P3L4).
P7L13	Please cite Garimella (2016) instead of Welti et al. (2009). Garimella (2016) investigated 300 and 700 nm CFA particles, not mineral dust, and found that the immersion freezing efficiency does not scale with the surface area as the smaller particles were relatively more efficient than the larger ones.
P7L17	Please cite Grawe et al. (2018) instead of Hiranuma et al. (2018). Firstly, the manuscript by Hiranuma et al. (2018) is still under review. Secondly, the study by Grawe et al. (2018) is more relevant for the here presented work as they discuss the methodology-dependent freezing behavior of CFA particles, not cellulose.
P8L11-13	Does this mean that 1.2 % of the particles contained pores suitable for PCF? If yes, then please say so.
P8L14	Please check the Mahrt et al. (2018) reference. Mahrt et al. (2018) indeed describe PCF, but they did not conduct temperature cycling experiments. They saw a stepwise increase in the activated fraction of one type of soot particles due to condensation in pores and subsequent homogeneous freezing.
P8L23	Figure 6 is discussed before Fig. 5. Please arrange the order of the attached figures accordingly.
P8L38-39	Please check this sentence for correctness. It does not relate to the previous statement and it seems that something is missing.
P9L5-7	Change beginning of the sentence to "**This** suggests..".
P9L7-8	"Confirm" is a very strong word here, given that the data of this example is not even shown and given that no error estimation for the f_{ice} error is provided.
P9L9	Change to "droplet activation". Also on P9L17.
P9L16	Please omit "One thing is extremely clear that …".
P9L19-30	This paragraph would profit tremendously from the inclusion of a 3-panel-plot of the measurement that you are describing here.
P9L25	I do not understand the use of the word "although" here.
P9L28-29	"ice formation occurred in a shorter temperature step". I am not sure what you mean here. The temperature at which $f_{ice,max}$ was registered is of interest, not the temperature range. Please reword.
P9L32	Change "comparison" to "ranking".
P9L33	Change "f_{ice}" to "$f_{ice,max}$".
P9L33	"which summary". Change to form a grammatically correct sentence.
P10L21-23	Please reword this sentence.
P10L25	Is it realistic that cenospheres or plerospheres would be filled by capillary condensation under the conditions in your experiments? How large are the spheres and how large are the openings? According to Marcolli (2017), large pores need very high RH or very low temperatures to be filled.
P10L26	Fischer et al. (1976), who first discovered cenospheres and plerospheres, is the more appropriate reference here.

P9L27-30	I suggest to change the formulation in such a way that it becomes clear that an estimation of the pore size and geometry is **not possible** for CFA. This is due to the heterogeneity of the particles. Other INP types might be better suited for such an estimation. Avoid using the word “pointless”.
P10L37	“Rainout” is probably not the right term for cases where only the ice phase is involved.
P10L37-38	I cannot find this statement in the given reference. Please check and remove if necessary.
P11L3-4	This is shown in a very confusing way in Fig. 8. Please adjust.
P11L12-13	“Currently, this is not well understood and requires further research.” This sentence can be omitted. The following sentence is completely sufficient.
P11L14	Change “clouds formation” to “cloud formation”.
P11L15	Change “studying the dominance of this occurrence” to simply “the occurrence”.
P11L16	Change “cloud system” to “cloud system**s**”.
P11L21	“However” does not seem like an appropriate transition word. The statement is not in contrast to the previous one. Please reword.
P11L22-23	I am aware that there are lots of different pore types (“pores”, “crevices”, “cavities”), but it might be best to define one term in the beginning and stick to it throughout the manuscript.
P11L25	Change “ice formation” to “ice nucleation potential”.
P11L33	What is meant by “their”? The particles? The pores? Please clarify.
P11L35-36	It should be mentioned here that CFA is not a suitable substance for the investigation of the effect of different pore geometries on PCF.
P11L40	Omit “in this theme”.
P12L3	Change to “On which time scale does a potential INP need to…”
Fig. 1	Please change “stuff” in the figure caption to a more scientific word.
Fig. 3	Please include the actual Greek letters in the caption, not the written-out names.
Fig. 5	Please explain the meaning of the blue dashed line in the caption.
Fig. 6	Change to “dark cyan bar” in the caption. There is only one.

<u>References (which are not already included in the manuscript):</u>

Fisher, G. L., D. P. Y. Chang, and M. Brummer (1976). “Fly ash collected from electrostatic precipitators: microcrystalline structures and the mystery of the spheres”. *Science* 192.4239, pp. 553–555.

Losey, D., S. K. Sihvonen, D. Veghte, E. Chong, and M. A. Freedman (2018). “Acidic Processing of Fly Ash: Chemical Characterization, Morphology, and Immersion Freezing”. *Environmental Science: Processes & Impacts* 20, pp. 1581–1592.

Parungo, F. P., E. Ackerman, H. Proulx, and R. F. Pueschel (1978). “Nucleation properties of fly ash in a coal-fired power-plant plume”. *Atmospheric Environment* 12, pp. 929–935.

Seames, W. S. (2003). “An initial study of the fine fragmentation fly ash particle mode generated during pulverized coal combustion”. *Fuel Processing Technology* 81.2, pp. 109–125.