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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Coal fly ash: Linking immersion freezing behavior and physico-chemical particle properties" *by* Sarah Grawe et al.

Anonymous Referee #1

Received and published: 25 July 2018

The study reported by Sarah Grawe and her co-authors on linking the immersion freezing behaviour of CFA particles to the physicochemical properties of coal fly ash (CFA) is an interesting and timely investigation. For a long time, the study of CFA as ice-nucleating particles (INPs) has been overlooked and this is one of the recent efforts to understand the intrinsic behaviour of this group of aerosol particles as INPs. This report has given an insight into the chemistry of CFA when immersed in water, which typifies the atmospheric process that these particles undergo in different cloud conditions. Although only a few samples are investigated here, the study has highlighted the deactivation of the ice-nucleating potential of CFA particles due to alterations in the chemical properties of the ash indicated by the two generation systems that they

employed in this study – dry and wet generation methods. The deactivation in the IN abilities of these particles observed for all the wet-generated CFA particles points to the possible chemical and physical changes that could occur in this scenario. Again, it is very striking to see that the IN ability of CFA can be compared to some mineral dust/mineral particles. This leaves an open question - what if the ice residue measurements attributed to mineral dust could also be contributed by CFA because of some similarities in their mineralogy? At the moment, I could not agree less with Grawe et al. that it is difficult to ascertain the atmospheric abundance as well as the transport of these particles in the atmosphere and hence, estimating its impact on clouds based on these new results will be a daunting task. On a general note, the manuscript is relatively well-composed, logically presented, and well-referenced – aside from the few major and minor comments that I have suggested below to enhance the quality of this work, I have no reservations in recommending this study for publication in ACP.

Minor Revisions

1. The differences between the efficiencies of CFA_dry and CFA_wet are really huge, some up to 6 orders of magnitude (Fig. 4) e.g. CFA4, do you think that only wet chemistry of the CFA can explain this difference? At least for CFA4, there are no needle-shaped particles observed. Are there other works that you can refer to that might give useful information to substantiate your hypothesis? Other workers in the ice nucleation community have seen these differences (though not this much). Please, can you explain more on these observations?

2. The authors should be consistent with the use of 'needle-shaped crystals or particles' rather than just needles unless clearly predefined. The ESEM images referred to in Figure S5 is of poor quality and that makes it highly difficult to appreciate the differences. The so-called 'needle-shaped' crystals are not well-shown in a convincing way. Please, do you have high quality or better ESEM images with high resolution that you can present to really buttress the findings that the report is making most references to? Please, could you clearly state how the particles from the wet aggregation method

were collected and treated before the ESEM imaging? One would expect a bit of aggregation of the particles if they were allowed to dry out from the droplets – otherwise, isolated particles will be seen. Figure S12 - further calls for a better interpretation of the morphology of the particles, Already, the scale shown is rather large for this type of study. Although there are crystalline pins present on the slide, there are also light-coloured regions, which may be CFA particles too. Please, could you throw more light on this?

3. For a better/easier readability, I would kindly recommend that Fig. 3 be modified following these suggestions: (1) show error bars in ns rather than temperature for CFA1-4 samples such that they can be easily compared with Garimella's work. Again, for the CFA3 panel, some selected data points can show the error bars to avoid obscuring its readability. (2) the legend should be kept together for an easy reference. (3) if possible, increase the data points size for Garimella's CFA and try to put a fit through the data points for an easy comparison.

4. The current title is a bit ambiguous for the results presented in this present study. The authors might consider focusing the title more on the 'reduction in the efficiency of CFA ice nucleation in the immersion freezing mode due to modifications/changes in the chemical properties'. OR another main idea that this work presents as a strong salient point is 'the difference between dry- and wet-generated CFA particles on their ice nucleation behaviour'. From this present investigation, it is not quite clear how the physical properties such as size, morphology and others change the ice nucleation behaviour rather attention should be focused on the unravelled chemical compositions and transformations. The authors might want to consider revising the title to carry the main idea of the article.

5. Figures (S6 – S9) - Please give more explanation in the plot's description, label the ordinates and abscissas correctly, and indicate the meaning of the legend codes (I.e. numbers in braces). Please, could you show the various classifications of CFA probably in a table format for readers to follow the discussion with ease? Indicate the equations

of the fit for Figure S11. Please remove the error numbers ($\pm$xxx) - they are irrelevant to the apparent BET surface areas as shown in Table S3. The errors are not realistic to the material rather to the fit/model performance hence, they are not needed (you may want to discuss with experts in this field). The adsorption model used in obtaining the specific surface area can vary considerably even with the same material. It really depends on how good the fit is and the number of points on the Isotherm considered.

Minor technical suggestions

Page 1, L4: This line should read '...physico-chemical properties of particles can influence...'.

Page 2, L1&2: Please replace "ice nucleating" with "ice-nucleating". This correction should be applied to such instances in the entire manuscript.

Page 2, L5: Please change 'there is ongoing discussion...' to 'there is an ongoing discussion...'.

Page 2, L6: Add Chen et al., 2018 to the reference.

Page 2, L9&10: Please restructure the sentence such that 'ice nucleation active' would be changed to something like 'act as ice nuclei'.

Page 2, L12: Please use past tense when describing past works in contexts like this one. e.g. Hoose and Möhler (2012) summarized...'. This has reoccurred in several places in the manuscript (next case is Page 2, L25 and so on). Please change "soot is a generally worse ice nucleus..." to "soot is generally a worse ice nucleus...".

Page 2, L17: Please give a better definition of bottom ash to distinguish the two forms of the ashes – one can also have bottom ash from the coal power plants, burning of agricultural fields, etc.

Page 2, L22: Please change '...gases from Coal Fly Ash.' to '...gases of Coal Fly Ash.'

Page 3, L1: I would omit the adjective ‘perfectly’.

Page 3, L7: There are other works on ice nucleation of CFA captured by Umo et al., 2015 and Grawe et al. 2016 that preceded Havlicek’s work. Please briefly mention them here or you can use an annotation like ‘references therein’ in an appropriate place.

Page 3, L13: Put a space before any unit e.g. -15 oC. Please correct this throughout the manuscript.

Page 3, L14-18: Please recast these statements – there are a bit confusing to me.

Page 3, L20: misspelt word “properties’.

Page 3, L26: This statement can read better as “Garimella (2016) investigated the freezing behaviour of four different CFA samples from the USA using the SPectrometer for Ice Nuclei (SPIN; Droplet Measurement Technologies, Inc.)”.

Page 3, L28-29: Please could you indicate the relative humidity that 1% ice-activity was reported and same for Havlicek’s study?

Page 3, L30: Please edit this line to read “. . .measurements of CFA by. . ..”.

Page 4, L1: Please restructure this line.

Page 4, L6: Please omit ‘previously investigated’ from this line.

Page 4, L12: These are very broad scientific questions. This part should be presented as hypotheses rather than as elaborate questions, which this project alone may not give all the answers.

Page 4, L14: Please specify the sort of deactivation referred to here. e.g. ‘deactivation in the ice nucleation properties’

Page 4, L25: Please change ‘consisted’ to ‘consists’ and ‘size selected’ to ‘size-selected’.

Page 4, L26: Please change ‘multi Micro’ to ‘multi-micro’.

Page 5, L2-4: Can these pieces of information be obtained from the company? If not, ignore and recast the sentence in such a way to reflect the fact that your team was unable to get the information rather than connoting that it is not known.

Page 5, L8: ‘Lime’ – since this is a very generic term. Please distinguish between quicklime and slaked lime. . .I think ‘CaO’ is mostly referred to as quicklime. Stick to the right one all through the manuscript.

Page 5: I am not sure if footnotes are allowed in ACP – if not, integrate this information into section 2.1. Please check with the Editors.

Page 6, L11: Please change ‘multiply charged’ to ‘multiply-charged’. Make this change in subsequent ones.

Page 6, L23: Please edit ‘0.5 wt% of CFA’. Did you mean that 0.5 g of CFA was dissolved in 100g of distilled water? Please check. Same for L33-Page 7, L1.

Page 7, L12: Please define ‘fice’ before use.

Page 7, L18: Please insert a comma after this statement ‘The ice nucleation active surface site density’

Page 8, L20: Please correct to “. . .produced by a microfluidic device and subsequently arranged into. . .”

Page 8, L20: Please change ‘pl’ to ‘pL’.

Page 8, L31: Please change “. . .the uncertainties of Vdrop, . . .” to “. . .the uncertainties in the measurement of Vdrop,. . .”

Page 9, L4: Please change “. . .in the following, . . .” to “. . .in the following sections, . . .”. Also, change ‘analysis’ to ‘analyses’. Apply this to similar cases. E.g. Page 11, L17, etc.

Page 9, L5: Please recast the sentence to improve its readability. E.g. . . .in the discussion of . . . OR . . .in discussing. . .

Page 9, L12-14: Please recast these statements.

Page 9, L24: Please correct 'CFA1 contains most Ca and S' to 'CFA1 has the highest concentration of Ca and S'. Please check the use of "most" and "least" in the entire manuscript. Sometimes I think you intended to use "highest" for "most" or "lowest" for "least".

Page 9, L28: Please correct "A more detailed' to 'A more-detailed'.

Page 10, L4: Include the company and country of the instrument in a parenthesis.

Page 10, L8-10: The information here is clear but check the use of tenses, verb agreements and possibly improve on the logical presentation of the observations here. E.g. The first sentence on L8 would read better as: 'CFA1 was the only sample that a clear difference was observed between the dry and wet particle generation methods'. However, check if this statement should come first.

Page 10, L31: Please include state symbols in this equation and all others in the manuscript where possible. E.g. CaO(s). . .This will help readers to understand the chemistry better.

Page 11, L9: This line should read 'the occurrence of needle-shaped particles in wet-generated CFA1 could. . .'.

Page 11, L18: Please recast this sentence. Maybe, refer to the other samples as 'samples from the USA.

Page 12, L1: I am not sure what you referred to as "inhomogeneous ice nucleation properties". Please clarify.

Page 12, L8: Please include the temperature range e.g. at T< -xxx oC.

Page 13, Fig. 2: Please improve the colour-coding of the line type to distinguish them easily. A dashed line might be better.

Page 13, L12: Please change 'We compare the CFA results to cold stage measurements by compare' to 'We compared the CFA results to cold-stage measurements of Quartz by. . .'.

Page 14, L1-2: Please provide a reference to the statement about the ns values of dry-generated quartz particles.

Page 15, L16 – 19: Please rephrase these sentences for clarity. Were you referring to the 'particles soluble in the pure water'?

Page 16, L23: Please, are there previous references that you can point us to?

Page 16, L24: I would be a bit cautious in making the assertion that there is a good agreement for results from WISDOM at -35 oC because homogeneous freezing of pure water kicks just before this temperature as reported by Reicher et al., 2018 (Fig 5).

Page 16, L33: Please check this range '-15oC<T<-20oC'. . .did you want to write '-15 oC > T > -20 oC'? Please change 'levels off for. . .' to 'levels off from. . .'.

Page 17, L1-3: Check the statement - it seems there is no point stating this here if we cannot point to the data somewhere.

Page 18, L15: Please explain further what you mean by a layer (of what?). Please change 'In case of dry particle generation' to 'In the case of dry particle generation method'.

Page 20, L33: Delete the extra 'the'.

Page 21, L15: Please change 'l-1'to 'L-1' and in all other instances.

Page 22, L5,6,15,28: I would suggest the summary and conclusions section be revised to carry the main findings of the article without the questions. Some of the questions

are not well-answered by this single study as even argued by the authors (see Page 22, L9-14).

Page 23, L3: Please change '. . .decrease quickly in contact with water' to '. . .decrease quickly when in contact with water'.

Page 25, L8: Write out the 'US' in full.

S_Page 25, L20: Steenari et al., is listed in the references but not cited anywhere in the text. . .please check.

Associated References to this Review Report

Chen, J., Wu, Z., Augustin-Bauditz, S., Grawe, S., Hartmann, M., Pei, X., Liu, Z., Ji, D., and Wex, H.: Ice-nucleating particle concentrations unaffected by urban air pollution in Beijing, China, Atmos. Chem. Phys., 18, 3523-3539, https://doi.org/10.5194/acp-18-3523-2018, 2018.

Reicher, N., Segev, L., and Rudich, Y.: The WeIzmann Supercooled Droplets Observation on a Microarray (WISDOM) and application for ambient dust, Atmos. Meas. Tech., 11, 233-248, https://doi.org/10.5194/amt-11-233-2018, 2018.

Grawe, S., Augustin-Bauditz, S., Hartmann, S., Hellner, L., Pettersson, J. B. C., Prager, A., Stratmann, F., and Wex, H.: The immersion freezing behavior of ash particles from wood and brown coal burning, Atmospheric Chemistry and Physics, 16, pp. 13 911–13 928, 2016.

Umo, N. S., Murray, B. J., Baeza-Romero, M. T., Jones, J. M., Lea-Langton, A. R., Malkin, T. L., O'Sullivan, D., Neve, L., Plane, J. M. C., and Williams, A.: Ice nucleation by combustion ash particles at conditions relevant to mixed-phase clouds, Atmospheric Chemistry and Physics, 15, pp. 5195–5210, 2015.

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