Review of “The immersion freezing behavior of ash particles from wood and brown coal burning” by Grawe et al.

The authors present the immersion freezing ability and efficiency of combustion ash particles from the laminar flow tube study. The authors provide the immersion freezing dataset in two metrics, f_{ice} and n_s, in the temperature (T) range of -38 °C < T < -24 °C. More specifically, this study suggests the followings: (1) the brown coal burning ash particles, which is the proxy of anthropogenic combustion ashes, are more ice nucleation (IN) active/efficient as compared to the wood burning products (the natural proxy), (2) the fly ash particles are more IN active/efficient as compared to the bottom ash particles, (3) two aerosolization processes, namely dry and wet dispersion, result in different $f_{ice}(T)$ and $n_s(T)$ spectra, (4) the ultrasonic bath application prior to particle generation increases the IN activity/efficiency of a ash sample, presumably due to the presence of fewer agglomerates in the sonicated sample than the non-treated one.

General comments

The topic itself is an important addition to ACP, and the authors’ new IN results potentially complement the results from previous study (*Umo et al*., 2015, ACP), in which the droplet-freezing assay was used to investigate in the immersion freezing ability and efficiency of combustion ashes in the T range of -11 to -36 °C. In general, the authors conducted a careful study, with their dedicated effort to examine a variety of sample preparation methods, e.g. atomization vs. dry dispersion, ultrasonic bath application. Unfortunately, such care was not taken in the preparation of the manuscript, with the manuscript containing a number of ambiguous statements, non-intuitive figures and over-interpreted results (e.g., Sect. 4, P5 L19-30). I have numerous critical revisions as listed below. Major revisions/suggestions are listed first, followed by the section-based specific and technical revisions. I would urge the authors of the manuscript to thoroughly proof read their manuscript as this list is too long.

While authors may be able to address these issues, I do believe that the revision of the manuscript could be time consuming and result in a significantly different paper. For these reasons, I encourage the authors to resubmit it with a completely different format.

Specific comments

I suggest the following major revisions.

***Discuss the representativeness of 300 nm diameter ash particles* -** Justification of selecting 300 nm diameter (P3 L26-28) is missing. The authors state that the ash samples are a composite material (e.g., P15 L22), but do not discuss why 300 nm diameter is representative for their IN analyses. Different size of particles may possess different composition and/or IN behavior (e.g., Wheeler et al., 2014, J. Phys. Chem. A). I strongly suggest the authors to conduct additional IN measurements and surface characterization with different sizes. Having another set of measurements for e.g. 600 nm (or even with polydispersity aerosol population) would add clarity.

***Provide the results (no hype) to support your data interpretations and conclusions* -** One of the major findings out of this study is that the immersion behavior of brown coal ash particles changes depending on the sample preparation methods. The authors need to **investigate and discuss** in-depth physical reasons of why the observed difference appears. It seems not meaningful to attribute the reason to just the ‘sample preparation and particle generation’ (P11 L14-16), speculate potential reasons (e.g., P12 L1-3; P13 L10-14) and put it off as future work (e.g., P14 L28-32; P15 L20-25). To date, there have been some recent publications attempting to identify potential reasons of the data diversity due to different experimental methods and sample preparation methods (e.g., Hiranuma et al., 2015, ACP, Emersic et al., 2015, ACP). I suggest the authors to elaborate what can be further clarified on top of given previous findings. Reporting only the IN observations seems not novel enough to complement the previous ash IN study (i.e., Umo et al., 2015).

***Consider removing Sect. 4* -** The atmospheric implications (P14 L8-17) sound too speculative and ambitious. The abundance data (concentration and size distribution) with some spatio-temporal distributions seem necessary to estimate the ambient ash-derived INPs. The back of envelop calculation presented here seems not novel enough for you to support your sub-conclusion, which appears in P14 L13-14 ("In conclusion,…") and P1 L13-14 ("ash from brown…a regional scale"). If the authors wish to keep the atmospheric implication section, the difference between airborne (fly) ash and surface (bottom) ash with respect to their mixing state, degree of agglomeration and atmospheric lifetime should be somehow discussed. Also, discuss the contribution of natural ashes to ambient INPs vs. that of anthropogenic ones. Otherwise, the authors may consider removing the entire section.

***Tighten up the writing by removing unnecessary words* -** Improving the language, structure, presentation seems necessary. The authors should avoid making a review question how careful the research team is.

For example, I suggest minimizing ambiguous (and unnecessary) adverbs and adjectives to make the manuscript more scientifically sound than the current form. Such words should be replaced with specific and explanatory descriptions/values. Otherwise, the authors should reinforce them by adding proper citations. My suggestions include, but not limited to:

P1 L6: more (specify how much in what *T* range?)
P1 L14: at least
P2 L12: major
P2 L15: rough
P2 L20: for a long time & large
P2 L22: strongly
P2 L24: very similar
P2 L32: lower (than what?)
P3 L4: slight
P3 L23: some
P3 L24: mostly (define which samples)
P3 L30: larger & more (than what?)
P4 L30: exactly
P5 L12: most (amongst what?)
P5 L13: slightly
P5 L14: significantly
P5 L17: most striking
P5 L19: small
P5 L23: perfectly (I do not think so) & most
P5 L24: significantly less (is it fair to say this by inspecting a single snapshot picture?)
P5 L27: similar
P5 L30: small
P5 L31: small
P6 L1: supposedly & obviously
P6 L5: possibly & weakly
P8 L10: almost entirely
Fig. 4 caption: at least
P10 L2: significant & low
P10 L4: most effective & least & rather similar
P10 L6: small & more (than what?)
P10 L7: more (than what?)
P11 L2: certain (specify)
P11 L15: considerably
P11 L16: by several tens of percent (just give a number)
P11 L20: probably exclusively & completely
P12 L1-2: most likely
P12 L24: numerous
P12 L25: large
P12 L26: higher (as compared to what?)
P12 L29: larger (how much?)
P13 L12: likely
P14 L15: significantly low
P14 L24: significantly (how much?)
P15 L3: barely
P15 L4: significant
P15 L6: likely
P15 L 11: eventually
P15 L20: most likely

***Improve the figure and table presentations* -** In general, all figures and tables should be self-explanatory. My suggestions include the followings:

Fig. 1: It seems that more than 50% of mass are composed of materials that are not listed in the figure. The authors need to clarify this point to the reader by adding descriptive text or adding another group of

bars showing the sum of the other components in the figure. The authors implies such contribution may in part come from ‘amorphous’ material (P11 L1). I suggest the authors to give an idea of what they are (perhaps carbonaceous materials?). I also suggest the authors to give a proper reason of why beech ash composition is not shown (P5 L9). Perhaps, presenting data (± uncertainty) with the table format may be more intuitive to the reader than using the figure format. In addition, the figure caption should read “bottom ashes from spruce, birch…”.

Fig. 2: I see at least six particles that have >1 μm diameter in the panel b. As stated in P5 L24-26, the doubly charged particles of 300 nm cannot be >1 μm. The authors state that “…the number of particles with three or more negative charges was negligible…” (P3 L32-P4 L2), but it seems not negligible and contradicting. In terms of the number, those large particles may have only a small contribution. However, they may substantially contribute to the total surface. If that is the case, they should be accounted for the immersion freezing parameterization. Otherwise, your ice nucleation active surface site density would be overestimated because of overlooking the presence of large particles. Adequate surface estimation is one of the important keys for the n_s parameterization. Ultimately, the authors may want to assess if such correction can explain the discrepancy between dry and wet (or not).

Just to start with, you may first estimate the particle size distributions by analyzing SEM images (i.e., estimate the area equivalent diameter for several hundreds of particles; see Hoffmann et al., 2013, AMT). This approach may be better than relying only on the USHAS measurements. In addition, such work will help clarify the vague statement in P5 L24-30.

Fig. 4: The authors need to explain the factor of 4.54 in text at the first appearance of Fig. 4. I also suggest clarifying what the ‘clay mineral baseline’ means. Better presentation may be made with multiple panels. For example, the authors may use individual panels for ash type comparison, dry vs. wet, +US vs. –US. The same may apply to Fig. 5.

Fig. 5: Specify if your n_s metric is based on the BET specific surface area or the geometric surface. Though I agree with your statement in P13 L8-10 (i.e., the influence/difference is small anyway), it is important to compare the results with a same metric. If this figure contains both BET-based n_s and geometric n_s spectra, I suggest presenting all data and spectra using either one of two metrics. The authors may simply apply a factor of 4 (P13 L9) for the conversion.

Add proper references – I suggest the authors to give a careful look at the followings:
P1 18: Add citation after “…and climate models”.
P1 L21: Replace Murray et al., 2012 with Koop et al., 2000 (Nature); Murray et al., 2010 (Phys. Chem. Chem. Phys.); Rosenfeld and Woodley, 2000 (Nature).
P2 L5: Add citations after “…been conducted”.
P3 L1-2: Whale et al. (2015, AMT) may be a good reference to add here.
P3 L20: Add reference for your dry dispersion method.
P4 L8: Add reference for “water contamination”. The authors may also want to reduce the tone and call it as a background contribution or something similar.
P7-8: Provide the reference for R1 & R2.
P10 L17: Any reference for insoluble K to be highly ice active? You should not speculate for all insoluble materials to be IN active.
P12 L1-3: multiple citations seem missing.
P12 L8: Look into references given in Zolles et al. (2015). There have been a few other studies of active sites and their influence on IN activities.
P12 L16: e.g., Connolly et al., 2009 (ACP), Niemand et al., 2012 (JAS)

Other specific and technical suggestions sorted out for each section are listed below.

Abstract
P1 L2: …trigger ice nucleation when they interact with water vapor and/or supercooled droplets.
P1 L4: …worldwide, and…
P1 L6-7: I suggest separating this sentence into two sentences.
P1 L6: ice active in the immersion mode
P1 L8: …the effect of various particle generation methods on…
P1 L8: For this → For instance
P1 L14: heterogeneous ice nucleation → immersion freezing in the *T* range of XX to YY °C

Sect. 1
P1 L21-23: The authors may focus on immersion freezing by rephrasing L21-23 to, "At water saturation, this temperature limit of droplet freezing … referred to as immersion freezing.". Otherwise, describe heterogeneous IN and then immersion freezing. Note that the deposition nucleation can occur at temperatures below -38 °C.
P2 L4: However, up to now only a very few → To date, only a few
P2 L5: → material, which
P2 L12: contribute to
P2 L12: → Furthermore, the ash from natural source is…
P2 L13-14: Awkward sentence. Rephrase.
P2 L18: I wonder where the authors find the 7% number in DeMott et al. (2003).
P2 L19-20: I suggest clarifying that the result presented in DeMott et al. (2003) is from a limited time segment of measurements in cirrus clouds.
P2 L23-26: I do not understand what this sentence mean. Please clarify.
P2 L27-29: I suggest separating this part into two sentences.
P2 L33: What are water soluble components? Sugars? Any biological materials? How important are they for IN as compared to the insoluble components?
P2 L35-P3 L2: Provide more information regarding Umo et al. (2015). At least the investigated *T* ranges for individual ash materials and their IN efficiency/activity with some quantities.
P3 L2: Reword "however". I do not find smooth transition.
P3 L5: Reword "assumed". e.g., suggested/postulated
P3 L11-12: Move this part to the method section.

Sect. 2.1.1
P3 L21: as → along with
P3 L21-23: Subdivide the sentence ("Variations caused … transported downwards.") into two.
P3 L23-24: Clarify if glass beads have any influence on modification of particle surface (e.g., by scratching) and IN behavior.
P3 L24-26: I suggest rephrasing the complete sentence ("In addition … dryer unit."). Just say you used a custom-built atomizer. Is it perhaps the one used in Wex et al., 2015, ACP? If so, add it as a reference.
P3 L31: efficient → active due to the presence of large surface

Sect. 2.1.2
P4 L4-5: Awkward sentence. Rephrase. The LACIS reference is repetitive.
P4 L6: "LACIS offers … nucleation processes."; please provide the reference showing the 'surface' (of the droplet assay plate - I assume this is what you mean) interferes with IN measurements. If not, I suggest rephrasing the sentence.
P4 L14-15: I suggest briefly clarifying how the phase discrimination can be done in text.

Sect. 2.2

P4 L18-23: I suggest to summarize your ash samples using a table along with columns of ash type (bottom or fly), source (natural or anthropogenic), particle generation method (dry or wet), and information regarding your IN experiments (e.g., examined T range and IN observed T range).
P4 L25-26: “It has to be noted that…”; not much adding. I suggest removing this sentence.
P4 L27: If it is commercially available, specify it.
P4 L27: Explain how you “extracted” it. Provide some information regarding the electrostatic precipitator (or reference). What is the cutsize? What is the collection efficiency? etc.
P4 L28: → station, which
P5 L4: affected → modified
P5 L5: “one fly ash suspension sample”; specify which one and why the authors choose this one in text.
P5 L9: Provide brief description of atomic adsorption methods along with proper reference(s). The rest of the paragraph (up to L18) may better fit in the results section. Consider reorganizing the sections.
P5 L11: obtained → estimated
P5 L19-30: I suggest the authors to minimize over-interpretation from snap shot pictures. The authors may consider providing the reader with the proxy of particles’ sphericity. For example, a particle aspect ratio of individual particles can be estimated by the 2D SEM images. Inspecting several hundreds of particles and providing statistically valid data in the result section will strengthen the paper.
P5 L23: Irregular shape may suggest the predominance of carbonaceous compounds (e.g., Hiranuma et al., 2008, Atmos. Environ.). Do the authors have any information regarding its organic fraction and content?
P5 L23-24: “…most show significantly less surface defects…”; it is hard to judge the presence of defects by looking at given SEM pictures with low magnification. Can the authors provide the image with high magnification as an example? Better option would be measuring BET surface of both bulk samples and comparing each other.
P5 L25-26: I wonder why UHSAS was not able to measure them.
P5 L27-28: “…similar particle losses should have occurred.”; I suggest removing any opinion statements. The authors may provide the results instead if available.
P5 L33-35: “It is reasonable to assume … additional fly ash particles.”; I do not understand your logic here. Please clarify.
P6 L3: → all components are dissolved in droplets
P6 L5 to the end of this section: this part seems not belonging to the method section. Should be moved to the discussion section?
P8 L9-10: Awkward sentences. I suggest rewording.

Sect. 3

P8 L13-16: Subdivide this sentence to two parts.
P8 L17-19: Why don’t you look at only quasi-spherical ash particles on the SEM images? Analyzing the SEM images, you should be able to distinguish ash particles from the recrystallized components, which seem possessing high aspect ratios. This procedure perhaps enables you to estimate the contributions of multiple charge components. The same applies to your statement in P11 L12-13. The correction seems feasible and important.
P8 L21: → in Fig. 4. These calculations are based on…

Sect. 3.1

P10 L3: Specify the T range for the reader.
P10 L4-6: Discuss why all the wood burned ash particles have similar IN behavior. There seems difference in SiO_2 content for spruce (~10%) and birch (<5%). Based on your statement in P5 L12-13 (i.e., the higher SiO_2, the more IN efficient), could the SiO_2 content be responsible for the observed result of $n_{s\_spruce} > n_{s\_birch}$ in Fig. 5? If this holds true, the bulk beech ash should contain the highest SiO_2. Would you consider carrying out the atomic adsorption measurement of beech ash (currently missing without any intuitive explanation) to support your idea?

P10 L9 - P11 L3: The authors suggest that the fraction of SiO_2, Hg and insoluble K has some contributions to determine the immersion freezing behavior of ashes based on their bulk observation of atomic adsorption technique (P10 L9-22). In the following sentences, the authors introduce the hypothesis, which infers that the amorphous material content is also important as a determining factor of IN behavior. Discuss which one is more dominant. Further, what is the mixing state of your ash samples? What is the relative importance of the mixing state as compared to the “bulk” composition?
P10 L10-12: Rephrase. Not easy to follow.
P10 L14: → act as INP. This previous observation may be relevant to our study as…
P10 L14: Is the atomic adsorption technique used in this study sensitive to iodine? If so, please show I in Fig. 1 too.
P10 L16: Why soluble? Presumed? Or measured? Please clarify.
P10 L18-22: “Apart from the chemical composition, other properties such as ice active sites…”; Discuss the relative importance of what you found to the other potential factors. I suggest rephrasing and clarifying the last sentence. I do not understand what the authors mean here.

Sect. 3.2
P11 L12-13: I disagree. The correction is possible and feasible, and the authors should account for it. See my comment in Sect. 3.
P11 L13-14: This sentence seems not needed here. I suggest removing.
P11 L14-16: The authors need to **investigate and discuss** physical reasons of why the influence of the US application on IN behavior is **material dependent** rather than just saying ‘sample preparation’ methods resulted in the difference. The same goes to P13 L3-4.
P11 L18: meaning → suggesting
P11 L17-30: Multiple topics seem to be squashed within this short section. Reorganize and rephrase the sentences. Again, the scaling factor of 4.54 should be introduced prior to its first appearance in Fig. 4.

P12 L1-3: Sounds too speculative. Any experimental evidence of a destruction of former active sites? I do not understand the last sentence. How do water soluble components play a role in what?
P12 L8-13: What is the atmospheric implication of your findings here?
P12 L23-24: Repetitive. Delete.
P12 L24-30: Rephrase. This part may better fit in the introduction section as part of an example of previous work regarding ash IN characterization.

Sect. 3.3
P12 L15: ice nucleation active surface site density
P13 L5: nucleation spectrum → n_s spectrum
P13 L10-14: Sounds too speculative. I suggest removing the opinion statements (that is, must be, expect, likely) and rephrasing the sentences.

Sect. 4
P14 L2-4: The authors may consider removing this paragraph, which seems not adding much.
P14 L5-8: These sentences better fit in the introduction section (e.g., P2 L15) rather than here.

Sect. 5
P14 L21: at the
P14 L23: differences (in what?)
P14 L28: “a decisive factor…”; I disagree. The authors need to provide much more comprehensive composition data (e.g., beech ash data, bulk vs. single particle, mixing state, organic speciation) than what are presented in this manuscript to have this statement as your conclusion.
P14 L28-32 & P15 L20-21: I agree with the authors that multiple particle properties inherently influence particle’s immersion freezing behavior, and it is not easy to understand what the controlling(s) factor

is(are). With some extra experiments suggested above, the authors may be able to shed light on the questions raised here.
P15 L9: nucleation spectrum → f_{ice} and n_s spectra; the same applies to elsewhere, e.g., P15 L17
P15 L12-13: What is its atmospheric implication?