We thank the referee for the useful comments, all of which we considered carefully. In the following, we respond to them separately, where the original comments are colored, while the answers are given in black.

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

In this study the authors examine the immersion mode freezing efficiency of combustion ashes from different woods and brown coal burning using LACIS. Ashes from brown coal burning are found to exhibit higher nucleating abilities than those from the ashes generated from wood burning. The results presented here also seem to indicate that sample preparation can have impacts on ice nucleation efficiencies; an important point which will need to be considered in future studies.

My major comments below surround increasing the specificity and clarity of statements made. In particular, there are some vague statements made in attempting to account for observations in this work, and how it compares to others such as Umo (2015). Sentence and paragraph structure can also at times make it difficult to make out what is being said without multiple rereads of certain passages. While I recognize that investigating the nature of nucleating sites in a mixture as complex as ash is challenging, I suggest the authors could discuss the difficulties surrounding this endeavor and limit sweeping statements.

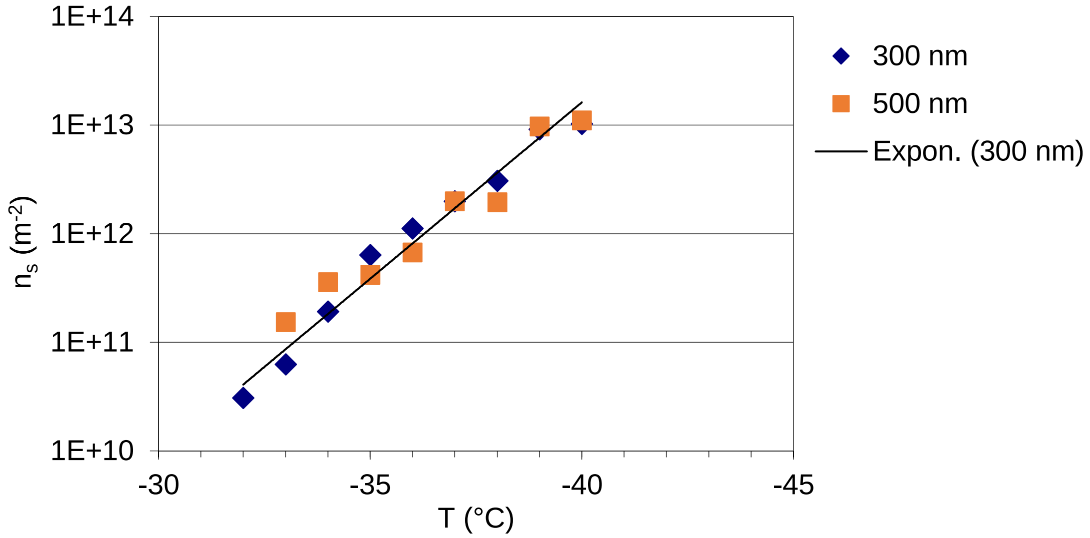
I am of the opinion that, following careful consideration of the points below and improvement of the manuscript in the areas listed, this could be accepted in ACP.

Main comments:

- The authors need to evaluate the use of 300 nm particles in this paper. It can be anticipated that physical and chemical composition varies with particle size, and in turn, perhaps the ice nucleating efficiencies. Without further experiments on larger particles it is difficult to see how the results of this study can be generalized to larger particles. I suggest that at the points in the manuscript where the authors are referring to size selected particles, they explicitly state this for clarity (e.g. section 3.1 L1-8).

  From size distribution measurements during coal combustion, we know that there is a bimodal distribution: one submicron peak below 0.1 µm and one broad supermicron peak in the range from 3 to 50 µm (Damle et al., 1981, Aerosol Science and Technology 1:1). As particle collection techniques are less efficient for submicron particles (Flagan and Seinfeld, 1988, Fundamentals of Air Pollution Engineering), we decided to select particles smaller than 1 µm. 300 nm particles were chosen because we could get sufficiently high and stable number concentrations from the variety of samples when selecting this size (the mode diameters vary from 130 to 200 nm for dry particle generation). While there are a lot of different particle types included in bulk fly ash (i.e., Ramsden and Shibaoka, 1982, Atmos. Environ. 16, 9), it has also been found from single particle analysis that the chemical composition of fly ash particles with aerodynamic diameters between 0.2 µm and 4.8 µm is remarkably consistent (Kaufherr and Lichtman, 1984, Environ. Sci. Technol., 18). Hence, we would not assume to see a difference in n_s, would we select another particle size.
  In case of bottom ash, exemplarily, measurements were performed with 500 nm brown coal bottom ash particles which showed no difference in n_s within the range of our measurement uncertainty compared to the measurements with 300 nm particles (see below, now also added in Fig. 4 as green triangles). As LACIS measurements are very time consuming and we do not expect

to see a difference in n_s in the size range we are able to select, we would like to avoid performing further experiments with other particle sizes.
In the manuscript, a paragraph explaining why 300 nm were chosen was added (P4 L17-28).



- P2L12: "As a result, coal ashes contribute a major proportion…..". This strong statement needs a reference.

Since another referee requested an estimate, which we cannot provide, we now only state that ash is the primary coal combustion product and cite a report of the US Geological Survey (Kalyoncu and Olson, 2001) on P2 L16-17.

- P2L13-15: On the one hand, "the importance of ash particles as potential INPs must be put into perspective by comparing with concentrations" yet in the next sentence an emission rate is given, not a concentration. While both sentences on their own are fine, having these sentences one after the other could be misleading.

This was reworded to: "The impact of ash particles as potential INPs must be put into perspective by comparing ash emission rates to those of other INP containing aerosols, e.g., mineral dust…" (P2 L18-19)

- P4L6: Why is this important? Reference to publications demonstrating that surfaces typically used for ice nucleation assays interfere with the nucleation process would seem to be appropriate here, bearing in mind that many studies have been performed where droplets are supported by substrates and this does not appear to be an issue.

The half sentence in question was omitted.

- P4L7-8: This statement also needs referencing and elaboration: what size droplets are you speaking of? Homogeneous nucleation CAN be probed in picolitre sized droplets on cold stages.

We changed the sentence to: "Furthermore, as water is brought into the system via the gas phase, impurities which are known to cause the freezing of pure water droplets above the homogeneous freezing limit on cold stages (Budke and Koop, 2015, AMT; Whale et al., 2015, AMT), can be ruled out for our experiments." (P5 L9-11). In citing these two studies, it is made clear that we are not relating to picolitre sized droplets.

- P4L24: only three woods are investigated in this study; is this representative of all “deciduous vs. coniferous” trees?

“Deciduous vs. coniferous” was omitted.

- P5L1-2: What power does this sonicator deliver to the sample?

The ultrasonic bath has a peak output of 320 W and is operated at 35 kHz. We did not include this information in the manuscript as it is not needed for a better understanding and none of the other referees asked for it.

- P5 L6-7: is there any effects based on how long the samples are left to stir for? Also, what about aggregation in solution? Could you be removing particles smaller than 200 nm by filtration that have formed aggregates over the course of 24 hours of stirring?

The aim of the filtration process was to remove insoluble material and leave a solution. So if particles smaller than 200 nm aggregated and were removed, this would actually be a positive effect (in terms of removing the insolubles). We did not study the effect of stirring duration as we wanted to prepare the samples in the same way as described by Umo et al. (2015, ACP). From our point of view, this does not necessarily have to be mentioned in the manuscript.

- P5L6: Define “ice activity”

We chose to avoid using this term and replaced it with “ice nucleation efficiency” which is more precise and, from our point of view, does not need further explanation.

- P5L8: Can the authors say anything on the efficiency of these filters and pore size distribution? Can particles larger than 200 nm sometimes make it through? Also, are the authors defining “water soluble material” as any particle which will make it through a 200 nm filter? This should be stated if so.

We do not have any information about the pore size distribution. The manufacturer only states that the filters have a “sharply defined pore size”. We define anything coming through the filter as water soluble because we collected particles from this solution and only found crystals on the filters. However, you are right in saying that some insoluble material smaller than 200 nm might make it through. Those particles could also be inside the crystals so that we cannot identify them on the SEM images. We added the following sentence: “We are referring to the remaining compounds as "water soluble" even though we are aware that insoluble material smaller than the filter pore size of 200 nm might still be present. This is justified, because the selected 300 nm particles predominantly include soluble substances.” (P11 L15-17).

- Figure 4: How is the “homogenous” region here determined? Citation of the appropriate paramaterization(s) should be added.

We define homogeneous nucleation according to the freezing behavior of highly diluted ammonium sulfate droplets which has been investigated with LACIS but was not shown in the original manuscript as we did not want to overcrowd the plots. However, we now changed Fig. 4 (now Fig. 3) to a 4 panel figure. This gives us the opportunity to show the ammonium sulfate data (Fig. 3d). From these measurements we see homogeneous nucleation becoming the dominant freezing mechanism below -38 °C. We added an explanatory sentence in the figure caption.

- Fig 4: State in the legend and text exactly what the “clay mineral baseline” is; i.e. what clays were used?

The used dusts were not all clay minerals. We included the following sentences in the manuscript for further explanation (P14 L27-P15 L1): "…measurements with an untreated feldspar sample (76 % microcline, K-feldspar, and 24 % albite, Na-feldspar, Augustin-Bauditz et al., 2014), […]. Also shown is the curve for different kinds of mineral dust particles (same feldspar sample, Arizona Test Dust, NX-illite, Fluka kaolinite) coated with sulfuric acid (Augustin-Bauditz et al., 2014). The coating caused the dusts to show a similar immersion freezing behavior even though differences were observed without coating, presumably due to different amounts of K-feldspar contained in the samples. Weathering feldspars turns them into clay minerals and it was argued in Augustin-Bauditz et al. (2014) that the coating had a comparable effect, i.e., consuming all feldspars in the different samples and leaving clay minerals only. Hence the line on which the data from all the different coated mineral dusts fell was termed the "clay mineral baseline"."
A short version of this is now also included in the caption of Fig. 3 (former Fig. 4). We did not add an explanation in the legend as this would overcrowd the plot.

- Fig 4: Harrison et al. ACPD (2016) show that K-Feldspar can have different activities: specify exactly which K-Feldspar was used.

The used sample is not pure K-feldspar but a mixture of 76 % microcline (K-feldspar) and 24 % albite (Na-feldspar). This was determined by X-ray diffraction measurements (Augustin-Bauditz et al., 2014, GRL). This was added to the manuscript (P14 L28-29) and the caption of Fig. 3.

- P10L7-8: I don't have an issue with this statement as such, but I think it's important to point out that onset freezing temperatures cannot be used for others to compare with. A simple phrase along the lines of "For within these experiments we can compare our onset freezing temperatures, which…."

Done.

- P10L9-13. This section is vague, and should be strongly caveated by noting that the authors don't know what the explanation for the differing nucleation activities is, or further experimental evidence showing that SiO2 is indeed responsible for this behaviour should be added. For both this point, and the point below, a statement explaining why it is difficult to conclusively identify the active site in such a complex sample at the beginning would definitely help here!

Such a statement has been added at the beginning of the paragraph (P14 L1-3): "To date, there is no experimental evidence on the ice-nucleation-determining compound in ashes, presumably because it has rarely been studied and because it is a very complex mixture (Ramsden and Shibaoka, 1982; Umbria et al., 2004; Zhang et al, 2011)."). As we cannot provide evidence to our SiO2 hypothesis on a time scale of weeks, we adopt your first proposal by saying that: "…even though this holds true for the ashes presented here, a larger number of samples would have to be investigated to make a conclusive statement." (P14 L10-12).

- Page 10L 14- Page 11L3: All of this section is very speculative and at points vague, and I suggest it be rewritten to make it more concise or removed. After providing several possible explanations for their observations, the authors note "other properties such as ice active sites on the particle surface might affect the ice nucleation ability of a substance." What does this mean? Taking the Vali (2015) definition of a site being a "Preferred location for ice nucleation on an INP", this statement is rather meaningless.

We agree that the cited sentence does not add to the paragraph. It was hence removed. We adapted the point about the potential influence of K on the immersion freezing behavior to be more precise

(P14 L14-17). Also, the point about the potential effect of amorphous components in the fly ash is now discussed in more detail (P14 L21-26).

- Page 11 L5: again, which K-Feldspar was used?

This was specified.

- Page 11 L6: Is it reasonable that clay minerals treated with sulfuric acid are termed the "clay mineral baseline"? Surely this should be justified. Also, if justified, what it is should be stated explicitly in figure 4.

We added further explanation. See P4 of this document.

- Page 11 L17-page 12L3: There are a lot of concepts in this rather long paragraph: separating into at least two smaller paragraphs would help readability greatly

Done.

- P12L1-3: If it's not the physical or chemical particle properties changing and leading to a destruction of active sites, what else could it be? This non-specific nature of this statement makes it vacuous. The word "likely" doesn't help here either.

This sentences has been reformulated. We also added some additional information (P16 L6-12): "These differences are, as for brown coal bottom ash but apparently not for spruce bottom ash, related to a change of physical and/or chemical particle properties due to the change in particle generation. A change in particle composition has been observed before for mineral dust particles which featured different hygroscopicities when being generated firstly via dry dispersion and secondly via atomization (Herich et al., 2009; Sullivan et al., 2010). It was assumed that soluble material present in a fraction of the dry particles was redistributed across all particles contained in the droplets as a coating (Herich et al., 2009). Sullivan et al. (2010) state that changes in surface structure and chemistry from dry to wet particle generation might not only affect the hygroscopycity but also the ice nucleation behavior of the particles."

- Section 3.3: Discussion of possible differences in composition and hence ice nucleating abilities due to size selection of particles should be presented here.

This is fair point. In Sec. 2, we stated that the composition of fly ash particles is consistent in a size range from 0.2 to 4.8 µm (Kaufherr and Lichtman, 1984, Environ. Sci. Technol.) and that we do not see a difference in n_s between the selection of 300 nm particles and 500 nm particles for brown coal bottom ash. However, much larger particles (up to 200 µm, mode diameters at 10 µm) are included in case of the experiments by Umo et al. (2015, ACP). We added the following (P19 L3-9): "Differences in ice nucleation efficiency between our samples and those investigated by Umo et al. (2015) could be related to differences in composition due to size selection. In our case, the immersion freezing behavior of 300 nm particles was investigated, whereas the suspensions examined by Umo et al. (2015) contained much larger particles (average volume-equivalent diameters of 10 µm and 8 µm for coal fly ash and bottom ashes, respectively). This might be relevant as there are studies indicating that the trace elemental composition in fly ash is inversely proportional to the particle size in the supermicron range and not strongly size dependent for submicron particles (Davison et al, 1974; Smith, 1979)."
The last sentence of this paragraph from the original manuscript ("In addition to the stated possible reasons, the fact that our samples were not completely identical to the samples investigated by Umo et al. (2015) concerning their chemical composition and morphology might contribute to the observed differences in n_s.") was deleted.

- Page 13L12: Agreed, but explain why you would not expect it. Reference where appropriate

We changed the sentence to: “Although a time-dependence of the nucleation process has been observed before (Ervens and Feingold, 2012; Welti et al., 2012; Wex et al., 2014), this effect is too small to describe the here found discrepancies.” (P17 L34-35).

- P13L13-14: Again, vague. Is there nothing more which can be said here other than the samples were not “completely identical”

We added the following (P18 L5-P19 L2): “There are recent studies investigating the effect of different experimental methods on the ice nucleation behavior of mineral dust particles where most cold stage methods yielded lower n_s values than dry dispersion methods (Hiranuma et al., 2015, ACP, Emersic, 2015, ACP). These findings could be relevant for ash samples as well. Hiranuma et al. (2015) argue that a high degree of agglomeration in the dry-dispersed particle measurements leads to a larger surface area being exposed to liquid water and consequently larger n_s values in comparison to the rather de-agglomerated suspensions. On the other hand, Emersic (2015) present the hypothesis that particles may coalesce in suspension leading to a reduction of the surface area available for ice nucleation.”

- P14 L26: All clay minerals? Which K-Feldspar?

Specified.

Typos/other:

- P3L1: Is the cold stage(s) used by Umo (2015) the same as that used in Murray 2010(a)?

The cold stage used for the experiments by Umo et al. (2015) is described in Murray et al. (2010a). We added Whale et al. (2015, AMT) where additional information concerning the setup is provided (P3 L10).

- P1L3: Largest rather than biggest

Done.

- P8L26 and fig 4. SMB should be SBM no?

Yes. This was changed.

References cited in our answers:

Augustin-Bauditz et al., GRL (2014)
Budke and Koop, AMT (2015)
Damle et al., Aerosol Science and Technology (1981)
Davison et al., Environ. Sci. Technol. (1974)
Emersic et al., ACP (2015)
Ervens and Feingold, ACP (2012)
Flagan and Seinfeld, Fundamentals of Air Pollution Engineering (1988)
Herich et al., Phys. Chem. Chem. Phys. (2009)
Hiranuma et al., ACP (2015)

Kalyoncu and Olson, US Geological Survey (2001)
Kaufherr and Lichtman, Environ. Sci. Technol. (1984)
Murray et al., Phys. Chem. Chem. Phys. (2010)
Ramsden and Shibaoka, Atmospheric Environment (1984)
Smith et al., Environ. Sci. Technol. (1979)
Sullivan et al., Aerosol Science and Technology (2010)
Umbría et al., Atmósfera (2004)
Umo et al., ACP (2015)
Welti et al., ACP (2012)
Wex et al., ACP (2014)
Whale et al., AMT (2015)
Zhang et al., Chinese Science Bulletin (2011)