Answers to comments by Anonymous Referee #2:

We would like to thank Referee #2 for his/her helpful comments that certainly increase the quality of our manuscript. In the following, the referee comments will be given in green, our answers and adjustments to the manuscript in black. When referencing page and line numbers, we are always referring to the original versions of manuscript and SI.

This is a well-written paper concerning immersion freezing of water droplets triggered by coal fly ashes (CFA). This is a timely topic which fits very well into ACP. The authors compare samples from different sources concerning their ice nucleation activity. They use different set-ups (LACIS, WISDOM, SPIN, LINA) to do so. They correlate their findings with the physical-chemical properties of the particles. They conclude that CaSO4 and CaO are the crucial mineral components and that thus surface hydration of these fractions can have an important impact on the ice nucleation activity of CFA.
Particularly, the physical-chemical characterization of the ice nucleation particles (INPs) makes the importance of this paper. Therefore, the precise application of the different methods in use is crucial. Therefore, I have listed here my concerns regarding the different techniques:

1. Alabama: I am not an expert in aerosol mass spectrometry. Therefore, I have no comments.

2. ESEM. The special resolution of the microscopic pictures is very low. I highly recommend transmission electron microscopy (TEM) pictures. This is of particular importance when investigating the spherical shaped combustion products, which are thought to origin from organics. TEM could provide the internal structure of the particles and will allow a correlation between structure and chemistry, which both have an impact on the ice nucleation (see e.g. Häusler et al. who have investigated typical constituents of soot and coal, i.e. graphenes, which have similar ns values like some coal fly ashes).
As stated on P2L13-15 of the main text, CFA is largely composed of non-combustible constituents in the fuel, i.e., mineral inclusions, and not organics. This is a fundamental difference between ash and carbonaceous particles. Graphene might be a typical constituent of coal, but it is not common in CFA. The ESEM instrument is currently upgraded and not available for further analysis. We agree that TEM analysis would be interesting, however, we would have to resample because the used boron substrates are not suitable for TEM. Resampling and analyzing the eight different particle types (CFA1-CFA4, dry and wet, respectively) would be a time-consuming process. Considering that the focus of the paper is on the investigation of the immersion freezing behavior of CFA, and considering that new images would not change the main message of the study, performing these additional measurements would be beyond the scope of this work. We now cite Gieré et al. (2003) who performed TEM with CFA in the SI (Sec. S2): “Gieré et al. (2003) who performed transmission electron microscopy of class F CFA particles found both, smooth spherical particles and irregularly shaped particles in the size range of several hundred nanometers. The irregularly shaped particles were made up of crushed glass, or glassy spheres with small crystals attached to their surface which concealed the spherical shape.”.

3. EDX. Is a valuable technique in order to gather the chemical composition of materials and is easily accessible in combination with SEM. However, at concentrations below 0.1% the signal to noise ratio of this technique in unsatisfying and the results are untrustworthy. I highly recommend using micro X-ray fluorescence analyses (μ-XFA).

We assume that the absence of, e.g., Ba, Ti, Sr, and Pb in the EDX results can be largely attributed to the weak statistics (~20 particles were investigated for each sample) and not to the detection limit of the EDX detector. Weinbruch et al. (2010) detected Ti in CFA particles using EDX. As stated in the SI (P8L21-22), our substrates were unfortunately not loaded ideally which is why resampling would be necessary to provide more information. EDX was included in addition to ALABAMA because, as you correctly stated, it is easily accessible in combination with the ESEM.

We are quite certain that μ-XRF would not yield satisfactory results when applied to 300 nm particles. Also, further information concerning trace metal occurrence in single 300 nm particles, which we already have from ALABAMA, is not needed from our point of view.

4. XRD. The powder diffractograms shown in the supplement are of excellent quality. Therefore, the authors can easily apply a Rietveld refinement of their data.

As stated in the main text (P10L22-23) “quantitative phase identification was done by Rietveld refinement using reference patterns from the Crystallography Open Database (Gražulis et al., 2009)”. We now include a table (new Table S2) showing the identified phases for each sample in the SI.

5. Bulk chemical composition analysis. Please specify how this was done.

Please refer to the main text (P11L5-7).

6. DMPS. No comments.

7. Light microscopy. Eventually, polarization microscopy could help to differentiate the components of the particles (amorphous vs crystalline).

The light microscopy images were included to show that needle-shaped particles exclusively occur in the aqueous environment of the CFA1 suspension. Further polarization microscopy images would most certainly show the same as the XRD results, i.e., that CFA3 contains most amorphous material. A more conclusive statement about the amorphous fraction is not expected to change the interpretation of the immersion freezing results, which is why nothing was changed in this regard.

We added the following paragraph to Sec. S6 for further explanation of the light microscopy images: “Images of liquid CFA suspension droplets were taken with a digital camera coupled to an optical microscope (Primovert, Carl Zeiss Microscopy GmbH, Jena, Germany). The magnification is 200x and unpolarized light was used. The suspensions were prepared in the same way as for the LACIS measurements and pipetted onto a glass microscope slide. A second slide was put on top of the liquid droplet to increase the amount of particles in focus and to avoid evaporation. Figure S13 a shows that needle-shaped particles are present in the aqueous environment of the CFA1 suspension, suggesting that they precipitate in the suspension and are not or only weakly water-soluble. The needle-shaped particles are several tens of microns long. In addition to the needle-shaped particles, smaller spherical and irregularly shaped particles can be seen. Droplets from the CFA2, CFA3, and CFA4 suspensions do not contain needle-shaped particles, only irregular and spherical particles. Generally, the number of irregularly shaped particles visible in Fig. S13 is much higher than the number of spherical particles for all samples. Coagulation of particles can be observed to some extent for all samples and might affect the surface area available for triggering immersion freezing in the cold stage experiments as described by Emersic et al. (2015).”.

8. BET. Specific surface areas about 1 m2 g-1 are often not precisely accessible. Please, describe the detection limit of your instrument.

The detection limit of the instrument (Nova 2200e, Quantachrome Instruments, Boynton Beach, FL, USA) is 0.01 m^2 g^{-1}. This was added in Sec. S8.

The authors should discuss in more detail the impact of internal structure, morphology and chemistry of the INPs on the ice nucleation activity. In particular, I miss a discussion of the carbonaceous particles. This can easily been performed with the data at hand and with some modifications described above. Therefore, I rate this manuscript as "accepted, subject to minor revisions".

Concerning the internal structure of the particles, we only have very limited knowledge from the BET measurements, i.e., that CFA4 classifies as porous whereas the other samples are non-porous. Hence, it is difficult for us to discuss the ice nucleation efficiency of the samples in connection with their internal structure. From our point of view, the discussion of morphology (see Sec. S2, S6), crystallography (Sec. S3), and especially chemical composition (Sec. S1, S4) and possible links between immersion freezing behavior and physico-chemical particle properties (see Sec. 3.1.2, 3.2.2, 3.2.3, and especially 3.3) is very detailed in our study already.

As stated in the introduction of the main text (P2L13), CFA only contains a limited amount of carbon. This is due to the very efficient and almost complete combustion of pulverized coal in power plants. Loss on ignition values, which are now included in the SI and shortly discussed in the main text, clearly show that carbon is a minor component of the CFA samples. Only the freezing behavior of CFA4, which contains 8 ± 5 % of unburnt fuel might be influenced by the occurrence of carbonaceous particles. The following sentences were added to the main text (Sec. 3.2.1): “According to LOI measurements (see Sec. S4), CFA4 contains the highest amount of unburnt fuel, which is presumably made up of carbonaceous particles. The low immersion freezing efficiency of CFA4 in the investigated temperature range could hence be related to the occurrence of carbonaceous particles, which have previously been found to be inefficient at nucleating ice in the immersion mode (e.g., Chen et al., 2018)”. The following sentences were added to the SI (Sec. S4): “In addition to the bulk chemical composition analysis, Loss On Ignition (LOI) values were determined. The LOI value is a measure of the amount of unburnt fuel, presumably carbonaceous particles, in the CFA samples and hence useful to assess the completeness of combustion in the power plant. The LOI values of the four CFA samples are -0.8 ± 5 % for CFA1, 0.2 ± 5 % for CFA2, 0.8 ± 5 % for CFA3, and 8.1 ± 5 % for CFA4, i.e., apparently only CFA4 still contains a relevant amount of unburnt fuel after combustion in the power plant. Particles with high C content tend to form irregular structures because of enhanced aggregation (Hiranuma et al., 2008). The specific surface area of CFA4, which is more than one order of magnitude higher than that of the other samples (see Sec. S8), could hence be in line with the comparably large LOI value. The fact that CFA4 has the lowest immersion freezing efficiency of all samples in the LINA experiments might be related to the amount of unburnt fuel in this sample. Carbonaceous particles, such as soot, have previously been shown to possess limited ice nucleation efficiency in the immersion mode (e.g., Chen et al., 2018).”.

Reference

Häusler, H., Gebhardt, P., Iglesias, D., Rameshan, C., Marchesan, S., Eder, D., Grothe, H.: Ice Nucleation Activity of Graphene and Graphene Oxides, The Journal of Physical Chemistry C 122 (15), pp. 8182-8190, 2018. DOI: 10.1021/acs.jpcc.7b10675 Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-583, 2018.

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Hiranuma, N., Brooks, S. D., Auvermann, B. W., and Littleton, R.: Using environmental scanning electron microscopy to determine the hygroscopic properties of agricultural aerosols, Atmospheric Environment, 42, pp. 1983–1994, 2008.

Gieré, R., Carleton, L. E., and Lumpkin, G. R.: Micro-and nanochemistry of fly ash from a coal-fired power plant, American Mineralogist, 88, 1853–1865, 2003.

Weinbruch, S., Ebert, M., Gorzawski, H., Dirsch, T., Berg, T., & Steinnes, E.: Characterisation of individual aerosol particles on moss surfaces: implications for source apportionment. Journal of Environmental Monitoring, 12(5), 1064-1071, 2010.