Atmos. Chem. Phys. Discuss., 14, C10379–C10382, 2014
www.atmos-chem-phys-discuss.net/14/C10379/2014/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ice nucleation by combustion ash particles at conditions relevant to mixed-phase clouds" *by* N. S. Umo et al.

Anonymous Referee #2

Received and published: 19 December 2014

The authors present a thorough study of the heterogeneous ice nucleation behavior of four different bottom and fly-ash samples and make the case of missing information on the emission strength of Coal fly ash from different combustion sources as far as their ability to nucleate ice, hence their influence on climate, is concerned. They combine the droplet freezing experiments with physical characterization of the fly ash and classical (bottom) ash samples in order to better understand the relationship between freezing behavior and surface composition of these complex materials which represents a laudable effort in itself. Apart from a few required clarifications and questions I have not found a major "show stopper" in this report which would prevent me from withholding recommendation to publish. However, Sections 6 and 7 are way too wordy and lengthy for the (trivial) content that the authors want to convey to the read-

ers at the end whereas the core results on the droplet freezing experiments are not discussed at length. They should essentially concentrate pages 28862 to 28864 to at most two succinct paragraphs as the conclusions are really quite simple and not especially earthshaking, namely that (a) CFA (Coal fly-ash) has an ice nucleating (IN) ability comparable to most mineral dust samples, (b) whose IN ability falls short of K-feldspar, and (c) that therefore one may (perhaps) make a case for additional measurements of these materials on a global scale. However, this last point is by no means uncontested, for what error would we be making if the ice nuclei budget of CFA and mineral dust were confounded? Here are my critical remarks that I would like to see answered before publication of the present paper:

- Regarding the use of Millipore water in the preparation of the ash suspension I think that the authors took the worst possible solution: Millipore water has a minimum of ionic impurities, but is not specified as to the number of floating insoluble nanoparticles. Owing to the fact that Millipore water flows through a bed of solid ion exchange material the flow periodically "breaks off" chunks of that material. The authors may easily convince themselves by atomizing pure (Millipore) water, evaporating and counting the particles using a CNC (Condensation Nucleus Counter). Using doubly-distilled water (our "best" solution) we have found a particle count of 10 to 50 particles per cc occurring in a broad mode centered around 50 to 60 nm, varying from day to day, which is not very satisfying. This most probably does not influence the nL-NIPI, but could affect the subtraction scheme of the microL-NIPI results.

- Considering Figures 2 and 3 one must be careful when taking the results of Figure 2 as an illustration of the particle size distribution function: Taking row A, middle panel for CFA in Figure 2 as an example, one gets the impression that the number of large spheres are important in the CFA size distribution. It ain't so because these large particles of approx. 8-10 microns represent the tail-end of the distribution. A disclaimer is in order when comparing or illustrating Figures 2 and 3! They cannot be compared because one is a geometric diameter derived from an optical measurement, the other

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is based on the particle mobility in an electric field.

- Regarding the symbols in the formalism there is a certain inconsistency with Whale (2014) in that “sigma” in equation (1) corresponds to “A”, the total surface area in a droplet used in Whale (2014), whereas A in equation (4) is the specific surface area in units of square cm per g. Why use two different symbols in publications written in the same year? This is confusing.

- Regarding the experimental results the authors do not really undertake an in-depth discussion. Why haven’t there been repeat freezing experiments? How do sequential freezing curves look like when performed with the same droplet suspensions in place? What is the reason for the sometimes significant difference of the fraction of droplets frozen vs. average droplet diameter? See results in Figure 6 (nL-NIPI results) for CFA (upper left panel, green symbols). Is there a systematic contribution of the ”pure” water to the freezing behavior of the ash IN?

- In the display of Figures 5 to 8 the authors managed to sneak in some ophthalmological eye charts: Both the graphic material as well as the legends are impossible to read as submitted!! Please make sure the reader finds itself in a position to read and understand these Figures.

- Regarding the results of the number of interaction sites (ns) as a function of temperature displayed in Figure 7: What is the reason for the “saturation” behavior of CFA compared to the bottom ashes as well as with respect to mineral dusts displayed in Figure 8? The authors should advance a plausible reason as the results displayed in the upper left panel of Figure 7 (and 8) are distinct from all others. Any reason for the systematic deviation off the common parametric line for the bottom ashes in Figure 7? Somehow, the points from the two frozen droplet experiments (nL and microL-NIPI) do not want to overlap as they deviate from one another!

- A last point of contention concerns the relationship between the EDX mineralogical results and the expected freezing behavior of the bottom and fly-ash samples. EDX

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addresses one to a few nanometers of matter, especially in this case because carbon is a light and low-density material from which X-rays may escape from some depth. In contrast, the freezing behavior depends only on the composition of the interface, in the case of crystalline material embedded in amorphous carbon probably from one or two molecular monolayers. It is outrageously simplifying when the authors just compare the EDX signals of the ash samples and derive the surface composition, thus freezing behavior. A robust disclaimer or additional explanations are in order here.

- Reference "(Wilson (et al.?), 2012)" is missing (as is (Connolly et al., 2009) in (Whale et al., 2014)).

- The English is OK in most parts, but must be checked by a native English speaker. Frequent use of double plurals are distracting. "Warmer" temperatures? Top of pg. 28859: "...a cumulative nucleation site density..."Pg. 28847, line 11: "...as a CCN activates" (What is the meaning?)

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 28845, 2014.

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