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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Characterization of individual ice nuclei by the single droplet freezing method: a case study in the Asian dust outflow region" *by* Ayumi Iwata and Atsushi Matsuki

**Anonymous Referee #2**

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The manuscript "Characterization of individual ice nuclei by the single droplet freezing method: a case study in the Asian dust outflow region" by Ayumi Iwata and Atsushi Matsuki describes an application of a droplet freezing apparatus to the characterization of the ice nucleating (IN) particles sampled during two Asian dust events. The authors report on the application of several microanalysis techniques (AFM, Micro-Raman, SEM, EDX) to reveal the chemical composition and morphology of the most IN active particle in a subset of a sample, identified by the droplet freezing technique.

A combination of the single-particle microanalysis techniques with droplet freezing assay methods is a very promising development in the field of the ice nucleating particle



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research. An important advantage of the method described in the manuscript is the realization of a "single IN particle per water droplet" approach, which greatly reduces uncertainty associated with preparation of suspensions, characterization of particle size and surface distribution, and variability of particle properties across the droplet population, which are the common issues in a conventional cold stage experiment. However, before starting characterizing the most active ice nucleating particles with all the modern and expensive single particle techniques, one has to be completely sure that the particles identified as the most IN active are really such particles. To be honest, I am not convinced that this is the case. I would nevertheless support the publication of the manuscript provided that authors carefully address the multiple critical issues listed below. This might require a tedious re-evaluation of the results or even new experiments because some issues cannot be resolved without repeating the experiments.

General remarks:

1. I would like to draw the author's attention to the both papers of Schrod at al., AMT 2016, and ACP 2017, who essentially describes a similar but much better-characterized setup (FRIDGE) to study the deposition freezing of ice on the atmospheric IN particles collected with an unmanned aircraft over eastern Mediterranean. This group has gone a long way improving their instrument and achieving reliable results, you can learn a lot from them. These papers have to be mentioned and discussed.

2. The method description is incomplete. Many important details are missing, preventing the objective evaluation of method applicability. The only reference supposedly describing the setup (Akizawa et al., 2016), refers to an application of a Linkam stage for mineralogical samples. I wonder how is that related to the IN study discussed in the manuscript. Peckhaus et al., ACP 2016, also used a Linkam stage for a cold stage experiments.

3. The method described in the manuscript allows identifying the first particle within the

field of view that initiated the freezing. This particle is then labeled the “ice nucleating” particle, and the others as “non-nucleating” particles. I wonder what happens with all other particles on the substrate? Do they initiate freezing too? Please explain this clearly in the manuscript.

4. The setup description in the manuscript doesn’t have it very clear, but if I understand correctly, the method has a very important limitation. In a closed cell with the humidified gas disconnected from the cell, the droplets are in equilibrium with the water vapor. The moment the first crystal appears, it grows very fast because the vapor is supersaturated with respect to the ice surface. Now that the system contains all three phases of water, droplets start evaporating and some of them would evaporate completely without having a chance to freeze. To prevent complete evaporation, you use the very fast cooling rate (30 K/min), but this reduces the time remaining for the other droplets to freeze to less than 20 s (if the first droplet freeze at -30°C and the homogeneous freezing is over at -40°C). Ice nucleation is a stochastic process described by a rate equation, so that the probability of freezing at given temperature is a function of time spent at this temperature. At such cooling rate, the freezing of “second-best” IN particles can be inhibited by this time-dependent issue and all the droplets will freeze homogeneously concealing the potential freezing activity of the IN particles. A chance of freezing is further reduced by droplets evaporation.

5. In this way, only one ice nucleating particle can be identified per sample. The other, just very slightly less active ice nucleating particles would have no chance to initiate freezing and would be labeled as non-nucleating. This would result in a wrong statistics of the IN vs the non-IN particles, and as a consequence in a biased composition of non-IN active particles. If I am wrong, please show your results in form of “the number of frozen droplets as a function of the substrate temperature”. Such curves can be used to retrieve the so-called ice nucleating active site (INAS) densities, that can be better compared with the measurements of other groups.

6. The critical issue discussed in the above comments can be also a consequence of





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the Linkam stage design. The standard cell of a Linkam stage has the metal coolant tubing exposed to the environment, making this tubing the coldest spot inside the cell. Water condensed on the tubing during the condensation step must freeze first during the cooling. As explained above, such ice surface would immediately become a strong sink for the water vapor. If the cooling rate is too slow, the liquid droplets condensed on the residual particles would evaporate before having a chance to freeze. I suspect that this is the reason for using a cooling rate of 30 K/min. If this is the case, it is a serious drawback of the system and has to be clearly stated in the manuscript. For the future work, I would recommend enclosing the substrate with the collected particles into a separate cell, so that just this area of the substrate is exposed to the supersaturated vapor.

7. At the cooling rate this high, a strong temperature gradient across the substrate can arise. The freezing temperature can be biased towards low values. Was temperature measured on the surface of a substrate or taken from the Linkam stage internal measurement? How was the temperature of the freezing onset determined? Have you been recording the microscope images? If yes, what was the image acquisition rate? Was it synchronized with temperature measurements? Since this is the first time you report the measurements with the new setup, you should convince the reader that the setup is well characterized.

8. What is the relationship between the field of view of the microscope and the sampling area containing droplets condensed on the aerosol particles? What if the first ice crystals are located outside of the view area? In this case, the initial ice crystals would not be detected but the local vapor pressure would be reduced due to the vapor deposition on the growing crystals, leading to evaporation of droplets and inhibition of freezing. Please give a detailed assessment of this effect.

Given the uncertainty of the method of identifying the most active IN particles, I don't see the point of discussing the single particle microanalysis. If possible, give the maximum detail of the cold stage operation and detection techniques. If the measurements

data permit, present your data not just in form of on-set freezing temperature, but in form of temperature dependent freezing curves. Otherwise, the measurements have to be repeated with a lower or variable cooling rate, and the results analyzed as discussed above.

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