The authors attempted to characterize the physico-chemical properties of atmospherically relevant ice-nucleating particles with the new off-line approach (i.e., a combination of several off-the-shelf techniques), which could potentially complement the in situ approach of ice residual studies. The topic itself is an important addition to ACP and the atmospheric science community. However, the experimental and analytical methods are unfortunately poorly explained and partly erroneous. Further, the manuscript contains a number of ambiguous statements and over-interpreted results without proper quantitative analyses as well as conclusive performance verifications. I have numerous suggestions for critical revisions. Additional tests of IDFM are necessary, and I do believe that the revision of the manuscript could be time consuming and result in a significantly different paper.

First of all, we would like to express our gratitude to the reviewer for carefully going through our manuscript and providing highly relevant remarks and suggestions for improvements. We took the comments very seriously, and hence made substantial efforts to conduct additional tests on our method (IDFM). We believe that the major concerns raised in the comments are now addressed. Please find our response to each of the comments below (in blue italic).

The title is misleading. "Characterization of individual ice nuclei: : :" should read ": : :ice residual: : :" unless the authors could provide the evidence of particular individual particles repeatedly form ice over several cooling-thawing cycles. The properties of the particle may alter during/after ice activation, and the particle should be considered as a residual after thawing.

In a strict sense it is true that it is an ice residual particle that we characterized. We changed the title as suggested and now we use the term "ice residual particle". Now the title appears as:
'Characterization of individual ice residual particles by the single droplet freezing method: a case study in the Asian dust outflow region'

In the introduction section, the authors need to logically address why it is particularly important to study the aerosol mixing state to improve our understanding of atmospheric ice nucleation in mixed-phase clouds. What is special about the mixing state on ice nucleation as compared to other general properties, such as size and bulk composition?

The authors may want to do a careful and rigorous literature review, digest the contents in a diplomatic manner and describe your thoughts to the reader along with your own story line.

The extremely small fraction of IN particles in the total atmospheric particles precludes us from using bulk aerosol sample for characterizing the IN property. In addition to the various external mixing states

expected in the ambient aerosols, we believe that the internal mixing commonly found in the atmosphere is equally important. Therefore, the detailed information on the individual particles is indispensable for better understanding the ice crystals formation in the real atmosphere. *This is now explained more clearly in the introduction (Page 3,Lline 20) of the manuscript.*

'Internal mixing of aerosols commonly takes place during long-range transport in the atmosphere (e. g. Zhang et al., 2003, Sullivan et al., 2007, and Iwasaka et al., 2009). The surface properties of the internally mixed particles following atmospheric processing (reaction, coagulation and aging) can dramatically change from their original properties (Maring et al., 2003; Trochkine et al., 2003). The internal mixing of particles is an important factor that contributes to the complexity of atmospheric aerosol particles. Although efforts have been made to address the effects of internal mixing on the IN activity of aerosols under conditions relevant for the mixed phase cloud formation (Sullivan et al., 2010; Kulkarni et al., 2014; Augustin-Bauditz et al., 2016), the complexity of the ambient aerosol has not yet been fully represented by the laboratory generated aerosols. Therefore, detailed investigation based on the individual particle analysis is necessary to relate the internal mixing state of aerosols in the actual atmosphere and their IN activity.'

Why did the authors arbitrarily pick -30 dC as the end cooling T (no explanation given)? Why didn't the authors carry out the T-binned analyses (e.g., up to -20 dC cooling vs. up to -30 dC cooling)? Such capability (seemingly feasible) and approach can resolve the issue, which the authors point out in the manuscript (e.g., P15L15-23).

We observed that the atmospheric particles started to form ice crystals only below -25 °C. The reason why we did not go below -30 °C is that it was difficult to keep track on the Non-IN and IN particles due primarily to the fact that initially formed ice crystals were growing too big and the impact on the surrounding particles became too obvious (scavenging and evaporation of droplets around the rapidly growing ice crystals). Also, if we start dividing the already few number of total IN particles into different temperature bins, it further degrades the counting statistics and makes the comparison of particle types more difficult. Therefore, we had to give up discussing on the problems that require the statistical comparisons by the T - bin analysis in the narrow temperature range (e.g. "P15L15-23" which need to clarify the detailed freezing temperature difference among various organics in atmospheric particles).

Because differences in particle composition may be correlated with particle size, it is difficult to determine which characteristic fundamentally drives cloud-nucleating ability. Why didn't the authors

conduct the size dependent analysis (i.e., coarse vs. fine) to examine if the size can be a

nucleation-triggering factor? It is not appropriate to generalize the results based on all-size population.

We agree on the importance of size dependent analysis. However, the number of IN in the atmosphere is generally extremely small, and as a result the total number of particles we could identify as ice residues became rather limited. If we further group and divide the already few ice residues into different size groups, it becomes even more difficult to compare the ice-nucleating ability among the particles with diverse mixing states and chemical compositions. All of the particles analyzed in this study are already larger than 1.1µm due to technical limitations, and the largest size was 5.47 µm, thus our result is representative only for this rather narrow range of the coarse particles, and it is now explained more clearly in section 3.1 as follows:

'With respect to the particle size detection/limit, the impactor already size segregates particles and limit the test particles in the super-micron range. The diameter of the collected atmospheric particles whose ice crystal formation could be monitored ranged between 1.16 and 5.47 µm through the identification by the optical microscope. Meanwhile, the laser spot size (i.e. spatial resolution) of micro Raman spectroscopy approaches the diffraction limit of approximately 1 µm in diameter. All in all, the size of IN active particles that can be analyzed by this method is limited to super micron particles.'

The cooling rate of 0.5 K/s seems aggressive and not atmospherically relevant (i.e., 1

K/m may simulate a typical convective cloud updraft). Why not 1 K/min just like other numerous cold

stage techniques do?

It is a very important point. We admit that our cooling rate is considerably faster when compared with the typical cooling rate in the convective cloud updraft. Part of the reason we selected the higher cooling rate is to minimize the chance of scavenging and drying nearby droplets because if we select a slower cooling rate, the resulting ice crystal size became too large. To avoid this from happening and facilitate precise isolation of the ice-nucleating particles, we had to choose the faster rate. However, we did confirm that pure water droplets do not freeze until the stage reaches down to -36.5 degrees even at this cooling rate, which coincides rather well with the results by several previous laboratory experiments (Pruppacher and Klett, 1997;Koop et al., 2000; Murray et al., 2010; Murray et al., 2012) and the observations of deep convective clouds (Rosenfeld and Woodley, 2000). The reason for selecting this cooling rate is now explained in section 3.1 as follows:

'The advantage of IDFM is that we can keep track and be sure which of the collected single particle was actually nucleating ice. Thus the IN active particles identified by IDFM can be studied in detail by various particle analysis techniques. Comparing IDFM with the other methods such as FRIDGE used

primarily to measure ice nuclei concentration (Ardon-Dryer and Levin, 2014; Schrod at al., 2016; Schrod at al., 2017), we have to compromise the accuracy and quantitative evaluation of IN activity since the evaporation of droplets around frozen particles by the Bergeron-Findeisen effect can affect the activated fraction. Therefore, by selecting the higher cooling rate and -30 ˚C as the end cooling temperature, we minimized the evaporation and the scavenging of the droplets around the rapidly growing ice crystals in the experiments of atmospheric particles. By this way, most of the atmospheric particle (excluding those very close to the ice crystals) were not dried and remained as droplets until temperature reached -30 ˚C. Note however, that the selected cooling rate is considerably faster when compared with the typical cooling rate found in the convective cloud updraft. Also, we cannot fully rule out the possibility that droplets very close to an ice crystal may had been fully evaporated.'

Show the profiles of dew point and T throughout the experiment rather than show snapshot pictures (i.e., Fig. 1).

We added the corresponding temperature profile and the time when the images were taken as follows. As described in the manuscript, moist air supply is stopped and the cooling stage is isolated during the cooling process, so the dew point is expected to vary and closely follow the stage temperature while the saturated vapor continued to condense onto the activated droplets.
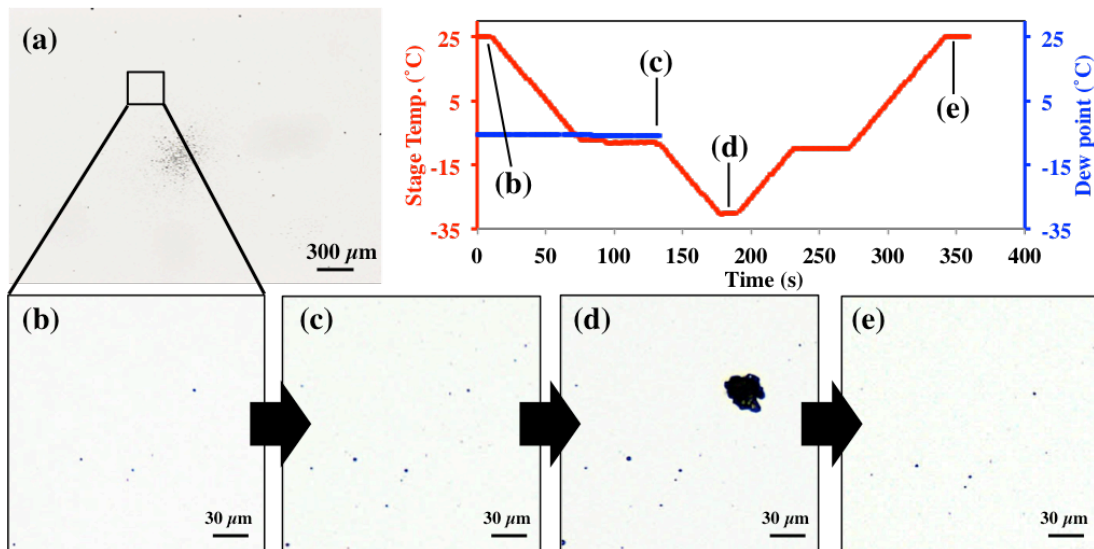

Figure 1: Optical images of sample particles deposited on Si wafer substrate before the freezing experiment (a, b), after exposure to water super saturation conditions at -9 ˚C (c), after cooling to -30 ˚C (d), and after sublimation and evaporation by dry air (e). The inset graph shows the stage temperature and the dew point of the wet air introduced into the cell before exposing the stage to water super saturation.

Quantitatively evaluate the capability of immersion/condensation freezing method relative to other cold stages using the ice nucleation parameters, such as frozen fraction or ice nucleation active surface site density. The onset discussion (P711-18) seems qualitative, speculative and over-simplified.

We have to admit that our technique is not a perfect method that can resolve all technical issues encountered in the ice nucleation experiments. The biggest advantage of course is that we can keep track and be sure which single particle was actually nucleating ice. In return, we have to sacrifice the accuracy and quantitative evaluation of freezing temperatures based on INAS in relation to the evaporation of droplets in the vicinity of the frozen particles (Bergeron-Findeisen effect), as well as due to the limited number and size (d>1.1µm) of the particles that can be analyzed.

The number of ice crystals formed are compromised especially at lower temperatures as the number and size of ice crystals increase and more droplets in the vicinity of the growing ice are subjected to evaporation. When comparing our results with those found in literature, we must also note that strict comparison is difficult because of the uncertainties and differences related to the size distribution and composition of dust particles used in different experiments. Assumptions made to calculate the surface area can also be a source of bias. The K-feldspar used in this study as a reference mineral dust was purchased from the same supplier, but the lot number is different (from different source rock) from the K-feldspar used in Atkinson et al (2013). Therefore, composition of K-feldspar used in the current study and that used in Atkinson et al. (2013) are not exactly the same. Nevertheless, we added the ice nucleation active sites (INAS) of the 4 standard mineral particles measured by the current IDFM (Fig. S-2).

The ice nucleation active sites (INAS) obtained in this study agreed within an order of magnitude difference compared to those found in the literature (despite many different experimental conditions). Further, we would like to emphasize that the relative order of the onset temperatures found for different particles is always consistent (i.e. K-feldspar > Na-feldspar > quartz > kaolinite >> pure water) and even the range of the freezing temperatures are not far off from the reported values.

It was probably not clearly stated in the manuscript, so the following change was made with regard to the onset temperatures:

'Heterogeneous ice nucleation observed in all standard mineral samples tested in this study (K-feldspar, Na-feldspar, quartz, kaolinite) consistently occurred at higher temperatures than the homogeneous freezing temperature. The reference mineral samples were milled to fine grains before being collected on Si wafer substrate by an impactor. Three set of samples were made for each reference mineral to ensure large enough observation area for the IDFM. *The total number of the particles monitored during the ice*

nucleation experiment by IDFM was 4,509, 2,271, 4,759, and 1,435 particles, respectively. In this study, the freezing onset temperature of the sample was defined as the temperature at which the IN active fraction of the total observed particles reached 0.01. As a result, the freezing onset temperatures for K-feldspar, Na-feldspar, quartz, and kaolinite ranged between -22.2 to -24.2 °C, -24.7 to -25.7°C, -24.8 to -26.8 °C and -27.2 to -29.2 °C, respectively (Fig. S-1). Therefore, the ice nucleation activity of K-feldspar was the highest and that of kaolinite was the lowest. The order and the range of observed onset temperatures for these minerals were consistent with the results found in the literature (Atkinson et al., 2013; Murray et al., 2011).'
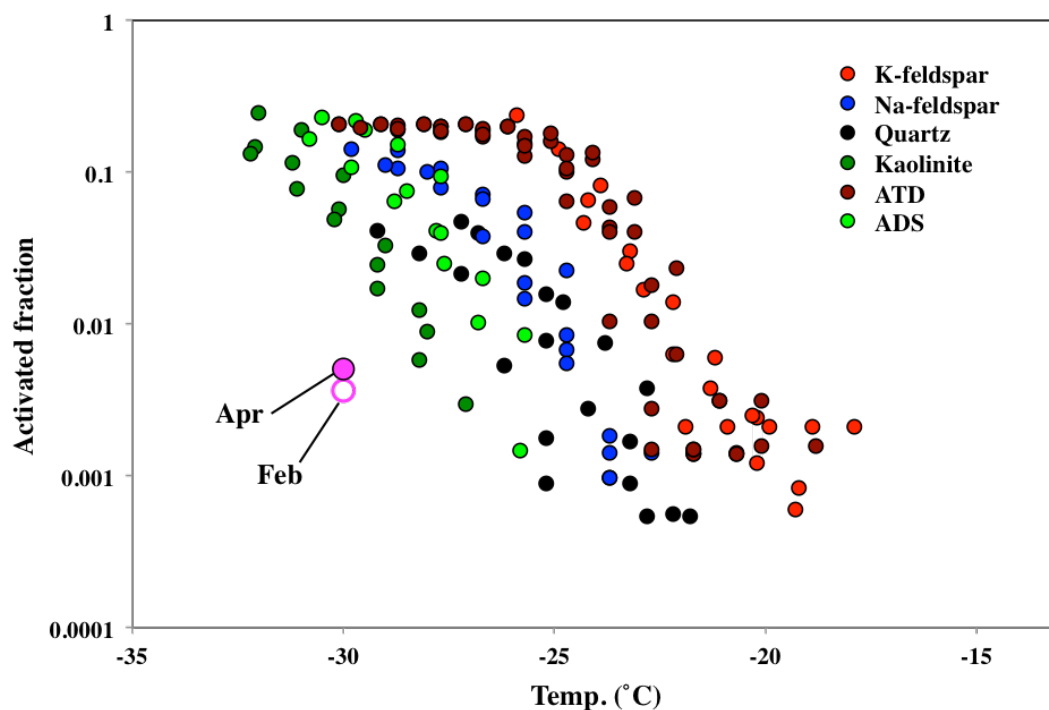

Figure S-1: Activated fractions of the reference mineral dust particles. Results of the atmospheric samples collected in February and April are also shown for comparison.
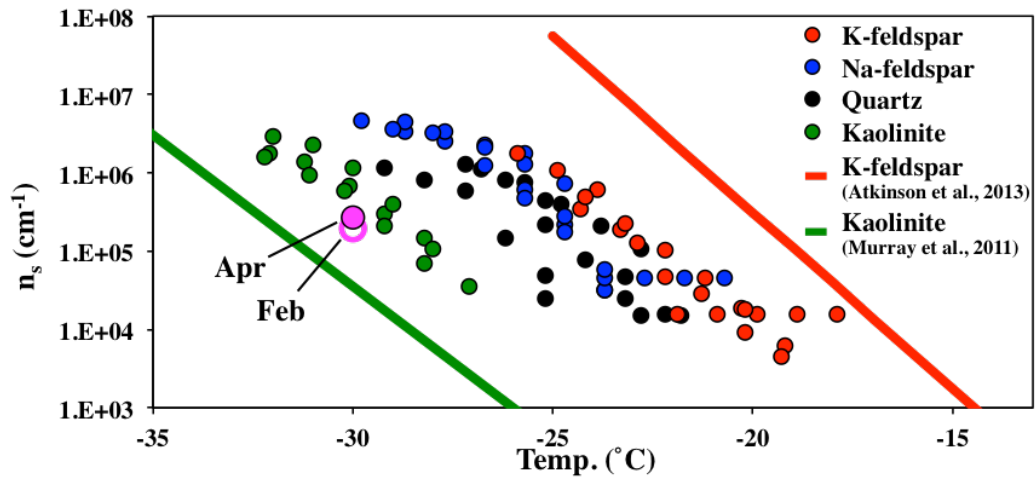
Figure S-2: the ice nucleation active site (INAS) densities for the reference single component mineral dust samples. These INAS densities were calculated from the activated fractions (Fig. S-1) and the averaged sphere equivalent surface areas obtained from the 2D silhouette of each particles in the microscopic image.

Description of the background contribution (contamination/impurity) should be included. The authors can assess it by putting soluble salts (e.g., NaCl) on the silicon wafer and cooling the cold stage down to the homogeneous freezing T.

We are aware of the importance of the background contribution (contamination/impurity). As suggested, we conducted additional measurements on the atomized NaCl particles and the activated fractions as a function of temperature are shown in Fig. S-4. At least, the ice nucleation was not observed above -34 °C for both NaCl particles and pure water. Therefore, we believe that there is no significant impact from contamination/impurity both during the water vapor condensation and the cooling processes affecting the ice nucleation down to -30 °C.
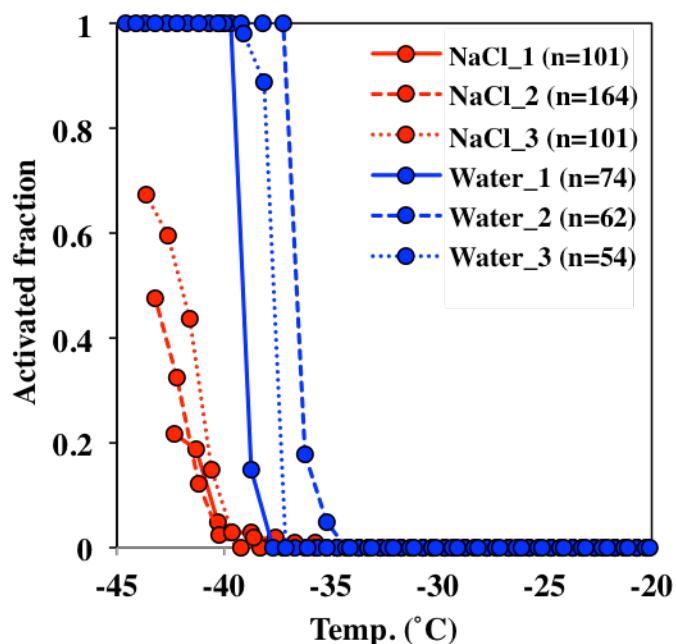
Figure S-4: Activated fractions of NaCl and pure water droplets. Three set of samples were tested for both NaCl and water. The number of particles and droplets observed under the microscope is shown as n. The test NaCl particles were aerosolized by atomizing their solutions (0.005g/ml) and collected on the substrate with an impactor. the pure water droplets were also collected by spraying directly onto the substrate..

Why the homogeneous freezing occurs over 3.5 K (P7L6-8)? It should be abruptly spontaneous in a narrow range of T, if the water saturation condition is well-controlled.

The size of droplets might not be a substantial factor for the observed deviation. Technical validations seem necessary.

We believe there was an obvious lack of explanation. In the same freezing run, all droplets freeze in a much narrower range and almost spontaneously at the same temperature, like the reviewer points out (Fig.S-4). -36.5 degrees is the highest $T_{0.5}$ (temperature when freezing fraction is 0.5) that was recorded among the multiple freezing experiments, and all the droplets were frozen before the temperature reached -40 degrees. This explanation is added in the manuscript (Page 7, line 6-8) as follows:

'Before evaluating the ice nucleation activity of the standard samples by IDFM, we measured the freezing temperature of pure water droplets using the same method, which can be regarded as the onset temperature of homogeneous freezing. As a result, homogeneous ice nucleation was initiated at approximately -36.5 ˚C or below, and all droplets spontaneously froze in a narrow temperature range within the same experimental run. All droplets froze before the temperature reached down to -40 ˚C in all

experimental runs. This homogeneous freezing temperature coincides with those reported by several previous laboratory experiments (Pruppacher and Klett, 1997; Murray et al., 2010; Murray et al., 2012) and from observations of deep convective clouds (Rosenfeld and Woodley, 2000).'

Fig 1: What particles are they? Regardless, the immersion freezing active fraction at -30 dC is 1/16. Is it comparable to other cold stage techniques?

The particles shown in Fig 1 are atmospheric particles collected in April, 2016. The original image shown in Fig. 1 was for a small area on the substrate which was enlarged for better visibility. Now Fig. 1 is modified (as shown above in response to earlier 9 comment) and the entire observation area is also shown. The actual activated fractions was 5.6E -03 as stated in the manuscript, which was significantly smaller than 1/16.

The authors may want to test reference samples (K-feldspar, quartz etc.) and estimate their n_s for to quantitatively compare to Atkinson et al. (2013, Nature).

As shown in response to earlier comments, the INAS obtained in this study agreed within an order of magnitude difference compared to those found in the literature (Fig. S-2).

Fig. 6: Two more pie charts should be added. Show the composition of total aerosols measured before cooling as well as that of after thawing to eliminate the artifact of cooling-thawing.

It would be better if we can show the additional two pie charts, however, conducting analysis before the cooling-thawing experiment will be an additional source of artifacts, for example, SEM analysis involves electron irradiation under high vacuum and can potentially damage the sample and evaporate semi-volatile materials. In addition, it is already quite labor intensive and very difficult to repeat three multiple individual particle analyses on the same particles. The idea was to preserve the original particle properties as much as possible until the cooling experiment. We cannot fully rule out the possibility of the impact of cooling-thawing on the particle properties, but it is beyond the scope of our current study, and must be incorporated in the future course of the study.

Sea salts are not ice nucleation inhibitors (P1L23), it is just not as active as other known INPs (e.g., aluminosilicate).

We believe there is also a lack of explanation and overstatement here. The results showed that the particles grouped as mineral dust were the most abundant ice residues in our study, with no obvious dependence on the elemental composition (EDX). On the other hand, most of the particles internally

mixed with sea salt were not found as ice residues. This internal mixing counterpart included mineral dust. Therefore, (instead of clearly placing them as an inhibitor) we suggest the internal mixing of mineral dust with sea salt may reduce the chance of the mineral dust to act as ice nuclei.

P2L9: Koop, 2000 (Nature) missing

Thank you for pointing out the error. We added it in the reference.

How were reference sample powders dispersed/aerosolized onto silicon wafers?

We added the following line to be more explicit on the preparation of the standard mineral samples:

'The reference mineral samples were milled to fine grains before being collected on Si wafer substrate by an impactor. Three set of samples were made for each reference mineral to ensure large enough observation area for the IDFM.'

Some details of single particle techniques (laser intensity of Raman, and its influence on composition detection) are also missing.

We added following information in the method section:

'The Raman spectra of individual particles were obtained using a 532 nm excitation laser with the intensity fixed at 4.906 mW. This laser wavelength was used to detect C-H vibrational mode that appears as peaks or a broad peak in the range 2,800 cm^{-1} and 3,100 cm^{-1}, and the laser intensity was chosen to minimize damage to the sample.'

Describing the experimental uncertainties in temperature measurement, particle size detection/limit etc. would be beneficial to the reader.

The temperature measured on the surface of a substrate and the Linkam stage internal measurement is calibrated based on the melting point of materials with known properties as described in Akizawa et al., 2016. The temperature difference between the substrate surface and the stage, as well as the temperature gradient is less than 0.3 ˚C based on the observation of melting pure ice. This explanation is added in the section 2.1 as follows:

'The sample particles were deposited onto a Si wafer substrate with hydrophobic coating (Glaco, Soft99 Corporation, Japan). Particles were observed for their position, size, and shape under an optical microscope with x50 magnification (Olympus, Japan) as shown in Fig. 1a. Subsequently, the substrate was transferred onto a cold stage in a closed cell (THMSG600, Linkam Scientific Instruments, UK). Since the cold stage used in this study is cooled by liquid nitrogen, the exposed tube through which the liquid

nitrogen passes in the cold cell becomes a cold trap which can act as an additional sink for the water vapor. Therefore, in this study, all cooling parts except the cold stage surface were covered by insulating material. The temperature measured at the cold stage was calibrated by the substances of known melting points (Akizawa et al., 2016). Furthermore, we confirmed that the temperature gap between the substrate and the cold stage was consistently smaller than 0.3 ˚C by observing the melting of pure ice. During the ice nucleation experiment by atmospheric particles, the stage temperature and the dew point were recorded every 1 seconds. The temperature measurement and the images were synchronized with the PC internal clock.'

Experimental limitations related to the particle size is discussed earlier in response to the comment made in relation to the size dependent analysis.

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