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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ice nucleation properties of mineral dust particles: Determination of onset RH_i, IN active fraction, nucleation time-lag, and the effect of active sites on contact angles" *by* G. Kulkarni and S. Dobbie

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We thank the anonymous referee 1 for providing constructive comments in improving the contents of this paper. Please read our comments as follows, and the corresponding changes are included in the revised manuscript.

General comments:

1) We apologize for any confusion. In the Kulkarni et al. 2009 AMT paper we clearly mentioned that bottom half portion of the chamber is not been affected by the optical port of the top plate. The contact between the copper rod and, the plates and ice layer is not important as we are only interested in the surface (the substrate surface) temperature of the rod. Every precaution had been taken to seal the rod such that no outside air leaks inside the chamber. The substrate surface temperature is measured and calibrated using the temperature sensor (thermistors) and deliquescence point of ammonium sulfate respectively. It is observed that the temperature distribution in the bottom half portion of the chamber varies linearly with height. This confirmed the linear variation of the temperature, next, using literature deliquescence relative humidity (DRH) values at respective DRH temperatures we checked for the validation of the relative humidity with respect to ice (RHi) profile. To calculate the uncertainties' on RHi values we measured the deviation of observed temperature from the DRH temperatures, and using these deviation values we calculated the uncertainties in RHi. This procedure has been described in detail in the revised manuscript of AMTD, 2009 (Kulkarni et al. 2009).

2) It should be noted that our chamber benefits from that there is a continuous supply of water vapor to the substrate surface. The chambers mentioned by the referee 'Dymarska et al., Eastwood, et al,' work on different principle than ours. These chambers have fixed volume of water vapor at any time, if nucleation occurred this will deplete the certain amount of water vapor and thus RHi drops. Whereas in our chamber the top plate ice layer provides the continuous supply of water vapor.

3) We agree with the error analysis procedure mentioned by the referee, and we also have performed the similar analysis. The table C1 illustrates the combination of temperatures and the corresponding maximum uncertainty in terms of RHi.

The uncertainty calculations are performed as follows. Initially we calculate the max RHi (let us call as RH1) without considering the temperature uncertainty. Next, we calculate max RHi (let us call as RH2) due to the temperature uncertainty of the plates,

which is $\pm$ 0.4 deg C. Then we subtract RH1 from RH2 to obtain the max RHi uncertainty, which is tabulated in above table. These uncertainty values are used in the paper. It should be noted that all formulae's used for these calculations are described in the paper.

4) The dust particles investigated for the ice nucleation are not used for subsequent experiments. Every experiment had been performed on different dust particles, therefore there is no preactivation phenomenon occurring as described by the referee. We will add this note in the revised manuscript. In each Fig. 3 to 6, three different combinations of plate's temperatures were used to obtain the onset RHi data. At each combination of plate temperature total 15 experiments were performed. This means data from 45 experiments was plotted in each Fig. 3 to 6. Therefore total 180 experiments were carried out to plot the data in Fig.3 to 6. In reality more experiments are performed but the results did not vary from shown in Fig. 3 to 6, and thus we had obtained good statistics. We have used the dry deposition technique to spread the sample over the substrate. The detailed experimental procedure is described in the Kulkarni et al. 2009.

Active IN fraction calculations are performed at constant RHi and temperature. Yes it is true that 48% of the total particles (5-15 in number) nucleated when they were exposed to one constant RHi and temperature (for example 110% and -20 deg C). To obtain the mean IN active fraction at each constant RHi and temperature we used the data from 15 experiments. The fraction is higher as normally observed by other groups, and we think it is mainly because of larger size of dust particles and probably could be the higher detection resolution of the microscope used here. It is also possible because of the smaller number of particles investigated for the ice nucleation, and the exposure time. The wide variation of $\pm$ 20 % observed in the active IN fraction can be due to the heterogeneity of the dust particle. As mentioned in the paper we did not have any tools to quantify the morphological heterogeneity, but each dust particle has different morphology than others as visualized under scanning electron microscope. One particular dust particle is shown in Fig. 2. We think it is still an open question how

morphological heterogeneity would influence the ice nucleation. We will incorporate these notes into the revised manuscript.

5) One of the benefits of the current ice chamber is that we can observe the dust particles at high resolution (the theoretical limit is 1.1 micron). It means if ice embryo grows to size larger than 1.1 micron it would get detected irrespective of dust size (but the dust size has to be larger than 1.1 micron). It should be noted that ice embryos are only observed to grow on the dust particles and not on the substrate. Therefore to observe the ice embryo the size of the dust particle is not important unless the dust size is less than 1.1 micron. The uncertainties associated with the time lag critical embryo calculations are described in the conclusions section. In the revised manuscript we will add them in the section 3.3.

We agree with the referee that uncertainty in the RHi values would influence the lag calculations. According to ice growth diffusion equation without kinetic corrections (Rogers and Yau, pp 103) given as, m = 4.π.r.D.$(\rho - \rho_r).t$.

The growth time is inversely proportional to the vapor density gradient. The calculations show the uncertainty of $\pm$ 2 Pa in vapor pressure would produce uncertainty of $\pm$ 2 seconds [These calculations are performed at plate temperatures top = -15 deg C and bottom = -25 deg C. The uncertainty in the vapor pressure is calculated at middle of the chamber due to the uncertainty in the temperature of the plates, which is $\pm$ 2 Pa. These pressure values are converted into density values to be used in the above equation at respective temperature]. Considering experimental uncertainties, like RHi, time lag calculations should be considered as the apparent estimations. The future work is needed to reduce these uncertainties, and the time lag calculations might be helpful to formulate the new parameterizations.

6) We agree with the referee. Ice nucleation is a phase change process, and is beyond the scope of this experiment to observe this process. To observe this phase change (from vapor to solid phase) one would require highly magnified microscope combined

with ice nucleation chamber. Similar to other ice chamber studies (for example Kanji and Abbatt, 2006) in our experiments we observe the ice formation process. We will modify the revised manuscript accordingly. Actually we do not assume the lag time between the ice nucleation and detectable ice grown is negligible. This time is calculated by using Maxwell diffusion growth equation. The calculations are described in the section 3.3.

Data analysis:

The Fig. 7 shows the active fraction data obtained at two different temperature and RHi values for Dakar-1 and Nigeria locations. It is quite possible to fit two different curves for each individual location and the individual curve analysis can be done. In reality the dust from these locations would mix in the atmosphere and it is then difficult to distinguish between the dust types. Therefore it could not be appropriate to fit the curve for each location and RHi value. Also a single curve equation would be simple to deploy in the global cloud models. It should be noted that we wanted to derive the equation that is independent of RHi, which would be useful to fit in our in-house cloud models. We have not performed any error analysis for the fitted curve, but would pursue this work if the cloud models show any significant sensitivity towards the curve fit equation. Total 60 experiments (each experiment had 5 to 10 particles and different particles in every experiment) were carried out to obtain the data points. We will add this note in the revised manuscript. In reality more experiments are carried out to check the statistics. It was observed that the results do not change.

One of the main goals of our work was to perform the process level studies and derive simple parameterizations. The Eq. 8 relates the ice crystal formation to the total number of aerosol particles and time. It is simple to deploy in the cloud models and, we also agree with the referee that it lacks information like surface area and chemistry. Similarly Eq. 7 lacks this information. But at this time where ice nucleation field is not

completely understood, and the modeling community requires a simple parameterization scheme. We think development of such simple schemes should be encouraged. The testing of these schemes in our in-house cloud models is underway. The recommendation obtained from modeling community would be then useful to improve such schemes. In the revised manuscript we would highlight these weaknesses and also the scope for further improvement.

For calculating the contact angle we used experimental nucleation rate, defined as follows,

$$J = N/(A.t)$$

where J is the nucleation rate, N is the number of ice nucleated particles in time t, and A is the surface area of the particles. The calculated rate coefficients are tabulated in the revised manuscript (Table 3). The equivalent diameter of dust particles was estimated using Hinds (1982) method, where they described the procedure to measure the Martin's diameter; the length of the line parallel to a given reference line that divides the projected area (silhouette) of the particle into two equal halves.

It should be noted that nucleation rates have units of 'nucleation events per unit area per time'. This means the rates become independent of individual dust particle surface area, but depends per unit surface area. Therefore in practical you can apply these rates to any particle size. Here we have assumed the 1 micron particles.

Specific comments:

The manuscript is revised accordingly. The focus of this paper was mostly to present the results and discussions from ice nucleation experiments. We would like to point to our previous paper Kulkarni et al 2009 to understand the detailed experimental set up

design and construction. Also this paper has added the references to old and present thermal gradient diffusion chambers.

The reference Flatau et al 1992 is added to the reference list. To calculate the RHi we use the ratio of vapor pressure to the saturated vapor pressure. During this calculation the effect of using different saturation vapor pressure scheme does not produce very different result (because we are interested in the ratio). Our other calculations are based on Flatau scheme, and therefore we would like to maintain the consistency across the results.

It should be noted that we have tested the linearity of temperature gradient across the gap between the two plates. The temperature values are calibrated and validated, they are not assumed.

Sample rod is 4 mm in diameter. The top (substrate surface) has a coating of Teflon surface. The rod is sealed at the bottom plate via O rings and compression fittings. The substrate surface temperature and RHi are important for the experiments, and these variables are validated and calibrated. Please see Kulkarni et al 2009.

While carrying onset RHi experiments the experiment is terminated once first nucleation event is observed. Whereas in the active IN fraction experiments the experiment is continued until no further nucleation events are observed.

After communicating with our cloud modeling community we concluded that both individual and bulk elemental compositions are important to understand. However considering the elemental composition heterogeneity among the single dust particles, also within the individual dust particles, and interests of cloud modeling community to represent the bulk properties than individual, it was thought to present bulk composition table. The comparison of every single dust particle elemental composition to the bulk elemental composition is beyond the scope of this paper. That saying we did compared few single dust particle composition spectra to the bulk composition and it is observed that they are within $\pm$ 20%. The field of view (FOV) of the scanning electron micro-

scope can be varied. To analyze the individual particle composition FOV is adjusted such that there is only one dust particle inside the FOV. Similarly FOV is adjusted to analyze the bulk composition, where 25-30 particles are inside the FOV.

We have added the following sentence. The similar elements were also observed by other studies for example, Krueger et al., 2004; Reid et al. 2003; Caquineau et al., 2002; Glaccum and Prospero 1980.

In the revised manuscript we have revised the explanation regarding the Eqn. 7 and Fig. 7 (the systematic variation with geographic location). Although Eqn. 7 do not take into account the surface area and chemistry, but considering the limited understanding of the ice nucleation at current time the development of such empirical simple schemes should be encouraged. We think they should be tested in the models, and using these modeling results they should be revised accordingly. We will highlight the weaknesses of this scheme into the revised paper.

The Eqn. 8 does not have the surface area term.

The reference (PK97, PP 341-345) for Eqn. 9 is added. The particle surface area is derived using Martin's diameter.

The contact angle is a measure of hydrophilicity or wettability of the aerosol particle. In the current paper we use this angle as measure of ice nucleation efficiency. A two dimensional detailed cross section of the particle, the particle surface consists of irregularities (cracks and dislocations etc.), can be viewed as shown in Fig. 8. In the present analysis we are only interested in the angle that solid embryo makes with the substrate. Finding the diameter and shape of this embryo is beyond the scope of this paper.

We have used 1 micron radius dust particles for the contact angle analysis, which is widely used size in the modeling community and also mean size diameter observed [Jickells et al., 2005; Hoornaert et al., 2003; Ginoux et al., 2001]

The conclusion section paragraph 2 is revised.

Technical comments:

All comments are included.

Our AMT (Kulkarni et al 2009) paper focused on the design, development and validation of the experimental set up, along with one sample result (onset RHi plot for dust particles). We have performed numerous experiments on these particles and produced lot of data. Most of the plots are identical. Also in the revised AMT paper we have added that these particles are from Nigeria location. It should be also noted that AMT paper was revised and accepted before ACPD referees published their comments. We would like to keep the onset RHi Fig 3 in this paper so that it becomes easy to compare these results with other onset RHi results (Fig 4 to 6). In the revised manuscript we will add the reference Kulkarni et al 2009 to the Fig 3 and text.

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Table C1: Showing the calculated RHi and uncertainty associated for different combination of TGDC temperatures.

Temperature deg C		Maximum	
Top plate	Bottom plate	RHi uncertainty	RHi
-10.0	-20.0	1.6 %	110 %
-19.0	-29.0	2.0 %	112 %
-26.0	-34.0	1.7 %	108 %
-29.0	-30.0	0.3 %	100.2 %