Atmos. Chem. Phys. Discuss., 9, C839–C846, 2009
www.atmos-chem-phys-discuss.net/9/C839/2009/

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

Anonymous Referee #1

Received and published: 14 May 2009

The paper presents ice nucleation (IN) relative humidity (RH) onsets, IN time-lags, and the active fraction of IN from three Saharan dust samples and one Spanish dust sample. The experimental method is based on novel design of a static thermal gradient diffusion chamber. It is found that Saharan dust activates ice at lower RHs compared to the Spanish dust sample in a temperature range between -16 C and -33 C for particle sizes smaller than 38 μm. An elemental analysis reveals that the Spanish dust sample contains a much higher fraction of Ca which might be one reason for the different RH onset values. This study observed significant time-lags in ice formation when a

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

specific RH was reached. A new parameterization is suggested to describe the ice formation time-lag and corresponding ice crystal formation rate. The effect of surface irregularities on the contact angle is discussed.

The topic of this manuscript fits nicely within the scope of ACP. However, the section on experimental method and procedure has to be elaborated to make sure that no experimental artifacts affect the data and the experimental uncertainty is correctly assessed. Also, the amount of data seems not to be sufficient to draw the conclusions presented here. The suggested new parameterizations describing ice crystal formation do not take into account the aerosol surface area and thus do not represent heterogeneous ice nucleation. Hence, these parameterizations can not be recommended to be used in cloud modeling studies. These major issues should be clearly addressed before publication of this manuscript can be recommended.

General comments:

1. A linear temperature gradient is assumed between the bottom and top plate of the chamber. However, Fig. 3 in Kulkarni et al., AMTD, 2009 indicates that the temperature gradient at the location where the particles are placed on the sample holder may not be linear. This is due to the large optical port which lacks controlled heating. For this reason the assumption of a linear temperature gradient and thus linear supersaturation field may not be correct. This issue gets more significant when introducing the copper rod into the chamber to expose the particle sample to ice supersaturations. As discussed below small uncertainties in temperature can significantly affect RH. It is also not clear if the copper rod is in contact with the ice at the bottom plate or isolated from it and if it is sealed against room air? How can it be assured that the particles have exactly the temperature at height d given by the temperature gradient between the plates when a very good heat conductor (copper rod) is in contact with a much larger fraction of the temperature gradient field and in addition is cooled from outside of the chamber? Besides that the copper rod affects the temperature gradient within the chamber, contact with ice could lead to a different sample temperature at height d with subsequent

ACPD
9, C839–C846, 2009

consequences for S_{ice} at d. Overall this experimental method may work, however, the uncertainties are larger than stated.

2. The authors terminate the experiment as soon as the first ice formation is detected since this ice particle will then scavenge the surrounding water vapor and further ice formation might occur at unspecified/uncontrolled ice supersaturations. However, a fundamental problem of the presented experiments lies in the fact that only a small fraction of the sample is observed. The field of view (FOV) is 0.13x0.1 mm. The overall sample size is at least 1x1 mm. If ice first forms outside the FOV the relative humidity at which the first ice is observed may not be correct for the above mentioned reasons. This problem pertains to all ice nucleation experiments where particles are deposited on substrates. For this reason previous studies monitor the overall sample area (e.g. Dymarska et al., Eastwood, et al, Bertram et al., Koop et al., Knopf and Koop etc.). Such an effect could significantly influence the measured onset relative humidities and ice formation time lags. Deliquescence experiments are insensitive to this kind of effect.

3. Regarding the experimental uncertainty. The temperature uncertainty is reported as $\pm$0.4 K. RH_i between a plate at -30 C and -29 C is about 111 %. A conservative error analysis would assume one plate at -30.4 C and the other one at -28.6 C which results in 121 % RH_i. This indicates an uncertainty in RH_i of about $\pm$10 % due to the temperature uncertainties of the plates. (For $\pm$0.2 C it still results in $\pm$5 % RH error). This would be the systematic error of the presented instrument. The previous literature on DRH values for ammonium sulfate, e.g. Braban et al., indicate a spread of about 7 % RH at about -18 C, not including the instrumental uncertainty. For these reasons, the overall data uncertainties of this study ought to be larger.

4. Regarding the experimental procedure. After the first ice nucleation event has been observed, was the sample heated above 273.15 K to ensure complete sublimation/evaporation of ice and water on the mineral dust? As shown previously warming the mineral dust to ensure ice sublimation, i.e. particle exposure to RH below 100 % RH_i but below 273.15 K may still leave the particles conditioned and may affect sub-

ACPD

9, C839–C846, 2009

sequent ice nucleation experiments of the same sample. Also, information is missing on how many ice formation events have been observed at each temperature for each sample. How many samples for each dust type have been investigated, i.e. what is the uncertainty due to sample preparation and dust heterogeneity? Since nucleation is a stochastic process as many ice formation events as experimentally feasible should be monitored before applying CNT, contact angle derivations, or other parameterizations. This affects Figs. 3-6 but also the results in Table 2. An active IN fraction of 48 %, does this mean 48 % of a sample containing 5-15 particles formed ice until the relative humidity was increased to 110 % RH_i? As mentioned above the RH may not be correct if more than one ice formation event is observed. In addition, how often was this experiment repeated? I would assume preparing a new sample of same dust and doing this experiment again will result in a different active IN fraction due to the heterogeneity of the dust. How significant are these reported values for Dakar-1 and Nigeria dust? Multiple samples of same dust should be investigated.

5. It is not clear if the time lag can be solely attributed to the formation of a critical embryo when taking all the uncertainties discussed above into account. 36 s are needed to grow an ice crystal to 1.1 μm. However, it may have to grow much larger to be distinguished against the 38 μm in diameter dust particles. The time difference of 36 s and observed 85 s is too close. A slight decrease in the water partial pressure due to formation of ice at a different location within the chamber could lead to longer growth times.

6. Strictly speaking you can not observe ice nucleation but ice formation. You assume the lag between ice nucleation and detectable ice growth is negligible under your experimental conditions.

Data analysis:

Figure 7: It is obvious that the data of Dakar-1 activates less ice particles compared to Nigeria dust at same time lags, in contrast to the statement in the document. Also,

ACPD
9, C839–C846, 2009

I am not sure if the data obtained at 110 % and 116 % can be treated combined. Individual parameterizations should be applied for each dust type. The shown fit does not describe the data well. What is the uncertainty of the presented fit? How often have these experiments been conducted and how many samples have been used? Is this only one sample, i.e. maximum about 15 ice nucleation events?

Derivation of Eq. 8 has to be elaborated, in particular when considering the large uncertainties associated with Eq. 7. Also in terms of CNT Eq. 8 lacks the fundamental parameter particle surface area. Obviously having 10 particles each with 1 μm or 1 mm in diameter will produce significantly different number of ice particles. This is not captured by Eq. 8. Overall the suggested parameterizations are insufficient to be reliable for application to model ice formation from dust particles and should not be published in this manner.

For Eq. 9 to be used for calculation of the contact angle, the experimentally derived heterogeneous ice nucleation rate coefficients have to be applied. These rate coefficients are not given in this manuscript. The derivation of these values should be given and explained. In addition, for calculation of the revised contact angle an aerosol diameter of 1 μm was assumed. This seems to be too much on the lower side when considering that most particles are in the size range < 38 μm. Applying a radius of 10 μm increases the surface area by at least 2 orders of magnitude and thus will yield a different contact angle.

Specific Comments:

Abstract: The abstract should mention the investigated particle sizes.

Page 11300, line 9: To what “in agreement”?

Page 11302, line 11: That ice particle numbers depend on SS_i has been also shown by Knopf and Koop 2006 and is given in textbooks such as Wallace and Hobbs.

Page 11303, line 22 following: I am missing references to previous literature on ther-

ACPD
9, C839–C846, 2009

mal gradient diffusion chambers. E.g. Elliott 1971, Saxena et al., 1970, Hussain and Saunders, 1984.

Page 11304, line 8: reference Flatau et al. is missing. Saturation water vapor pressures should be calculated using Murphy and Koop, QJRMS, 2005.

Page 11304, Eqs. 1-4: As mentioned above. Assumption of linear temperature gradient is not convincing.

Page 11304, line 22: What are the dimensions of the sample rod? How is it isolated and sealed against ice and ambient air, respectively? This will affect the temperature gradient at the bottom of the chamber. The rod also serves as a cold pool within the chamber since it is in contact with the colder air of the environmental room.

Page 11305, paragraph 1: See discussion above concerning uncertainties.

Page 11305, line 16: Previously in the text it is stated that the experiment is terminated when ice is observed. Here it seems that various ice formation events were observed and noted. See also discussion above.

Page 11306, line 26 and following: You should give the elemental surface composition of the dust particles in a table as well. This may be more important for your studies compared to the bulk composition. The particle bulk elemental composition is reported using the same analytical technique. How were the surface and the bulk of the dust particles probed? How does the surface and bulk composition differ?

Page 11307, line 9 and following: The interpretation and discussion of the elemental composition of the dust need more references such as Glaccum and Prospero, Esteve et al., Caquineau et al., Eltayeb et al., Reid et al.

Page 11307, line 24: “These particles. . .” can be omitted.

Page 11310, 2nd paragraph: Please see discussion above concerning the effect of ice particles depleting the water partial pressure outside FOV on nucleation time lag.

ACPD

9, C839–C846, 2009

Page 11311, last paragraph: Please see discussion above.

Page 11312, line 8: I do not agree with the statement that there is no systematic variation with geographic location after 300 s. Also Eq. 7 appears not to be the ideal description for the presented data sets. Please see discussion above.

Page 11313, Eq. 8 and following lines: How does aerosol surface area come into play using Eq. 8? Please see discussion above.

Page 11314, Eq. 9: This equation needs a proper reference. Also J_{het} in cm^{-2} s^{-1} should be given for the presented experiments. How is the particle surface area derived?

Page 11314, line 13: For one case the contact angle is assumed for a flat surface on the other hand for a rough surface. The question is, under which spatial dimension the concept of the contact angle holds. Even in a crack or cavity the contact angel may be associated with a smooth surface. Conceptually, I am not sure which is the correct micro- or macrophysical picture of a contact angle.

Page 11315, line 5: Chosen particle radius is too small. See discussion above.

Page 11315, 2nd paragraph of "Conclusions": The spread in onset RH_i is discussed but one sentence later it is stated that the dust particles were not sensitive to RH_i. Please resolve this. Address the discussion regarding the overall uncertainties.

Technical comments: Page 11310, lines 21 and 22: Missing "%".

Page 11314, line 8: Indexes in σ_{ij} must be in subscript.

Figures: Figure 1 has been already published in Atmos. Meas. Tech. The exact same figure may not be published again in ACP. I leave the final decision to the editor.

Figure 3 shows exactly the same results as Figure 7 in Kulkarni et al. Atmos. Meas. Tech. Discuss. 2009. However, here it is stated that it is dust from Nigeria. In Kulkarni et al. Atmos. Meas. Tech. Discuss. 2009 it is referred to as Saharan dust sample.

ACPD
9, C839–C846, 2009

As for Fig. 1, Fig. 3 may not be published in this form again in ACP. I leave the final decision to the editor.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 11299, 2009.