Responses to Referees

The authors wish to thank both reviewers for their useful suggestions and thoughtful comments. Below are our point-by-point responses to reviewers' comments.

Referee #1

Reviewer's comment: The most important point I would like to make is in regards to the use of hematite particles. Why was Hematite chosen as dust particles for cirrus clouds? Is there prior evidence of its presence in cirrus clouds?

Authors' response: We did not select hematite because it is a major atmospheric dust component in cirrus clouds. We chose hematite because it is a good model substance to infer n_s values over a wide T and RH_{ice} range (i.e., page 16500 lines 9-12 and lines 16-21 and Sect. 3.3). The atmospheric relevance was demonstrated by comparing the model hematite results with more relevant desert dust aerosol results (page 16506 lines 20-25).

Reviewer's comment: The author refers us to the a paper by *Matsuki et al*. (2010) which examined mineral dust particles from cloud residual and clear sky in Niger. Matsuki et al. shows in Fig 4 in their paper that out of the different types of mineral dust particles that were found in cloud droplets residual, hematite frequency was very small compared to all other mineral dust particles as clay minerals.

Authors' response: We cited *Matsuki et al*. (2010) to state that hematite is an example of atmospheric mineral dust particles that can be found as cloud-borne particles, not specifically to infer its presence in cirrus clouds. To clarify our point, we have rephrased "cloud-borne particles" to "cloud-borne particles in shallow stratocumulus clouds" on the page 16506 line 6 in the first manuscript version (now moved to the page 16497 line 21 after "…proxy for atmospheric dust particles).

Reviewer's comment: In addition hematite particles are different than most of the atmospheric dust particles (in term of mineralogy and shape), can that also affect their IN ability? Since the atmosphere does not only contain hematite particle but a combination of different dust particles type, why not then combine all dust measurements and try to get an isoline that will represent all of them?

Authors' response: In this work, we demonstrated that the formulated hematite n_s-isolines are reasonably comparable to that of desert dust samples, previously studied in AIDA (i.e., ATD and SD2; *Möhler et al*., 2006), at $n_s \sim 10^{-11}$ m^{-2} (Fig. 3A and associated text on the page 16506 lines 20-25; page 16507 lines 20-22). Nonetheless, we feel it is important to point out and re-emphasize that this work is a conceptual study with laboratory-synthesized hematite particles as a model aerosol for deposition ice nucleation over a wide range of T and RH_{ice}. In this study, we did not attempt to conclude how much hematite content contributes to ice formation in cirrus clouds. For clarity, we have added the following sentence on the page 16498 line 3 after "…existing parameterizations.":

"It is important to note that the purpose of the current study is to perform a conceptual study with laboratory-synthesized hematite particles as a model aerosol for deposition ice nucleation, over a wide range of T and RH_{ice}, but not to quantify how much hematite content contributes to ice formation in cirrus clouds."

Reviewer's comment: Another general comment is that this manuscript will substantially benefit if the author will start the paragraphs with words other than figure or we, in addition there are too many places that are written in first body (e.g. page 16505 lines 4 and 29, page 16506 line 9 etc.).

Authors' response: The authors appreciate the prior suggestion by the reviewer on means to improve the overall quality of the paper. As per reviewer's suggestion, we have modified the following sentences (starting with words other than "figure" or "we"):

Sect. 2.2. page 16498 line 23-page 16499 line 3: "For this study, a cooling rate of 5 °C min^{-1} was typically applied at the beginning. Then, the cooling rate decreased to <0.1 °C min^{-1} within 400 s for each pumping expansion experiment, which was mainly due to an increasing heat flux from the chamber walls. Afterwards, an almost constant temperature was maintained by the stirred and well-mixed volume of the cold chamber. During the experiment, the pressure in the vessel decreased from 1000 to 800 mb."

Sect. 2.3. page 16500 line 27: "The mean size and surface area of hematite particles were prescribed with an assumption that…"

Sect. 3.1. page 16504 lines 3-6: "The temporal profiles of deposition nucleation experiments from HALO campaigns, including N_{ice}, gas T, RH_{ice} and RH_{water} measured by the TDL as well as the polarized light scattering properties in near-backscattering direction measured by SIMONE, are shown in Figure 1."

Sect. 3.1. page 16504 line 20: "The initial n_s-isoline curves in the T-RH_{ice} space are illustrated in Figure 2."

Sect. 3.2. page 16505 lines 27-28: "The n_s-isolines of hematite particles were compared to previous measurements made using different aerosol species."

Sect. 3.2. page 16506 lines 9-14: "Comparison of the hematite n_s-isolines to previous deposition freezing observations are shown in Figure 3. More specifically, previous measurements were performed with natural Saharan desert dust (SD2, *Möhler et al*., 2006), reference Arizona test dust (ATD, *Möhler et al*., 2006; *Welti et al*., 2009), volcanic ash (*Steinke et al*., 2011), soot (*Möhler et al*., 2005), clay minerals (*Welti et al*., 2009; *Koehler et al*., 2010) and organics (*Shilling et al*., 2006; *Wang and Knopf*, 2011)."

Sect. 3.3. page 16507 lines 24-25: "Next, the ice nucleation efficiency of hematite particles was parameterized over a wide range of T-RH_{ice}."

Sect. 3.4. page 16509 lines 8-9: "The SCAM5 results for monthly mean profiles of the simulated in-cloud N_{ice} ($Ni \sim N_{ice}$) over the ARM SGP site for five cases are shown in Figure 5."

Sect. 3.4. page 16510 lines 7-8: "The results of the COSMO model for the vertical profiles of N_{ice} (presumably equivalent to the heterogeneous INP number concentration) are summarized in Figure 7. These results simulate…"

Reviewer's comment: A literature overview that shows the actual presence of hematite particles in cirrus clouds is missing. Only in section 3.2 the author mentions the present of hematite particles in the atmosphere but still not in cirrus clouds. It should be mentioned that *Matsuki et al*. (2010) did not mention that the dust particles measurements were taken from cirrus cloud, therefore we need to ask are we sure hematite particles can be found in cirrus clouds?

Authors' response: Discussed above.

Reviewer's comment: Additional information in the method part is needed. TSI mentioned on the SSPD 3433 web page that it can sufficient deagglomerate most dry particles in the range from 0.5 to 50 μm, in the paper the authors mention that they size selected 200nm, which is below the threshold of this equipment.

Authors' response: The previous AIDA study (Fig. 2 of *Skrotzki et al*., 2013) demonstrated the application of a SSPD for dry-dispersion of quasi-monodisperse (200 nm mode diameter) hematite into the AIDA vessel.

Page 16498 lines 16-17 now reads:

"A Small-Scale Powder Disperser (SSPD, TSI, Model 3433) was used to dry-disperse the quasi-monodispersed hematite particles into the AIDA vessel as demonstrated in *Skrotzki et al*. (2013)."

Reference:

Skrotzki, J., Connolly, P., Schnaiter, M., Saathoff, H., Möhler, O., Wagner, R., Niemand, M., Ebert, V., and Leisner, T.: The accommodation coefficient of water molecules on ice – cirrus cloud studies at the AIDA simulation chamber, Atmos. Chem. Phys., 13, 4451-4466, doi:10.5194/acp-13-4451-2013, 2013.

Reviewer's comment: In addition, did the author verify that the size that were selected by the DMA were similar to the size distribution that came out of the DMA?

Authors' response: DMA was not employed in our study. As described in lines 6-12 of the page 16498, we used laboratory-synthesized hematite particles that had been formed as a powder of equally sized hematite particles (~200 nm, 500 nm, 1000 nm area equivalent diameter; *Skrotzki et al*., 2013; *Hiranuma et al*., 2014). Hence, no additional size-segregation was necessary.

Reference:

Hiranuma, N., Hoffmann, N., Kiselev, A., Dreyer, A., Zhang, K., Kulkarni, G., Koop, T., and Möhler, O.: Influence of surface morphology on the immersion mode ice nucleation efficiency of hematite particles, Atmos. Chem. Phys., 14, 2315–2324, doi:10.5194/acp-14-2315-2014, 2014.

Reviewer's comment: Section 2.3 page 16500 line 27 to page 16501 line 3. Was a 1000nm surface area used for all three selected sizes, please clarify?

Authors' response: We chose only 1000 nm diameter as a simulated hematite size for our COSMO and SCAM5 modeling studies. Our choice of 1000 nm diameter and surface area is reasonable and representative for ice nucleation efficiency (inferred by n_s) of three different sizes of hematite particles studied at AIDA (page 16503 lines 18-25; i.e., different sizes of hematite particles were used to characterize ice nucleation efficiency, n_s, at a wide temperature range).

Reviewer's comment: The value of 1000nm that were taken from *Hiranuma et al*. (2014) does not represent size selected measurement but values from looking on the entire distribution, does the authors expect it to be the same value?

Authors' response: We use the term 'quasi-monodisperse' because of the presence of minor fraction of smaller agglomerates/fragments (Fig. 2 in *Skrotzki et al*., 2013; Fig. 1 in *Hiranuma et al*., 2014) within the sample, but this minor fraction have minimum influence on the surface-scaled n_s parameterization presented in the current work.

The geometric standard deviation (σ_g) from *Hiranuma et al*. (2014) is correctly 1.05. What we have reported (0.097) is "width of the distribution" (= $2.303 \cdot 2 \log \sigma_g$.; *Huffman et al*., 2010). Our COSMO and SCAM5 modeling studies were performed based on either assuming monodisperse size distribution of 1000 nm or mode diameter of 1000 nm with σ_g = 1.05. After all, the impact of introducing

such distribution on the simulation results was small as presented in the manuscript (page 16509 line 28-page 16510 line 1).

For consistency, we have replaced "($\sigma = 0.097$)" with "($\sigma_g = 1.05$)" on page 16501 line 2.

Reference:

Huffman, J.A., Treutlein, B., and Pöschl, U.: Fluorescent biological aerosol particle concentrations and size distributions measured with an Ultraviolet Aerodynamic Particle Sizer (UV-APS) in Central Europe, Atmos. Chem. Phys., 10, 3215-3233, doi:10.5194/acp-10-3215-2010, 2010 (the supplemental Online Material is available at: http://www.atmos-chem-phys.net/10/3215/2010/acp-10-3215-2010-supplement.pdf).

Reviewer's comment: Page 16501 line 13 The author mentioned that for T>-36 the parameterization from M92 was used in the model, however it is known (and also mentioned on the page 16496 line 21) that M92 parameterization is relevant for -7>T>-23, therefore I am not sure if the model can represent well the creation of ice for temperature between -23<T<-36.

Authors' response: We agree with the reviewer that the M92 parameterization, which was developed based on the INP concentrations from CFDC observations in mid-latitudes, is strictly valid only in the temperature and supersaturation range of the measurements, i.e., between -7 and -20°C and 2 and 25% ice supersaturation. However, it has been extrapolated beyond this range in numerous previous model implementations (e.g., *Morrison et al*, 2003; *Seifert and Beheng*, 2006), because some information is needed in the whole temperature range above homogeneous freezing conditions. Here, we implemented the M92 parameterization, for $T > -36$ °C, where hematite particles are not ice active, simply to ensure a reasonable spatio-temporal distribution of total water content (among water vapor, liquid and ice phase cloud particles) and to avoid unrealistic conditions (e.g., high supersaturations) in the lower troposphere in our model runs. Further, Figure 2 in *Seifert et al*. (2012) show the evidence that the deviation between the Phillips parameterization (*Phillips et al*., 2008) and the M92 parameterization can result in about an order of magnitude INP concentration mainly due to 'aerosol assumption' (i.e., number concentration). For these reasons, and given the inherent uncertainty of an aerosol-independent approach, we believe that the use of the M92 parameterization for $T > -36$ °C in our conceptual modeling study is appropriate and reasonable.

References:

Morrison, H., Shupe, M. D., and Curry, J. A.: Modeling clouds observed at SHEBA using a bulk microphysics parameterization implemented into a single-column model, J. Geophys. Res., 108, doi:10.1029/2002JD002229, 2003.

Seifert, A., Köhler, C., and Beheng, K. D.: Aerosol-cloud-precipitation effects over Germany as simulated by a convective-scale numerical weather prediction model, Atmos. Chem. Phys., 12, 709–725, doi:10.5194/acp-12-709-2012, 2012.

Seifert, A. and Beheng, K.D.: A two-moment cloud microphysics parameterization for mixed-phase clouds. Part I: Model description, Meteorol. Atmos. Phys., 92, 45–66, doi:10.1007/s00703-005-0112-4, 2006.

Phillips, V.T.J., DeMott, P.J., and Andronache, C.: An empirical parameterization of heterogeneous ice nucleation for multiple chemical species of aerosol, J. Atmos. Sci., 65, 2757–2783, doi:http://dx.doi.org/10.1175/2007JAS2546.1, 2008.

Reviewer's comment: Page 16506 lines 4-8 I think that this part should also be mentioned in the introduction part.

Authors' response: The referee makes a good point. We have updated and moved the following sentence on the page 16497 line 21 after "…proxy for atmospheric dust particles":

"Hematite is used as an example of atmospheric mineral dust particles, which can also be found in the form of cloud-borne particles in shallow stratocumulus clouds (*Matsuki et al*., 2010). Natural hematite often exists in supermicron-sized silt particles and accounts for a few percent of the total dust particle mass (*Claquin et al*., 1999)."

Reviewer's comment: Page 16507 lines 14-22 Can the author say something about some of the points on figure 3 that does not match the n_s isoline, spatially those measured by AIDA.

Authors' response: The reviewer is right. It may be indicative of isolines to be also as a function of composition. The authors, however, point out that the previous AIDA results for desert dust are in good agreement with the new n_s isolines, at least within an order of magnitude, and their agreement also supports the general trend of the isolines. There is one outlier for SD2 at about -50°C. The reason for which is not known. Furthermore, the soot data show a somewhat less steep increase to lower temperatures. But, it confirms the general trend of isolines for deposition nucleation. These premises must be further examined in comparing to atmospherically relevant substrates and their ice nucleation activities in controlled laboratory settings.

Reviewer's comment: Page 16508 lines 3 I think that the part of supplement material 3 should be part of the paper, since all the measurements represent measurement below water saturation the reader should see in detail how that isonline above water saturation were calculated.

Authors' response: The authors prefer to keep it in the supplement. To address the reviewer's concern, we now rephrased the sentences in the page16508 lines 1-3 as:

Original: "The lower bound of n_s value (10^6 m^{-2}) was set based on the minimum n_s observed during AIDA expansions. The method used to constrain the n_s-isolines above 100% RH_{ice} as discussed in the supplemental material (Fig. S3)."
→
Modified: "The lower bound of n_s value (10^6 m^{-2}) was set based on the minimum n_s observed during AIDA expansions. Since the certain regions of n_s-isolines (i.e., $n_s < 7.5 \times 10^{10}$ m^{-2}; blue lines in Fig. 2) can submerge below ice saturation, the correction was applied to shift them and maintain all isolines above 100% RH_{ice}. The procedure to constrain n_s to >100% RH_{ice} is described in the supplement (Fig. S3)."

Reviewer's comment: Page 16508 lines 12-17 (regarding Figure 4b) Why using a third degree polynomial if it does not represent the experimental work?

Authors' response: In later sections (i.e., Simulation A vs. Simulation B in Figs. 5, 6 and 7 in Sect. 3.4), we demonstrate that the third degree polynomial fit parameterization yield similar simulation results (with respect to yielded ice crystal concentration) compared to the interpolated parameterization. We intended to introduce this fit owing to its model friendly aspect.

Reviewer's comment: Page 16509 first paragraph The whole section is not clear. It is not clear, which figure represent figure 4b? Some of the sentence needs clarification as lines 14-20. There is hardly reference to figure 6.

Authors' response: To clarify our study cases, we have modified and updated the texts in the following sections:

Page 16509 lines 9-13:

Original: "These include the pure homogeneous ice nucleation case (Simulation A), three cases with contributions from both the homogeneous and heterogeneous ice nucleation (hereafter combined case) described in Fig. 4 (Simulations B, C and D) and the simulation of the different lower boundaries of RH_{ice} (RH_i^*, Simulation D)."
→
Modified: "These include (Case 1) the pure homogeneous ice nucleation case, (Case 2-4) cases with contributions from both homogeneous and heterogeneous ice nucleation (hereinafter referred to as the combined case) described in Fig. 4a-c (corresponding to Simulations A, B and C) and (Case 5) the simulation of the different lower boundaries of RH_{ice} (RH_i^*, Simulation D)."

Page 16509 lines 18-20:

Original: "The differences between the four parameterizations used in this study are small for both the combined cases and the pure heterogeneous cases."
→
Modified: "The differences between the three parameterizations derived from AIDA measurements, corresponding to Simulations A, B and D, are small for both the combined case and the pure heterogeneous ice nucleation case as presented in Fig. 6."

Page 16509 line 25:

Original: "The three parameterizations have largest differences…"
→
Modified: "The three parameterizations (i.e., Simulations A, B and D) have largest differences…"

Reviewer's comment: Discussions: The first paragraph is not so clear, the SCF was mentioned only briefly in secession 3.2. I recommend the authors to rewriting this paragraph again.

Authors' response: We now updated the first paragraph on the page 16511:

"As described in the previous section (Sect. 3.1), deposition mode freezing cannot solely explain the n_s-isoline observation below water saturation (-50 ˚C < T < -36 ˚C in Fig. 2). Although we presumed that SCF acts as a subset of immersion freezing and plays an important role in this region, further insight and evidence of SCF beyond cloud simulation chamber observations are required to correctly understand the contributions of both homogeneous and heterogeneous nucleation. High-resolution microscopic techniques with an integrated continuous cooling setup are needed to visualize the freezing process of a single particle and to fully understand the complex freezing processes involved in SCF on particle surfaces."

We feel the definition of SCF given in Sect. 3.1 (page 16505 lines 14-25) is sufficient and no repetitive discussion is necessary.

Reviewer's comment: Page 16511 lines 21-23 Not all the points on figure 3 match the hematite particles therefore I do not think it is correct to assume that all dust will behave in the same way is hematite particles.

Authors' response: To address the referee's concern, we now rephrased the related section.

Page 16511 lines 21-23:

Original: In fact, comparison between our AIDA n_s-based parameterization with hematite particles and *Möhler et al*. (2006) with ATD and SD2 (Fig. 3a) provides indication on the validity of the assumption to treat all dust as hematite in deposition mode."
→
Modified: "In fact, comparison between our AIDA n_s-based parameterization with hematite particles and *Möhler et al*. (2006) with ATD and SD2 (Fig. 3a) suggests that hematite has similar ice nucleation efficiency, inferred by n_s, as dust. The comparison between the observed profile of ice crystal number concentrations and the simulated ones (Figs. 5 and 6) also suggests the validity of the new parameterizations. These premises must be further examined in comparing to atmospherically relevant substrates (fresh and aged ones) and their ice nucleation activities in laboratory settings. In situ INP measurements, such as the number concentration and the types of INPs, at the upper troposphere can also help to constrain the parameterizations."

Reviewer's comment: Table 1:
Organize the table in a way that will be easier on the reader, for example based on *T* from warm to cold *T* or particle size.

Authors' response: Table 1 is now organized based on T(Evaluated n_s) - from low to high T(Evaluated n_s).

Table 1. Summary of aerosol measurements and AIDA ice nucleation experiments. All HALO experiments are from *Skrotzki et al.* (2013).

	Aerosol Measurements			Ice Nucleation Measurements				
Experiment ID	Hematite Diameter, nm	Total Number Conc., cm^{-3}	Total Surface Conc., $\mu m^2\ cm^{-3}$	Examined T Range, °C	Examined RH_{ice} Range, %	Evaluated n_s, m^{-2}	T(Evaluated n_s), °C	RH_{ice}(Evaluated n_s), %
HALO05_24	200	115.0	14.4	-76.1 to -81.9	100.6 to 164.8	10^{11}	-78.2	136.4
HALO04_09	500	112.5	26.9	-75.8 to -80.1	100.3 to 149.8	10^{11}	-77.5	128.3
HALO04_05	500	142.2	30.9	-61.8 to -65.5	100.2 to 135.6	10^{11}	-62.6	111.1
HALO05_18	200	161.9	21.8	-60.3 to -65.2	100.1 to 124.5	10^{11}	-60.8	106.0
HALO06_22	200	145.7	19.2	-50.2 to -53.9	100.3 to 123.4	10^{11}	-50.7	106.7
HALO06_21	200	245.0	32.9	-50.3 to -53.8	100.4 to 115.8	10^{11}	-50.5	102.2
INUIT01_26	1000	342.1	749.0	-41.0 to -47.1	100.2 to 103.9	10^{10}	-41.2	102.2
HALO06_20	200	168.7	22.4	-39.8 to -44.4	100.4 to 128.8	10^{10}	-40.7	111.3
HALO06_19	200	283.0	42.9	-39.7 to -44.5	100.2 to 121.6	10^{10}	-40.6	109.2
INUIT04_08	1000	193.0	647.0	-39.3 to -45.4	100.0 to 113.2	10^{10}	-40.4	110.1
INUIT04_10	1000	161.7	546.6	-37.5 to -43.7	100.0 to 124.1	10^{10}	-40.1	123.3
INUIT01_30	1000	414.5	889.7	-34.6 to -42.0	100.2 to 127.1	2.5×10^{8}	-37.0	122.8

Reviewer's comment: Please add to the table a column that will give information on which of experiments were taken from Skrotzki et al. (2013) and which one from Hiranuma et al. (2014) etc.

Authors' response: We have updated the table text as "Table 1. Summary of aerosol measurements and AIDA ice nucleation experiments. All HALO experiments are from *Skrotzki et al*. (2013).". Further information is given in text on the page 16503 lines 13-17.

Reviewer's comment: No information regarding how the evaluated n_s values of T and RH is mentioned in the text, why and how these value were chosen?

Authors' response: We thank the reviewer for pointing out this error. We have added information regarding "evaluated n_s, T and RH_{ice}", which were used to verify size-independency of the n_s values (page 16503 lines 18-25), in the following sections:

Page 16503 line 21

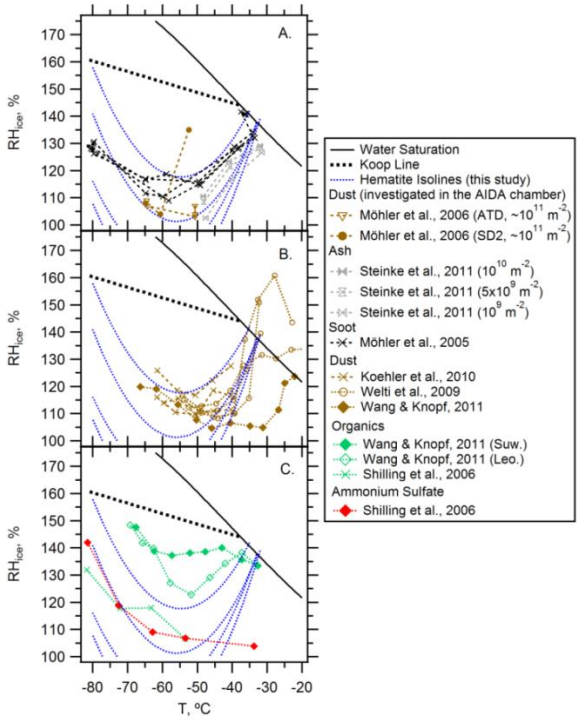
Original: "the n_s values"
→
Modified: "the evaluated n_s values"

Page 16503 lines 22-23

Original: "(i.e., INUIT04_08, 1000 nm, HALO06_19,200 nm, and HALO06_20, 200 nm)"
→
Modified: "(see corresponding RH_{ice} and T at Evaluated n_s in Table 1 for INUIT04_08, 1000 nm, HALO06_19, 200 nm, and HALO06_20, 200 nm)"

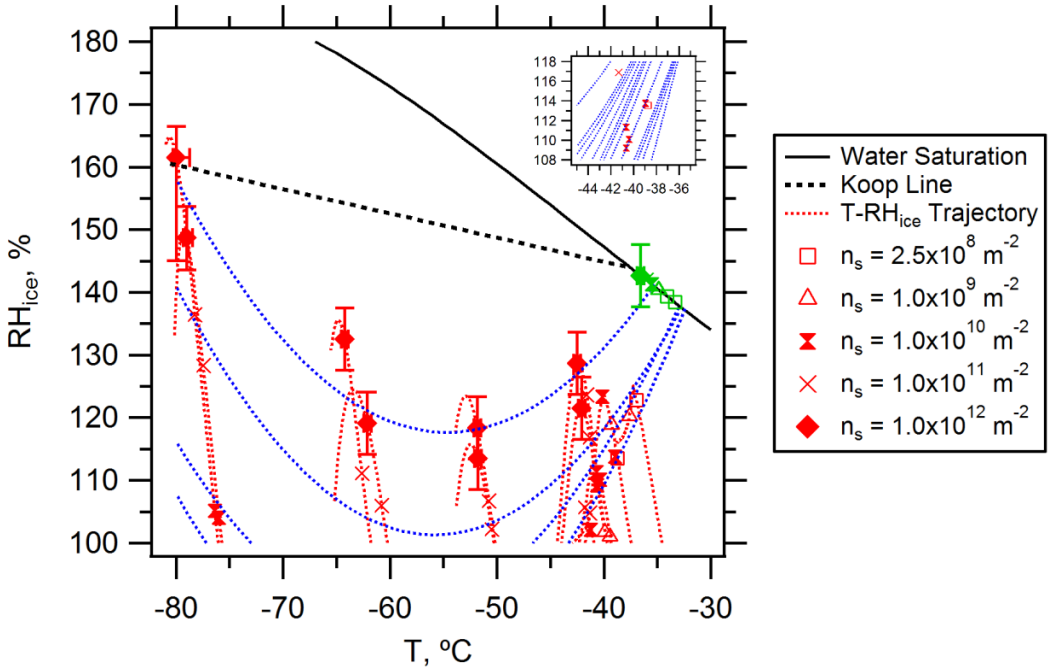
Reviewer's comment: Figure 2 and 3
It will be better to increase the figures size on the expend of the legend which take too much space of the figure, which does not allow to see all the values.

Authors' response: Modified with smaller symbols.



Reviewer's comment: Figure 2
It is very hard to distinguish between the different values; it might be the red color, especially around -40°C where the points are overlapping one another. Please mark them in a different marker or color. Please also mark in a different color the immersion freezing measurement so it will be easy to identify them from the one from this work (mentioned also on the page 16504 lines 23).

Authors' response: We modified Figure 2 with smaller symbols as well as its caption as:



Original caption: "…The data on the water saturation line represents the previously reported results of immersion freezing (*Hiranuma et al*., 2014)."
→
Modified: "…The data indicated by green color on the water saturation line represent the previously reported results of immersion freezing (*Hiranuma et al*., 2014)."

Reviewer's comment: Figure 5 and 6
It is very hard to distinguish between some of the lines. Perhaps using another color indicator or showing only pressure of 0-600 will highlight the differences. An addition line which will represent observation will be a nice addition for this plot, something that will represent the observation to show how the new parameterization is compared to it.

Authors' response: This is a good suggestion. We added the observed profiles of ice crystal number concentrations in the figure. The observational data were collected over the SGP site on eight days of April 2010 during the Small PARTicles In CirrUS (SPARTICUS) campaign (*Zhang et al*., 2013). See the figure 5&6 captions for details. Please note that for the aircraft measurements, we only consider samples when ice crystal number is above the detection limit (*Zhang et al*., 2013). Accordingly, for modeled profiles we replaced the grid-box mean values with the in-cloud values.

Reference:

Zhang, K., Liu, X., Wang, M., Comstock, J. M., Mitchell, D. L., Mishra, S., and Mace, G. G.: Evaluating and constraining ice cloud parameterizations in CAM5 using aircraft measurements from the SPARTICUS campaign, Atmos. Chem. Phys., 13, 4963-4982, doi:10.5194/acp-13-4963-2013, 2013.

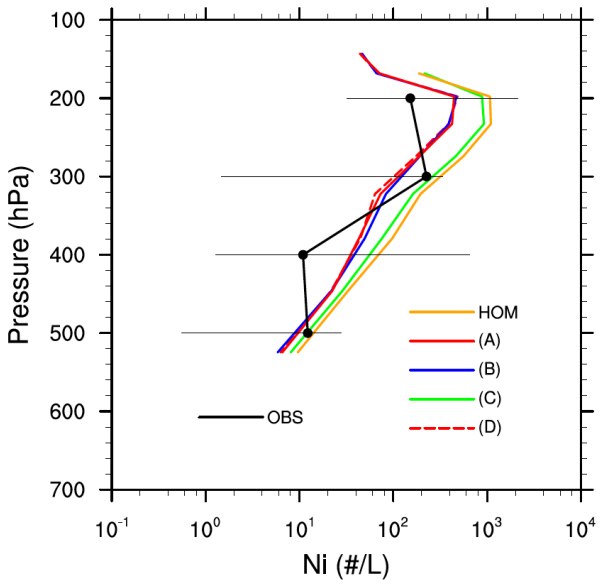


Figure 5. Monthly mean profiles of the simulated in-cloud ice crystal number concentrations ($Ni \sim N_{ice}$) over the ARM SGP site. The four cases shown in the figure include the pure homogeneous ice nucleation case (HOM) and four combined (heterogeneous + homogeneous) ice nucleation cases: (A) AIDA Interp. + Homogeneous; (B) AIDA Fit + Homogeneous; (C) P13 + Homogeneous; and (D) AIDA Interp. (RH_i^*=105%) + Homogeneous. Black dots show the observed mean profile of *Ni*. Left and right ends of the horizontal bars indicate the 10th and 90th percentiles of the observed *Ni* values at each pressure level.

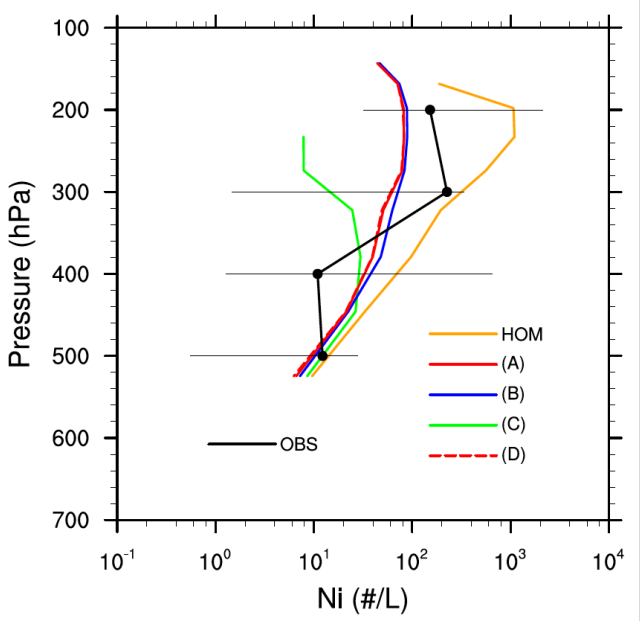


Figure 6. Monthly mean profiles of the simulated in-cloud ice crystal number concentrations ($Ni \sim N_{ice}$) over the ARM SGP site. The four cases shown in the figure include the pure homogeneous ice nucleation case (HOM) and four pure heterogeneous ice nucleation cases: (A) AIDA Interp.; (B) AIDA Fit; (C) P13; and (D) AIDA Interp. (RH_i^*=105%). Black dots show the observed mean profile of *Ni*. Left and right ends of the horizontal bars indicate the 10th and 90th percentiles of the observed *Ni* values at each pressure level.

We added the following sentence on the page 16509 line 13 after "… Simulation D).":

"In addition, the observed profile of ice crystal number concentrations is also shown in comparison to the simulations in Fig. 5. The observational data were collected over the SGP site on eight days of April 2010 during the Small PARTicles In CirrUS (SPARTICUS) campaign (*Zhang et al*., 2013)."

We added the following sentence on the page 16509 line 18 after "… heterogeneous nucleation.":

"The observed mean profile of in-cloud ice crystal number concentrations is in agreement with the simulated ones."

We also modified the sentences on the page 16511 lines 20-23:

Original: In fact, comparison between our AIDA n_s-based parameterization with hematite particles and *Möhler et al*. (2006) with ATD and SD2 (Fig. 3a) provides indication on the validity of the assumption to treat all dust as hematite in deposition mode."
→
Modified: "In fact, comparison between our AIDA n_s-based parameterization with hematite particles and *Möhler et al*. (2006) with ATD and SD2 (Fig. 3a) suggests that hematite has similar ice nucleation efficiency, inferred by n_s, as dust. The comparison between the observed profile of ice crystal number concentrations and the simulated ones (Figs. 5 and 6) also suggests the validity of the new parameterizations. These premises must be further examined in comparing to atmospherically relevant substrates (fresh and aged ones) and their ice nucleation activities in laboratory settings. In situ INP measurements, such as the number concentration and the types of INPs, at the upper troposphere can also help to constrain the parameterizations."

Reviewer's comment: Consider changing figure 5 and 6 to one figure as 5a and b, it will be easier for the reader to understand the comparison of the two.

Authors' response: We use another alphabetical sub-category (Simulations A-D), and we feel introducing another one will be confusing. We now modified the text and introduced Figure 6 explicitly at the reviewer's prior suggestion. So we would like to keep figure numbers as is.

Additional revision: In addition to addressing the reviewer's comments, other editorial corrections (major and non-miscellaneous ones) were made as below.

Since a temperature is a numerical measure, we would like to replace "warm or cold" with "high or low": page 16494 line 14, page 16494 line 16, page 16494 line 21, page 16500 line 21, page 16504 line 16, page 16511 line 13.

Abstract

Page 16494 lines 4-5: "critical in order to" → "important to"
Page 16494 line 8: "water saturated conditions that were realized" → "water subsaturated conditions. These conditions were achieved"

Introduction

Page 16495 line 2: "constitute" → now rephrased to "represent a"

Page 16495 lines15-19: now reads, “Briefly, deposition mode induces ice formation when water vapor is directly deposited onto the INP, immersion and condensation freezing can induce ice formation when freezing is initiated by the INP immersed within the supercooled droplet or solution droplet, and contact freezing can initiate at the moment when an INP comes into contact with a supercooled droplet.”
Page 16495 line 21: “is accounted for by” → now reads, “results from”
Page 16495 lines 22-24: “However, representativeness of freezing mechanisms in cirrus clouds is still ambiguous (e.g., *Sassen and Khvorostyanov*, 2008).” → now reads, “However, freezing mechanisms in cirrus clouds are still uncertain (e.g., *Sassen and Khvorostyanov*, 2008).”
Page 16496 line 19: “descriptions such as *Meyers et al*. (1992, henceforth M92)” → now reads, “descriptions given in *Meyers et al*. (1992, hereinafter referred to as M92)”
Page 16497 lines 4-6: now reads, “They showed that the heterogeneous INP number concentration obtained from a CNT-based parameterization is typically higher by several factors than that of Phillips’s parameterization under identical test conditions”
Page 16497 lines 19-20: “Herein, as part of the Ice Nucleation research UnIT (so called INUIT), we conducted a comprehensive investigations on examining the” → now reads, “Within the framework of Ice Nucleation research UnIT (INUIT), we comprehensively investigated”
Page 16497 lines 26-28: “Applications of the fitted n_s parameterization derived from these measurements to atmospheric modeling simulations were also performed.” → now reads, “In addition to developing the new dust parameterizations from these AIDA measurements (Sects. 3.1-3.3), the fitted n_s parameterization was also applied to atmospheric modeling simulations (Sect. 3.4).”

Method

Page 16498 lines 7-10: “well defined surface area, and are therefore good to investigate and relate T-RH_{ice} dependent ice nucleation efficiency to surface area (*Hiranuma et al*., 2014).” → now reads, “well-defined surface area. Hence, they are suited well for investigating T-RH_{ice}-dependent ice nucleation efficiency and relating it to the surface area (*Hiranuma et al*., 2014).”
Page 16500 line 19: “complementally covering” → now reads, “that complement each other and cover”
Page 16501 lines 12-14: “was used to simulate ice formation of background particles at T > -36°C. In specific, the aerosol-independent M92 scheme was used in this study. A combination of these parameterizations was advantageous…” → now reads, “was used to simulate ice formation of background particles at T > -36°C, namely, the aerosol-independent M92 scheme. These parameterizations were combined…”
Page 16501 line 18: “To better understand how the AIDA n_s-based parameterization compares to” → now reads, “To better understand to what an extent the AIDA n_s-based parameterization differs from”
Page 16502 lines 4-8: now reads, “The single column model resembles a single column of a GCM and can be derived from observations or model output. The complex feedbacks between the simulated column and other columns due to large-scale dynamics, except cloud detrainment from shallow and deep convection, are not considered. Therefore, the single column model is an ideal tool for testing ice cloud parameterizations.”
Page 16502 lines 20-21: “More specifically, COSMO is the high resolution limited-area model, which allows an assessment of clouds” → now reads, “COSMO is the high-resolution limited-area model to assess clouds”

Results

Page 16503 lines 13-14: “In the present study we also used the AIDA results reported in *Skrotzki et al*. (2013) and reconciled to n_s values” → now reads, “In addition, we used the AIDA results reported by *Skrotzki et al*. (2013) and reconciled them with the n_s values”

Page 16503 lines 25-26: “Further, an advantage of using 1000 nm diameter hematite particles was that, being of , comparatively larger surface area,” → now reads, “The advantage of using 1000 nm diameter hematite particles was that, due to their comparatively larger surface area,”
Page 16505 line 16: “Supportively,” → now reads, "To support this,"
Page 16505 line 21: “SCF may have plausible relevance” → now reads, “SCF may be of relevance”
Page 16507 lines 14-16: now reads, “As seen in Figure 3, the results from previous studies suggest the necessity of increasing RH_{ice} to maintain a constant n_s value below T ~-55°C. They also indicate that nucleation may be triggered by SCF…”
Page 16508 lines 7-8: “are necessary in order to” → now reads, “are required to”
Page 16508 lines 17-20: now reads, “The third approach (Fig. 4c) consisted in applying the equivalent n_s for deposition nucleation of hematite particles parameterized using the method introduced by *Phillips et al*. (2008 and 2013). In detail, we characterized the nucleation activity…”
Page 16509 lines 13-14: “We observe that ice crystal formation from” → now reads, “The results of our simulations suggests that ice crystal formation due to”
Page 16509 line 24: “balances” → now rephrased to “compensates”
Page 16510 line 21: “This enables us to estimate” → “This segregation allows for an estimation of”

Discussion

Page 16511 line 14: “and deserves more attention.” → now reads, “, and this highlights the need for further investigation.”
Page 16511 line 24 – Page 16512 line 2: now reads, “Finally, to further develop more atmospherically relevant parameterizations other than the fit-based parameterization with artificial test aerosol, the relationship between $1/T$ and $\ln S_{ice}$ for a constant nucleation rate or n_s based on the CNT can be analyzed (i.e., Eqns. A10-A11 in *Hoose and Möhler*, 2012). In this way, the composition specific $n_s(T\text{-}S_{ice})$ values, where the transition from SCF to deposition nucleation (or vice versa) occurs, may be better defined and can be then be used as an inexpensive model friendly parameterization.”

Conclusion

Page 16512 lines 21-23: “Elaborating observed suppression of SCF near water saturation and enlightening the physical processes on observed transitions in nucleation modes for various types of atmospheric particles are important as future works.” → now reads, “The observed active SCF near water saturation and physical processes at the transitions of nucleation modes still remain to be studied in detail for various types of atmospheric particles.”
Page 16513 lines 1-5: now reads, “Our new parameterization revealed a minimum deviation of N_{ice} values estimated by SCAM5 at minimum RH_{ice} values for ice formation (100 or 105%) compared to COSMO. This deviation suggests different sensitivities of the model to the lower bound of the RH_{ice} value owing to the presence of the model-resolved supersaturation…”
Page 16513 line 7: “suppression in ice nucleation” →now rephrased to “more ice nucleation”

References

Pages 16514-16519: All available doi numbers are now added in references.
Page 16517: Mishra et al., which is a study on optical properties, has been excluded.

Referee #2

Reviewer's comment: 1) Justification for using hematite to represent "atmospheric dust" at the start of the paper, or stating this as a point of evaluation in this manuscript.

Authors' response: We have updated the last paragraph of the introduction section with some more clarification on why we selected hematite particles as a test substrate as well as a proxy of atmospheric dust in this study.

We chose hematite because it is a good model substance to infer n_s values over a wide T and RH_{ice} range (i.e., page 16500 lines 9-12 and lines 16-21 and Sect. 3.3). The atmospheric relevance was demonstrated by comparing the model hematite results with more relevant desert dust aerosol results (page 16506 lines 20-25).

In this work, we demonstrated that the formulated hematite n_s-isolines are reasonably comparable to that of desert dust samples, previously studied in AIDA (i.e., ATD and SD2; *Möhler et al*., 2006), at $n_s \sim 10^{-11}$ m^{-2} (Fig. 3A and associated text on the page 16506 lines 20-25; page 16507 lines 20-22). Nonetheless, we feel it is important to point out and re-emphasize that this work is a conceptual study with laboratory-synthesized hematite particles as a model aerosol for deposition ice nucleation over a wide range of T and RH_{ice}. In this study, we did not attempt to conclude how much hematite content contributes to ice formation in cirrus clouds. For clarity, we have added the following sentence on the page 16498 line 3 after "…existing parameterizations.":

"It is important to note that the purpose of the current study is to perform a conceptual study with laboratory-synthesized hematite particles as a model aerosol for deposition ice nucleation, over a wide range of T and RH_{ice}, but not to quantify how much hematite content contributes to ice formation in cirrus clouds."

Reviewer's comment: 2) Recognizing the fact that P13 is at least inclusive of some atmospheric INP data, so the mystery of it not agreeing with lab data below -40 ˚C is neither a new discovery, nor is it explained by new data presented herein. As an explanation of lower temperature discrepancies with laboratory dust data, P13 offered that coatings are common and may limit deposition nucleation. This may not be the full reason, but this paper needs to better explain or speculate as to why the modeling community should use the new parameterization in preference to P13.

Authors' response: The referee makes a good point in stating the fact that we are not working on the premise that there is one true dust-derived $n_s(T, S_i)$ and thus we cannot conclusively say which parameterization does better job for predicting/estimating dust-derived INPs. To address referee's concern, we modified the relevant texts and also soften the tense of P13 vs. our new parameterization in the following sections:

Page 16510 lines 24-27:

Original: "Our result shows less ice crystal formation with P13 compared to the AIDA n_s-isoline-based parameterization. The observed discrepancy between the new parameterization and P13 may largely reflect the difference in parameterization based on lab- or field data. Furthermore, strong supersaturation dependence of n_s at cold T was not well constrained by P13, presumably due to a limited amount of data."
→
Modified: "Our results show diversity between P13 and the AIDA n_s-isoline-based parameterization. Ice crystal formation was less for P13 and more for the new parameterization. A possible explanation for the observed deviation may be due to the difference in parameterization based on lab- or field data. For

instance, atmospheric aging and processing (i.e., surface coating and associated heterogeneous surface reactions) may have altered ice-nucleating propensity and limited deposition nucleation of dust-derived INPs in the P13 parameterization for the field data-derived parameterization as discussed in *Phillips et al*. (2008)."

Page 16511 lines 14-23:

Original: "Substantial differences between the empirical approach of P13 and our parameterization developed in this study are presumably attributed to the difference in lab- or field data, highlighting the need for further characterizations of atmospherically relevant substrates and their ice nucleation activities in laboratory settings. Nevertheless, *Niemand et al*. (2012) demonstrated that different dusts exhibit similar n_s in immersion mode freezing and perhaps such a similarity remains true for deposition mode ice nucleation. In fact, comparison between our AIDA n_s-based parameterization with hematite particles and *Möhler et al*. (2006) with ATD and SD2 (Fig. 3a) provides indication on the validity of the assumption to treat all dust as hematite in deposition mode."
→
Modified: "However, it should be noted that there is some evidence for the atmospheric relevance and applicability of the new parameterization. First of all we demonstrated that the new n_s parameterization based on the experiments with hematite particles agrees well with previous literature results for mineral dust aerosol (e.g., *Möhler et al*, 2006; *Welti et al*., 2009; *Köhler et al*., 2010). Second, *Niemand et al*. (2012) demonstrated that different dusts exhibit similar n_s in immersion mode freezing and perhaps such a similarity remains true for the deposition mode ice nucleation of desert dusts. Lastly, the comparison between the observed profile of ice crystal number concentrations and the simulated ones (Figs. 5 and 6) also suggests the validity of the new parameterization. These premises must be further examined in comparing to atmospherically relevant substrates (fresh and aged ones) and their ice nucleation activities in laboratory settings. In situ INP measurements, such as the number concentration and the types of INPs, at the upper troposphere can also help to constrain the parameterization."

Page 16509 lines 3-6:

Original: "To conclude, the discrepancy between a new parameterization and P13 is substantially large, and the consequence of this discrepancy towards cloud properties is demonstrated in the following section."
→
Modified: "AIDA n_s-isoline-based parameterization suggests strong supersaturation dependence of n_s at low *T*. Observed diversity between a new parameterization (Figs. 4a and 4b) and P13 (Fig. 4c) may result in different ice crystal forming propensities and may predict different cloud properties. The potential consequence of observed diversity is demonstrated using conceptual models and discussed in the following section."

In addition, we also moved the following discussion of upper and lower *T* boundary (originally page 16508 line 24- page 16509 line 3) and inserted to the page 16508 line 17, after "… shown in Fig. 4b." since these boundaries are more relevant to n_s fit presented in Fig. 4b:

"Note that the upper temperature boundary of -36 ˚C was assigned as the interface between immersion mode- and deposition mode ice nucleation (*Hiranuma et al*., 2014), and the lower boundary of −78 ˚C is the limit introduced by interpolating the hematite-isoline curves."

Reviewer's comment: 3) Relatedly, the parameterization seems to drastically limit ice supersaturation at low temperatures in atmospheric situations, while still producing ample ice crystals. Some discussion of the realism of that result should be added.

Authors' response: The main reason for the higher ice number concentrations despite lower supersaturations is that our laboratory-based parameterization yields higher values of n_s at e.g. at ~110% than the P13 parameterization gives at e.g. ~130%. In addition, also with the new parameterization, supersaturations up to 120% are reached occasionally. One possible explanation for this simulated high ice formation is the contribution of updrafts, where supersaturation conditions are maintained. Nevertheless, since atmospheric measurements of supersaturations in cirrus regions seem still uncertain, and high atmospheric supersaturations are still under debate (e.g., *Peter et al*., 2006; *Krämer et al*., 2009), we cannot say for certain about the realism of this feature and, therefore, prefer no discussion in the current manuscript.

References:

Peter, T., Marcolli, C., Spichtinger, P., Corti, T., Baker, M. B. and Koop, T.: When dry air is too humid, Science, 314, 1399-1402, doi:10.1126/science.1135199, 2006.

Krämer, M., Schiller, C., Afchine, A., Bauer, R., Gensch, I., Mangold, A., Schlicht, S., Spelten, N., Sitnikov, N., Borrmann, S., de Reus, M., and Spichtinger, P.: Ice supersaturations and cirrus cloud crystal numbers, Atmos. Chem. Phys., 9, 3505-3522, doi:10.5194/acp-9-3505-2009, 2009.

Reviewer's comment: Lines 21-24, but also a general comment: The major question this begs is why we should deem that hematite is representative for cirrus, and why we should deem that the lab studies are relevant for atmospheric particles? This seems like a topic in itself.

Authors' response: We did not select hematite because it is a major atmospheric dust component in cirrus clouds, but we chose hematite because it is a good model substance to infer n_s values over a wide T and RH_{ice} range (discussed above). The compatibility between hematite particles and desert dust particles has already been demonstrated in the first version of our manuscript (i.e., Fig. 3A and associated text on the page 16506 lines 20-25; page 16507 lines 20-22).

To further clarify, we have updated the abstract. Modifications are performed to the old text as follows:

Page 16494 lines 5-7:

Original: "The surface-scaled ice nucleation efficiencies of hematite particles, inferred by n_s, were derived from AIDA…"
→
Modified: "The ice nucleation active surface-site density (n_s) of hematite particles, used as a proxy for atmospheric dust particles, were derived from AIDA…"

Page 16494 lines 16-19:

Original: "We implemented new n_s parameterizations into two cloud models to investigate its sensitivity and compare with the existing ice nucleation schemes towards simulating cirrus cloud properties."
→
Modified: "We implemented the new hematite-derived n_s parameterization, which agrees well with previous AIDA measurements of desert dust, into two conceptual cloud models to investigate their sensitivity to the new parameterization in comparison to existing ice nucleation schemes for simulating cirrus cloud properties."

Reviewer's comment: The parameterization you choose to compare to is constrained by measurements of atmospheric IN, and it notes already that the results are inconsistent with cloud chamber data for pure mineral dusts. Hence, it should be understood that this is not a new story, but a remaining mystery of sorts. This paper may shed some additional light on it due to the fact that it is hard to imagine a different situation for any pure dust aerosol, so perhaps the atmospheric measurements had some unresolved issues. Nevertheless, this paper needs to state more clearly what its goals are besides the new dust parameterization.

Authors' response: For clarity, we have modified the following sentence:

Page 16497 lines 26-28: "Applications of the fitted n_s parameterization derived from these measurements to atmospheric modeling simulations were also performed." → now reads, "In addition to developing the new dust parameterizations from these AIDA measurements (Sects. 3.1-3.3), the fitted n_s parameterization was also applied to atmospheric modeling simulations (Sect. 3.4)."

In addition, we have added the following sentence on the page 16498 line 3 after "…existing parameterizations.":

"It is important to note that the purpose of the current study is to perform a conceptual study with laboratory-synthesized hematite particles as a model aerosol for deposition ice nucleation, over a wide range of T and RH_{ice}, but not to quantify how much hematite content contributes to ice formation in cirrus clouds."

Reviewer's comment: Page 16496, lines 8-10: Regarding this statement, I do not understand what is meant by Welti et al. introducing this idea. The concept of a freezing mechanism of solutions on particles at below water saturation has a history in going back to Zuberi et al. (2002), Archuleta et al. (2005) and so forth. Welti et al. referenced this earlier work (exploring it in the context of CNT), as does the present paper later in the manuscript.

Authors' response: We thank the reviewer's suggestion for these useful literatures (*Zuberi et al*., 2002; *Hung et al*., 2003; *Archuleta et al*., 2005) and are now added on the page 16496 lines 8-10:

"Recently, *Welti et al*. (2014) introduced the relevance of soluble components of mineral dust (i.e., Fluka kaolinite) to condensation freezing below water saturation."
→
"Previous laboratory studies introduced the concept of a freezing mechanism of solutions on particles at below water saturation (*Zuberi et al*., 2002; *Hung et al*., 2003; *Archuleta et al*., 2005). More recently, *Welti et al*. (2014) explored the relevance of soluble components of mineral dust (i.e., Fluka kaolinite) to condensation freezing below water saturation in the context of classical nucleation theory (CNT)."

The CNT abbreviation is now used in the page 16496 line 24:

"Besides, classical nucleation theory (CNT)-based" → "Besides, CNT-based"

Added references:

Archuleta, C.M., DeMott, P.J., and Kreidenweis, S.M.: Ice nucleation by surrogates for atmospheric mineral dust and mineral dust/sulfate particles at cirrus temperatures, Atmos. Chem. Phys., 5, 2617-2634, doi:10.5194/acp-5-2617-2005, 2005.

Zuberi, B., Bertram, A.K., Cassa, C.A., Molina, L.T., and Molina, M.J.: Heterogeneous nucleation of ice in $(NH_4)_2SO_4$−H_2O particles with mineral dust immersions, Geophys. Res. Lett., 29, 1504, doi:10.1029/2001GL014289, 2002.

Hung H.-M., Malinowski, A., and Martin, S. T.: Kinetics of heterogeneous ice nucleation on the surfaces of mineral dust cores inserted into aqueous ammonium sulfate particles, J. Phys. Chem. A., 107, 1296–1306, doi: 10.1021/jp021593y, 2003.

Reviewer's comment: Page 16497, lines 7-9: There is no doubt that there is a need for better parameterizations for cloud models, but an issue not mentioned is if one can be certain that laboratory measurements are representative for the atmosphere. So actually, what this seems to argue for are more and better in situ measurements. Apparently, these may not be as straightforward as setting conditions in instruments and measuring INP. At least, I think the authors should be open to all possibilities.

Authors' response: The reviewer makes a good point. The efforts to constrain model uncertainties from both in situ measurements and lab experiments are important and might be complementary. We updated the text in the following section to address the referee's comment and to clarify our point.

Page 16497 lines 7-9:
Original: "Therefore, systematic laboratory measurements to develop water subsaturated ice nucleation parameterizations for the range of atmospherically relevant T -RH_{ice} conditions are needed to better represent ice nucleation processes in cloud models."
→
Modified: "To gain insight on what triggers such deviation and to constrain model uncertainties, more and better in situ measurements are necessary (*Cziczo and Froyd*, 2014). In specific, identifying and quantifying sources, global spatio-temporal distribution and mixing-state of INPs might support to reduce model assumptions. In parallel, systematic laboratory measurements are indeed needed to develop water subsaturated ice nucleation parameterizations for the range of atmospherically relevant T-RH_{ice} conditions for a better representation of ice nucleation processes in cloud models and to support in situ measurements."

Added reference

Cziczo, D.J. and Froyd, K.D.: Sampling the composition of cirrus ice residuals, Atmospheric Research, 142, 15−31, doi: 10.1016/j.atmosres.2013.06.012, 2014.

Reviewer's comment: Page 16498, line 6: What is the basis for selecting hematite particles as a proxy in this case?

Authors' response: Their uniform chemico-physical properties, such as shape (cubic), chemical composition (Fe_2O_3) and size (~200, ~500 and ~1000 nm diameter), which makes them as suitable test substrates to characterize ice nucleation efficiency (n_s) at a wide temperature range (i.e., page 16503 lines 18-25).

We have made the following minor modification on text (page 16498 line 6):

Original: "Laboratory-generated cubic hematite particles…"
→
Modified: "Laboratory-generated cubic hematite particles that have homogeneous chemico-physical properties…"

Reviewer's comment: Page 16501, lines 13-14: I am a bit surprised at the selection of use of the aerosolindependent M92 scheme to represent heterogeneous nucleation when applying a dust parameterization for cirrus levels. Can you please state if the values predicted by M92 are capped at some low temperature, or is it extended far beyond its usual valid (where data were represented in the original paper) temperature range? Is there a reason that the immersion freezing parameterization for hematite was not joined to the one for deposition?

Authors' response: We used the M92 parameterization only for T >-36 ˚C (discussed above; see the authors' response to the comment from reviewer 1 on the page 4). Immersion freezing is considered as a part of SCF (details discussed below) and incorporated in our n_s-isoline-based parameterization. Use of the M92 parameterization for T>-36°C is necessary in the model applications because hematite is a rather inefficient ice nucleus in this temperature range, where other INP (e.g., biological ice nuclei, feldspars, etc.) are likely to contribute significantly to ice formation. If the M92 parameterization was not used in this range, too much supersaturated air and supercooled water would be transported to cirrus levels, and the impact of INP in cirrus clouds would be overestimated.

Reviewer's comment: Page 16501, lines 21-24: Further clarification is also needed regarding the use of P13. First, does the parameterization allow initialization otherwise in accord with the present parameterization in terms of the numbers of dust particles? Second, even if ice nucleation below water saturation is used for mineral dust particles only, does not this create some likely overlap with the M92 scheme? That is, I would expect the P13 formulation to make ice prior to homogeneous freezing temperatures, where the M92 formulation is already generating ice.

Authors' response: Since we re-formulated the P13 parameterization in terms of n_s (Fig. 2c), P13 was implemented in the same way (i.e., same T and RH_{ice} ranges) as the AIDA-derived parameterization by assuming 200 dust particles per L with the identical aerosol surface area. With our approach, also no ice formation was allowed in the regime covered by M92. This makes the comparison of two parameterizations consistent, using M92 at T > -36°C.

Reviewer's comment: Page 16502, line 22: Is a time step of 20s reasonable or sufficient for cirrus simulations?

Authors' response: In contrast to a parcel model that actively resolves the depletion of water vapor through heterogeneous ice formation, we use the parameterization-scheme of *Kärcher et a*l. (2006) to parameterize the processes on small time scales, such as depletion of water vapor. *Kärcher et al*. (2006) demonstrated the implementation of their scheme into a global model with much longer time steps (~30 min).

For clarity, we now added the following sentence at the end of section 2.3.2 (page 16503 line 8):

"The latter was used to parameterize the competition of water vapor between homogeneous and heterogeneous freezing"

Reference:

Kärcher, B., Hendricks, J., and Lohmann, U.: Physically based parameterization of cirrus cloud formation for use in global atmospheric models, J. Geophys. Res., 111, D01205, doi:10.1029/2005JD006219, 2006.

Reviewer's comment: Page 16504, lines 23-25: Could you say a little more about how immersion freezing data is used to "constrain" fitting curves? Because immersion freezing is requisite at the warmer

temperatures? Or because you consider SCF as a subset of immersion freezing? Yet, you have not yet introduced the concept of SCF in the paper to this point.

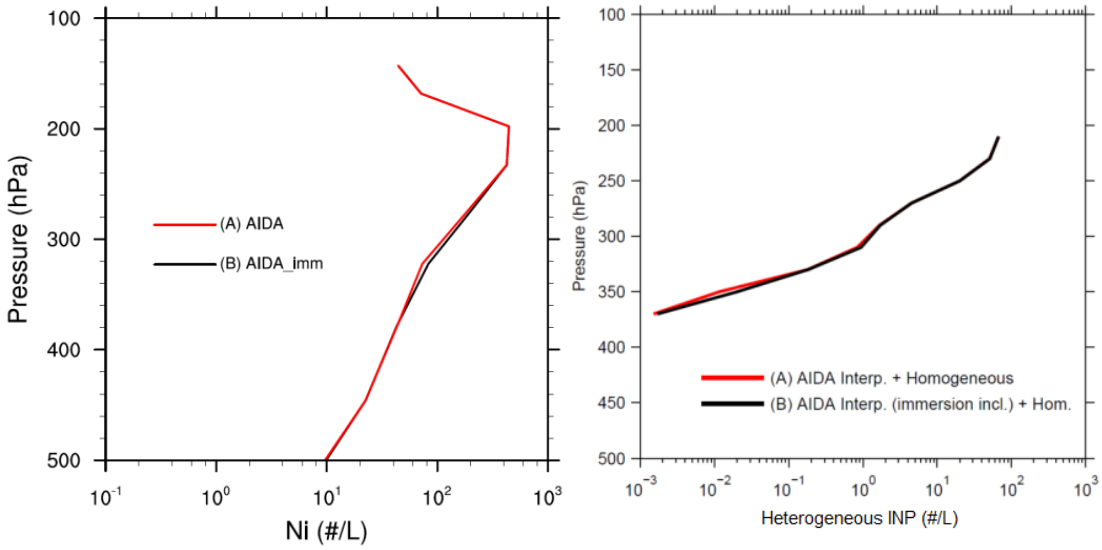
Authors' response: We thank the referee to raise this important point. We now describe how immersion freezing data are used on the page 16504 lines 23-25:

Original: "Previous AIDA measurements of immersion freezing (i.e., INUIT04_13 and INUIT01_28 from *Hiranuma et al*., 2014) are also shown and used to constrain the fitted curves."
→
Modified: "Previous AIDA results of two immersion freezing experiments (i.e., INUIT04_13 and INUIT01_28 from *Hiranuma et al*., 2014) are also shown on the water saturation line and used to constrain the fitted curves because immersion freezing is considered part of isolines. Since the n_s values presented in Fig. 3 of *Hiranuma et al*. (2014) only extends up to ~10^9 m^{-2}, the data points of higher n_s values were extrapolated based on the observed values from two measurements."

The review is correct in pointing out that SCF is considered as a subset of immersion freezing. We now updated the first paragraph on the page 16511:

"As described in the previous section (Sect. 3.1), deposition mode freezing cannot solely explain the n_s-isoline observation below water saturation (-50 ˚C < T < -36 ˚C in Fig. 2). Although we presumed that SCF acts as a subset of immersion freezing and plays an important role in this region, further insight and evidence of SCF beyond cloud simulation chamber observations are required to correctly understand the contributions of both homogeneous and heterogeneous nucleation. High-resolution microscopic techniques with an integrated continuous cooling setup are needed to visualize the freezing process of a single particle and to fully understand the complex freezing processes involved in SCF on particle surfaces."

We have evidence that both including immersion freezing data and not including them (but extrapolating the n_s-isoline fit to water saturation line) can reproduce similar (almost identical) simulation results in the simulations with SCAM5 and COSMO (please see figures below).



Extra Figure. Comparison of two parameterizations (i.e., including immersion data vs. extrapolating without immersion data) in monthly mean profiles of the simulated in-cloud ice crystal number

concentrations with SCAM5 (left) and the heterogeneous INP number concentration averaged over two days with COSMO (right).

We feel that we provide the definition of SCF given in right place (Sect. 3.1 on the page 16505 lines 14-25) and no earlier discussion is necessary.

Reviewer's comment: Page 16505, line 9: I suggest replacing "while concurrent" with "during"

Authors' response: Corrected.

Reviewer's comment: Page 16505, line 14: Considering this sentence ending, ": : :pointed to a new freezing process in this study" I believe that "point" would be more appropriate. However, there seems a basic problem in saying it is a new freezing process, when what is imagined is something much like what has been discussed explicitly in recent papers and has been alluded to in some previous ones. Should it say that these results appear to support the existence of a pore or surface freezing process, as discussed in recent literature (e.g., Marcolli , 2014). Then move on to define it as SCF, rather than PCF.

Authors' response: We agree. We now rephrased the sentence on the page 16505 lines 12-14 as:

"Therefore, other microphysical processes at the particle surface and/or perhaps even within the bulk phase may be responsible for this T -dependent behavior and these results appear to support the existence of a pore or surface freezing process, as discussed in recent literature (e.g., *Marcolli*, 2014)."

Reviewer's comment: Page 16506: I must question the semantics of what can be called "atmospheric dust particles" because I am not terribly convinced that the hematite results encapsulated by n_s fits show that they are comparable to actual atmospheric dust, but rather to soil dust samples brought into the laboratory. Are any of the referenced studies, for any temperature regime, actual measurements of atmospheric dust, rather than surrogates for such?

Authors' response: *Matsuki et al*. (2010) studied atmospheric dust particles. More specifically, the authors deduced that airborne dust residuals collected through the counter virtual impactor (*Ogren et al*., 1985) during flights in stratocumulus clouds over Niger contained hematite.

Reference:

Ogren, J. A., Heintzenberg J., and Charlson R. J.: In-situ sampling of clouds with a droplet to aerosol converter, Geophys. Res. Lett. 12, 121–124, doi: 10.1029/GL012i003p00121, 1985.

Reviewer's comment: Page 16506, line 9: "are" compared.

Authors' response: Corrected.

Reviewer's comment: Page 16506, line 16: Is "mobile" the right word for such ice nuclei counters? Mobile implies that they move, rather than the fact that they are movable or able to be installed on aircraft. Perhaps "portable"?

Authors' response: Thank you. We agree and corrected.

Reviewer's comment: Page 16508, lines 3-5: The lower bound was explained, but not the upper. What controls the upper bound, why physically does n_s remain constant up to the water saturation line, and why

presumably? It is explained rather obtusely at present. Does it mean simply that experimental data does not exist in this regime?

Authors' response: The answer is yes. Within our experimental conditions, the highest estimated n_s was ~10^{12} m^{-2} before the peak RH_{ice} (i.e., Fig. 2), even accounting for continuous increase in n_s after depletion of supersaturation (i.e., Fig. S2), and we simply did not want to extrapolate the isoline fit to 'unexplored' region.

We have now rephrased the sentence (page 16508 lines 3-5) to:

"Above the upper bound of 10^{12} m^{-2}, n_s presumably remains constant up to the water saturation line in T - RH_{ice} space (no experimental data is available in this range)."

Reviewer's comment: Page 16509: Variously here, the "three" and "four" parameterizations are mentioned. Please clarify.

Authors' response: To clarify our study cases, we have modified and updated the texts in the following sections:

Page 16509 lines 9-13:

Original: "These include the pure homogeneous ice nucleation case (Simulation A), three cases with contributions from both the homogeneous and heterogeneous ice nucleation (hereafter combined case) described in Fig. 4 (Simulations B, C and D) and the simulation of the different lower boundaries of RH_{ice} (RH_i^*, Simulation D)."
→
Modified: "These include (Case 1) the pure homogeneous ice nucleation case, (Case 2-4) cases with contributions from both homogeneous and heterogeneous ice nucleation (hereinafter referred to as the combined case) described in Fig. 4a-c (corresponding to Simulations A, B and C) and (Case 5) the simulation of the different lower boundaries of RH_{ice} (RH_i^*, Simulation D)."

Page 16509 lines 18-20:

Original: "The differences between the four parameterizations used in this study are small for both the combined cases and the pure heterogeneous cases."
→
Modified: "The differences between the three parameterizations derived from AIDA measurements, corresponding to Simulations A, B and D, are small for both the combined case and the pure heterogeneous ice nucleation case as presented in Fig. 6."

Page 16509 line 25:

Original: "The three parameterizations have largest differences…"
→
Modified: "The three parameterizations (i.e., Simulations A, B and D) have largest differences…"

Reviewer's comment: Page 16510, COSMO simulations: I find a lot missing in the discussion here. First, the averaging used to obtain the results is not totally clear. What defines a cloudy area for the results shown in Figures 7 and 8? Does it imply that areas with very low ice content and low ice concentrations are averaged along with others of higher optical depth or higher ice water content across the domain? The lower ice concentrations in P13, despite the inclusion of homogeneous freezing are striking and somewhat

surprising unless the small regions where stronger ice formation occurs (e.g., homogeneous freezing regions) are averaged out, while the higher values in the AIDA-based parameterizations surprise me if they are averaged over all cloudy parcels, even at low ice supersaturations.

Authors' response:

We thank the reviewer for pointing out that this discussion was too condensed and partly misleading. Regarding the averaging conditions, we have applied the following procedure in order to obtain consistent results for the different simulations:

The INP concentrations as well as T and RH_{ice} conditions allowing for hematite to nucleate through deposition mode, i.e. T<-36°C and RH_{ice} >100%, are extracted and binned in pressure intervals for subsequent averaging, which yields the data in Figure 7. This averaging procedure was implemented for both the AIDA-based parameterization and P13. In case of P13, this leads to averaging also over zeros, when temperatures are below -36°C, but the supersaturation is low enough that the parameterization returns $n_s = 0$ (white areas of Figure 4C).

Note that Fig. 7 shows only the heterogeneous INP concentration. Although contained in the simulation and calculated right afterwards heterogeneous ice formation, the homogeneously formed ice is not contained in the mean values of Figure 7. Here we compare only ice that is formed by deposition nucleation, rather than "total" ice occurring in the model. In this way, the effects of sedimentation, advection and turbulent diffusion of ice crystals (that had been formed earlier in the model and may be present in T<-36°C and RH_{ice}>100% regions due to transport) are disregarded in order to extract the heterogeneous ice formation.

We have modified the test on the page 16510 lines 9-13:

Original: "N_{ice} was spatially averaged over all cloudy areas of the model domain for freezing conditions of cubic hematite particles. As shown in Fig. 7, the mean N_{ice} resulting from the parameterization based on P13 is smaller than that from the AIDA n_s-isoline-based parameterization by more than two orders of magnitude."

→

Modified: "N_{ice} was spatially averaged over all areas of the model domain which in principle allow for deposition nucleation in our simulations, i.e. conditions below -36°C and above 100% RH_{ice}. Because not always n_s is larger than zero (white areas of Fig. 2), also areas without ice formation are contained. It is also noteworthy that only purely heterogeneous ice formation is presented rather than the total ice occurring in the model. As shown in Fig. 7, the mean N_{ice} resulting from the parameterization based on P13 is smaller than that obtained from the AIDA n_s-isoline-based parameterization by more than two orders of magnitude. This large difference results predominantly from the inactivity of P13 at low RH_{ice}."

The x-axis in Fig. 7 and caption have been modified:

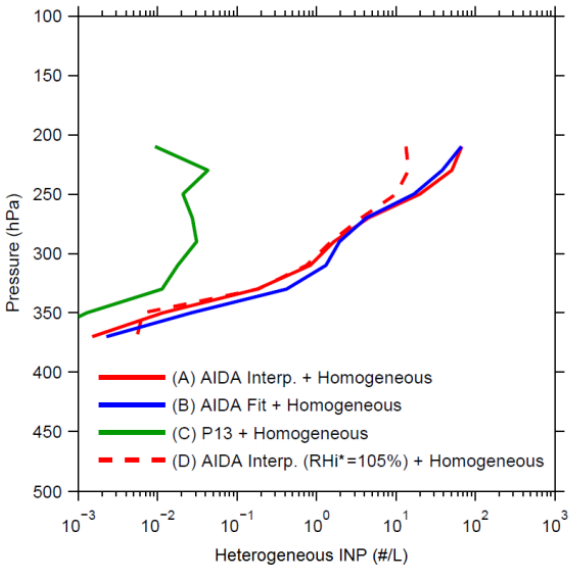


Figure 7. The mean heterogeneous INP number concentrations simulated in COSMO.

Reviewer's comment: Next, the results not only show a vast difference between the domain averaged ice crystal concentrations, but the relative picture of maximum supersaturation evident in Figure 8 is drastically different. If I follow this correctly, it would be highly unlikely to find an area supersaturated with respect to ice by more than 20

Authors' response: Our presentation is correct. Most of ice formation, in case of using AIDA-derived parameterization, is triggered below RH_{ice} 120% (Fig. 8A) owing to our n_s parameterization which shows non-negligible ice formation even at low RH_{ice} and simulated atmospheric conditions in COSMO.

Reviewer's comment: Page 16510, last sentence: The data in P13 are clearly limited at lower temperatures. That paper acknowledged this issue and also discussed discrepancies between field and laboratory data at temperatures below -35 ˚C, offering some speculation about this. Can you say that your results confirm these things and can you speak to whether or not the modeling provides any new insights?

Authors' response: What we see from the results of both models is that the modeled ice concentrations are very sensitive to deposition nucleation at low temperatures when heterogeneous INPs (hematite particles in this study) compete with homogeneous freezing. Because the low supersaturations have a high frequency of occurrence in the atmosphere, it is highly desirable that atmopherically relevant IN (mineral dust and others) are described more precisely with respect to their deposition nucleation ability in the cirrus regime.

Reviewer's comment: Page 16511, lines 14-18: I wonder if the discrepancies between the parameterizations noted here do not actually highlight most the need for more high quality atmospheric measurements of INP's in the upper troposphere. This is what stands out to me at least. The laboratory measurements seem consistent.

Authors' response: The authors believe that in situ measurements of INPs, such as the number concentration and the types of INPs, can constrain lab based parameterizations. Though direct observation of the aerosol freezing mechanism in the upper troposphere where coincides with the low water vapor pressure (*Cziczo and Froyd*, 2014), investigating chemical characterization of cirrus residual particles can

give a crucial hint and promote the investigation of ice formation mechanism by using laboratory instruments (e.g., AIDA).

We have rephrased the sentences on the page 16511 lines 14-23:

Original: "Substantial differences between the empirical approach of P13 and our parameterization developed in this study are presumably attributed to the difference in lab- or field data, highlighting the need for further characterizations of atmospherically relevant substrates and their ice nucleation activities in laboratory settings. Nevertheless, *Niemand et al*. (2012) demonstrated that different dusts exhibit similar n_s in immersion mode freezing and perhaps such a similarity remains true for deposition mode ice nucleation. In fact, comparison between our AIDA n_s-based parameterization with hematite particles and *Möhler et al*. (2006) with ATD and SD2 (Fig. 3a) provides indication on the validity of the assumption to treat all dust as hematite in deposition mode."
→
Modified"However, it should be noted that there is some evidence for the atmospheric relevance and applicability of the new parameterization. First of all we demonstrated that the new n_s parameterization based on the experiments with hematite particles agrees well with previous literature results for mineral dust aerosol (e.g., *Möhler et al*, 2006; *Welti et al*., 2009; *Köhler et al*., 2010). Second, *Niemand et al*. (2012) demonstrated that different dusts exhibit similar n_s in immersion mode freezing and perhaps such a similarity remains true for the deposition mode ice nucleation of desert dusts. Lastly, the comparison between the observed profile of ice crystal number concentrations and the simulated ones (Figs. 5 and 6) also suggests the validity of the new parameterization. These premises must be further examined in comparing to atmospherically relevant substrates (fresh and aged ones) and their ice nucleation activities in laboratory settings. In situ INP measurements, such as the number concentration and the types of INPs, at the upper troposphere can also help to constrain the parameterization."

Reviewer's comment: Page 16512, lines 14-16: I did not note anywhere in the paper where a hypothesis for the appearance of an RH-dependent ice nucleation below -60 ˚C was discussed. Can you suggest anything?

Authors' response: Discussed on the page 16504 lines 25-27:

For clarity, we have added "(i.e., RH_{ice}-dependent ice nucleation regime)" in the end of this sentence (page 16504 lines 25-27):

"Figure 2 shows several important features of n_s-isoline curves. First, below −60 ˚C, n_s-isolines showed an increase in RH_{ice} required to maintain a constant n_s (i.e., $n_s > 2.5\times10^8$ m^{-2}) with decreasing T (i.e., RH_{ice}-dependent ice nucleation regime)."

Reviewer's comment: Last sentence: Can you comment on whether or not you believe that the stronger ice nucleation at limited ice supersaturations on the basis of the new parameterization is realistic for the atmosphere? How might this be examined?

Authors' response: How strong ice nucleation at lower RH_{ice} can be examined and quantified by conducting 'direct' measurements of INP concentration as a function of T and RH_{ice}. This could ultimately verify how realistic the lab results are for the atmosphere. Nonetheless, both experimental and model results (Fig. 2 and 8A) suggest the new parameterization to induce substantial ice formation even at low RH_{ice}. Hence, the new parameterization strongly suggests the role of T and more ice nucleation when compared to the existing empirical parameterization, presumably allowing more ice activation under water subsaturated conditions.

Additional revision: In addition to addressing the reviewer's comments, other editorial corrections (major and non-miscellaneous ones) were made and listed above on the pages 11-13 of authors' responses.

All relevant changes made in the manuscript are indicated by the highlighted sections in yellow (as of September 30 2014) and green (added on October 1, 2014) below.

A Comprehensive Parameterization of Heterogeneous Ice Nucleation of Dust Surrogate: Laboratory Study with Hematite Particles and Its Application to Atmospheric Models

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Manuscript in preparation for *Atmospheric Chemistry and Physics*

ACP - Special Issue: Results from the ice nucleation research unit (INUIT)

October 1, 2014

Abstract

A new heterogeneous ice nucleation parameterization that covers a wide temperature range (-36 to -78 ˚C) is presented. Developing and testing such an ice nucleation parameterization, which is constrained through identical experimental conditions, is important to accurately simulate the ice nucleation processes in cirrus clouds. The ice nucleation active surface-site density (n_s) of hematite particles, used as a proxy for atmospheric dust particles, were derived from AIDA (Aerosol Interaction and Dynamics in the Atmosphere) cloud chamber measurements under water subsaturated conditions. These conditions were achieved by continuously changing the temperature (T) and relative humidity with respect to ice (RH_{ice}) in the chamber. Our measurements showed several different pathways to nucleate ice depending on T and RH_{ice} conditions. For instance, almost T-independent freezing was observed at -60 ˚C < T < -50 ˚C, where RH_{ice} explicitly controlled ice nucleation efficiency, while both T and RH_{ice} played roles in other two T regimes: -78 ˚C < T < -60 ˚C and -50 ˚C < T < -36 ˚C. More specifically, observations at T lower than -60 ˚C revealed that higher RH_{ice} was necessary to maintain a constant n_s, whereas T may have played a significant role in ice nucleation at T higher than -50 ˚C. We implemented the new hematite-derived n_s parameterization, which agrees well with previous AIDA measurements of desert dust, into two conceptual cloud models to investigate their sensitivity to the new parameterization in comparison to existing ice nucleation schemes for simulating cirrus cloud properties. Our results show that the new AIDA-based parameterization leads to an order of magnitude higher ice crystal concentrations and to an inhibition of homogeneous nucleation in lower temperature regions. Our cloud simulation results suggest that atmospheric dust particles that form ice nuclei at lower temperatures, below -36 ˚C, can potentially have a stronger influence on cloud properties, such as cloud longevity and initiation, compared to previous parameterizations.

1. Introduction

Ice clouds represent a significant source of uncertainty when predicting the Earth's climate change according to the recent Intergovernmental Panel on Climate Change report (i.e., *Chapter 7 of IPCC*, 2013; *Boucher et al*., 2013). Rare airborne particles that can act as ice nucleating particles (INPs) at supercooled temperatures indirectly influence the Earth's forcing by changing microphysical properties of ice clouds, such as reflectivity, longevity and precipitation. However, understanding ice cloud formation over a wide range of atmospherically relevant temperatures and humidity is challenging (e.g., *DeMott et al*., 2011; *Murray et al*., 2012), and our knowledge of ice formation through various nucleation modes is still scarce and limited, such that the ice nucleation processes are currently very poorly represented in global climate models (e.g., *Hoose et al*., 2010; *Liu and Penner*, 2005). In particular, heterogeneous ice nucleation processes proceed through various modes including deposition nucleation, immersion-, condensation- and contact freezing (*Chapter 9 of Pruppacher and Klett*, 1997; *Vali*, 1985). Briefly, deposition mode induces ice formation when water vapor is directly deposited onto the INP, immersion and condensation freezing can induce ice formation when freezing is initiated by the INP immersed within the supercooled droplet or solution droplet, and contact freezing can initiate at the moment when an INP comes into contact with a supercooled droplet.

A global model simulation of INPs in tropospheric clouds showed that more than 85% of heterogeneous ice nucleation results from freezing of supercooled cloud droplets, in which INPs are either immersed or condensed (*Hoose et al*., 2010). However, freezing mechanisms in cirrus clouds are still uncertain (e.g., *Sassen and Khvorostyanov*, 2008). It is understood that various INPs can nucleate ice at water subsaturation and a range of supercooled temperature conditions as comprehensively illustrated in Fig. 2 of *Hoose and Möhler* (2012). The potential importance of ice nucleation under ice supersaturated conditions below the homogeneous freezing threshold line (i.e., Koop line; *Koop et al.*, 2000; *Ren and MacKenzie*, 2005) has already been proved in earlier studies, suggesting the need for further investigations in the water subsaturated region. For example, *Christenson* (2013) experimentally showed that the capillary condensation of supercooled liquid on surface defects facilitated subsequent homogeneous nucleation and growth of ice below water saturation. *Marcolli* (2014) suggested that the inverse Kelvin effect below water saturation helps to form water in pores or cavities and hypothesized that this condensate

could freeze through the homogeneous- or immersion mode freezing. This freezing mechanism was referred to as pore condensation and freezing. Previous laboratory studies introduced the concept of a freezing mechanism of solutions on particles at below water saturation (*Zuberi et al*., 2002; *Hung et al*., 2003; *Archuleta et al*., 2005). More recently, *Welti et al*. (2014) explored the relevance of soluble components of mineral dust (i.e., Fluka kaolinite) to condensation freezing below water saturation in the context of classical nucleation theory (CNT). Further, recent aircraft-based field observations suggested that predominant heterogeneous ice formation at cirrus temperatures occurs under water subsaturated conditions, in particular when RH_{ice} is below 140% (*Cziczo et al*., 2013). In addition, *Storelvmo and Herger* (2014) demonstrated that forward modeling simulation with 50% of the mineral dust particles acting as INPs was in good agreement with an observation reported by *Cziczo et al.* (2013). Another airborne observation during an Asian mineral dust event suggested that ice nucleation in cirrus clouds occurs under water subsaturation conditions below 130% RH_{ice} (*Sakai et al*., 2014).

Previously, empirical descriptions given in *Meyers et al*. (1992, hereinafter referred to as M92) were derived from the limited field measurements of ice nuclei concentrations measured at -23 ˚C < *T* < -7 ˚C and 102% < RH_{ice} < 125%. Recently, *Phillips et al*. (2008, 2013) empirically parameterized the heterogeneous ice nucleation of various types of aerosols as a function of humidity (RH_{ice} > 100%) and temperature conditions (0 to -100 ˚C). Besides, CNT-based ice nucleation descriptions have also been widely used and implemented in cloud models (e.g., *Barahona and Nenes*, 2009a and 2009b; *Kärcher and Lohmann*, 2003; *Khvorostyanov and Curry*, 2004). These parameterizations can predict different cloud properties for identical environmental conditions. For example, *Barahona et al*. (2010) showed that the ice crystal number can vary by up to an order of magnitude in a global chemical transport model depending on the choice of the heterogeneous ice nucleation parameterization. The authors found the lowest global mean ice crystal concentration from the parameterization of *Phillips et al.* (2008). Moreover, sensitivity of ice cloud properties to the parameterization was observed by *Liu et al*. (2012). They showed that the heterogeneous INP number concentration obtained from a CNT-based parameterization is typically higher by several factors than that of Phillips's parameterization under identical test conditions. To gain insight on what triggers such deviation and to constrain model uncertainties, more and better in situ measurements are necessary (*Cziczo and Froyd*, 2014). In specific, identifying and quantifying sources, global spatio-temporal distribution and mixing-state of INPs

might support to reduce model assumptions. In parallel, systematic laboratory measurements are indeed needed to develop water subsaturated ice nucleation parameterizations for the range of atmospherically relevant T-RH_{ice} conditions for a better representation of ice nucleation processes in cloud models and to support in situ measurements.

Recently, *Hoose and Möhler* (2012) compiled previously reported aerosol-specific heterogeneous freezing efficiencies from laboratory experiments based on a single-parameter, n_s (e.g., *Niemand et al*., 2012; *Connolly et al*., 2009). In addition, the authors formulated ice nucleation efficiency by evaluating aerosol-specific "singular" freezing onsets when or after specific ambient conditions were met. Such time-independent and surface area-scaled n_s formulations can be further adapted to comprehensively assess the ice nucleation in a wide range of atmospherically relevant T-RH_{ice} conditions. Accordingly, the n_s concept was adapted to deposition nucleation at low temperatures (up to -80 ˚C).

Within the framework of Ice Nucleation research UnIT (INUIT), we comprehensively investigated the ice nucleation efficiency of pristine cubic hematite particles as a model proxy for atmospheric dust particles. Hematite is used as an example of atmospheric mineral dust particles, which can also be found in the form of cloud-borne particles in shallow stratocumulus clouds (*Matsuki et al*., 2010). Natural hematite often exists in supermicron-sized silt particles and accounts for a few percent of the total dust particle mass (*Claquin et al*., 1999). Ice nucleation efficiencies of cubic hematite particles were measured using the AIDA cloud chamber. We also re-examined the previously reported AIDA results of hematite ice nucleation (*Hiranuma et al*., 2014; *Skrotzki et al*., 2013) and combined them with the results from this work in order to examine the ice nucleation efficiency of hematite particles in the temperature range between -36 and -78 ˚C. In addition to developing the new dust parameterization from these AIDA measurements (Sects. 3.1-3.3), the fitted n_s parameterization was also applied to atmospheric modeling simulations (Sect. 3.4). We implemented the parameterization in the Single column version of the Community Atmospheric Model version 5 (SCAM5, *Neale et al*., 2010) and the COnsortium for Small-scale Modeling (COSMO, *Baldauf et al.*, 2011; *Doms et al.*, 2011) models to assess the newly developed parameterization and compare them with existing parameterizations. It is important to note that the purpose of the current study is to perform a conceptual study with laboratory-synthesized hematite particles as a model aerosol for deposition

ice nucleation, over a wide range of T and RH_{ice}, but not to quantify how much hematite content contributes to ice formation in cirrus clouds.

2. Method

2.1. Description of hematite particles

Laboratory-generated cubic hematite particles that have homogeneous chemico-physical properties were used as a proxy for atmospheric dust particles. These particles had a uniform composition, morphology and well-defined surface area. Hence, they are suited well for investigating T-RH_{ice}-dependent ice nucleation efficiency and relating it to the surface area (*Hiranuma et al*., 2014). Detailed information on the manufacturing process of cubic hematite particles is available elsewhere (*Sugimoto and Sakata*, 1992). Three different sizes of quasi-monodispersed hematite particles (~200, ~500 and ~1000 nm diameter, respectively) were used in this work. The morphology and size of the hematite particles were characterized by scanning electron microscopy and determined based on an equivalent circle diameter derived from the observed 2D particle projection area (*Vragel*, 2009; *Hiranuma et al*., 2014). A Small-Scale Powder Disperser (SSPD, TSI, Model 3433) was used to dry-disperse the quasi-monodispersed hematite particles into the AIDA vessel as demonstrated in *Skrotzki et al*. (2013).

2.2. AIDA cooling expansion

The AIDA expansion freezing experiments were achieved by mechanical pumping (*Möhler et al*., 2003). Mechanical pumps can be operated at different pumping speeds simulating atmospherically relevant adiabatic cooling of rising air parcels in the cylinder of 84 m^3 in volume (i.e., 7 m height x 4 m width thermally conductive aluminum vessel) installed inside the thermostatic housing. For this study, a cooling rate of 5 °C min^{-1} was typically applied at the beginning. Then, the cooling rate decreased to <0.1 °C min^{-1} within 400 s for each pumping expansion experiment, which was mainly due to an increasing heat flux from the chamber walls. Afterwards, an almost constant temperature was maintained by the stirred and well-mixed volume of the cold chamber. During the experiment, the pressure in the vessel decreased from 1000 to 800 mb.

The mean gas temperature in the AIDA vessel was determined by five thermocouples installed at different vertical levels. The sensors of these thermocouples were located about 1 m

off the vessel wall and, thus, fully exposed to the chamber air. Stirring of the air by the mechanical ventilator prior to and during pumping ensured a homogeneous temperature distribution in the vessel of ± 0.3 ˚C (*Möhler et al*., 2003). The relative humidities with respect to water (RH_{water}) and RH_{ice} were determined with an accuracy of ± 5% using the mean gas temperature and the mean water vapor concentration. The water vapor concentrations were measured in situ by tunable diode laser (TDL) water vapor absorption spectroscopy throughout the expansion experiments. Since this direct long path absorption technique is described and evaluated in detail in other publications (*Fahey et al*., 2014; *Skrotzki et al*., 2013), no further information is given here.

Under atmospheric pressure, prior to each expansion experiment, a combination of a Scanning Mobility Particle Sizer (SMPS, TSI, Model 3080 DMA and Model 3010 condensation particle counter), an Aerosol Particle Sizer (APS, TSI, Model 3321) and a condensation particle counter (CPC, TSI, Model 3076) collectively measured the total number and size distribution of aerosols at the horizontally extended outlet of the AIDA chamber. Subsequently, the total aerosol surface area was estimated as presented in *Hiranuma et al*. (2014). During expansion, we quantified the ice nucleation of hematite particles with two different light scattering instruments: an optical particle counter welas (PALAS, Sensor series 2300 and 2500) (*Benz* et al., 2005) and SIMONE (German acronym of Streulicht-intensitätsmessungen zum optischen Nachweis von Eispartikeln, which translates to the scattering intensity measurement for the optical detection of ice; *Schnaiter et al*., 2012). More details on the application of this specific combination of two instruments for the AIDA ice nucleation experiments are given in *Hiranuma et al.* (2014).

2.3. Ice nucleation parameterization and modeling

The size-independent singular ice nucleation efficiency, n_s, was calculated by normalizing the observed AIDA ice crystal concentration (N_{ice}) to the total surface area of aerosols, which can be calculated by multiplying the surface area of an individual particle (S_i) by the total number concentration of aerosols (N_{ae}) (e.g., *Niemand et al*., 2012; *Hoose and Möhler*, 2012). For size-selected hematite particles, this linear approximation (i.e., $n_s = (-\ln(1-\alpha))/S_i \sim \alpha/S_i$) was valid independent of the ice active number fraction ($\alpha = N_{ice}/N_{ae}$). An overestimation of ice due to the use of linear approximation only amounted up to about a factor of three at $n_s \leq 10^{12}$

m^{-2}. Subsequently, the n_s values estimated for the wide range of experimental conditions (-36 ˚C < T < -78 ˚C and 100% < RH_{ice} < water saturation) were used to depict and fit constant n_s contour lines. Here, these lines are referred to as the n_s-isolines or simply as the isolines.

The isoline-based parameterizations were derived (see section 3.3) and then implemented in two atmospheric models (a single-column version of a global scale model and a convection resolving model, see Sect 2.3.1. and 2.3.2. for model descriptions). The unique advantages of the use of both models in this study are (1) to demonstrate that our AIDA n_s-based parameterization can be directly applied on different scales of atmospheric models and (2) to estimate the number of ice crystals simulated in two different atmospheric scenarios that complement each other and cover a wide range of atmospheric temperature and saturation conditions (ice formation at higher RH_{ice}, up to ~180%, and lower T, down to ~-70 ˚C). More specifically, the former represents a finely resolved parameterization-oriented model embedded in the global model while the latter is a more physically based high-resolution grid scale model, typically used to analyze small scale complex systems for a fundamental understanding of ice formation. Altogether, results from two independent models were examined for a detailed modeling of atmospheric ice formation on all scales.

The mean size and surface area of hematite particles were prescribed with an assumption that either these particles are spherical and have a mean particle diameter of 1000 nm or the size of these particles follows a lognormal distribution, with a mean volume-equivalent diameter of ~1000 nm (σ_g = 1.05), which is consistent with the AIDA experiments described earlier (*Hiranuma et al*., 2014). The cloud microphysical sensitivity of these two size treatments was characterized. In addition, sensitivity simulations of two lower boundaries of RH_{ice} (i.e., 100 vs. 105%) were also carried out. This sensitivity analysis was specifically useful to examine uncertainty involved in the TDL measurement (RH_{ice} ± 5%) concerning the condensed n_s spacing (up to several orders of magnitude) in a narrow RH_{ice} range and a certain T region. In both models, hematite particle number concentrations are given to be 200 L^{-1}, which is about the average dust concentration simulated by the SCAM5 model over the Southern Great Plain (SGP) site in springtime. Since the n_s-isoline parameterization tested in this study is applicable at T below -36°C, an additional parameterization was used to simulate ice formation of background particles at T > -36°C, namely, the aerosol-independent M92 scheme. These parameterizations were combined to ensure more atmospherically relevant processes and conditions (e.g.,

distributions of water vapor) when compared to the application of the n_s-isoline parameterization alone.

To better understand to what an extent the AIDA n_s-based parameterization differs from other parameterizations commonly used in atmospheric models, the existing empirical parameterization of heterogeneous ice nucleation by *Phillips et al*. (2013, hereinafter denoted as P13) was implemented as well. The P13 scheme reflects the aerosol specific ice nucleation. In particular, the contribution of mineral dust with the background troposphere baseline surface area mixing ratio of ice-active mineral dust particles (=2.0 x 10^{-6} m^2kg^{-1}) was considered in this study. Ice formation occurring below water saturation only was considered and, thus, Eqn. 1 in *Phillips et al*. (2008) was used for parameterizing ice nucleation.

2.3.1. SCAM5

Single column models are widely used to test physical parameterizations for use in the general circulation model (GCM). The model has 30 vertical levels, and the model time step is set to 10 min. The single column model resembles a single column of a GCM and can be derived from observations or model output. The complex feedbacks between the simulated column and other columns due to large-scale dynamics are not considered. Therefore, the single column model is an ideal tool for testing ice cloud parameterizations. The SCAM5 model was modified to incorporate the new parameterization developed in this study. The *Barahona and Nenes* (2008, 2009a, b) scheme, which provides an analytical solution of the cloud parcel model equations (hereinafter called BN scheme), is used for calculating ice nucleation in cirrus clouds. The new AIDA n_s-isoline-based parameterizations as well as the P13 scheme were implemented in the model. The simulation was performed for one month (April 2010) at the United States Department of Energy's Atmospheric Radiation Measurement facility located at the SGP site (*Hiranuma et al*., 2014).

2.3.2. COSMO

The non-hydrostatic weather forecast model, COSMO, was adapted to systematically investigate the impact of hematite particles under the simulated upper tropospheric conditions.

COSMO is the high-resolution limited-area model to assess clouds and convection at a horizontal spatial resolution of 2.8 km with 50 layers of stretched vertical grids. The time step is set to 20 seconds. In this study, we simulated a period of two days (July 23 to July 25, 2011) on a domain of 450 x 450 horizontal grid points centered over the German Alps (longitude: 0.1°E to 18.7°E, latitude: 41.7°N to 53.2°N). The initial and boundary conditions were provided by the European Centre for Medium-Range Weather Forecasts. They are available at the Meteorological Archival and Retrieval System. In order to account for the spatio-temporal evolution of mass and number densities of six hydrometeor classes (i.e., cloud droplets, raindrops, cloud ice, snow, graupel and hail), the two-moment bulk microphysics scheme was incorporated in our COSMO model version following the method described by *Seifert and Beheng* (2006) and *Seifert et al.* (2012). Apart from the AIDA isoline-based freezing parameterization of hematite, two other ice nucleation modes, namely, M92 and homogeneous nucleation of cloud or solution droplets (*Kärcher et al*., 2006; *Ren and MacKenzie*, 2005), were considered in our COSMO simulations. The latter was used to parameterize the competition of water vapor between homogeneous and heterogeneous freezing.

3. Results

3.1. AIDA ice nucleation experiments

A series of AIDA experiments was carried out during the INUIT01 and INUIT04 campaigns to investigate the ice nucleation efficiency of well-characterized hematite particles under water subsaturated conditions at -47 ˚C < T. In addition, we used the AIDA results reported by *Skrotzki et al*. (2013) and reconciled them with the n_s values in order to parameterize the overall ice nucleation efficiency of hematite particles up to -78 ˚C. In total, 12 expansion experiments, 4 from the INUIT campaigns and 8 from *Skrotzki et al*. (2013), were studied. Detailed experimental conditions and aerosol properties for these expansion experiments are summarized in Table 1. The use of different sizes of hematite particles in different temperature regions was justified by calculating the size-independent n_s values of 200 and 1000 nm diameter particles at ~-40 ˚C. For instance, the evaluated n_s values (10^{10} m^{-2}) for these two sizes agreed very well within ± 1 % RH_{ice} and ± 0.3 ˚C of chamber conditions (see corresponding RH_{ice} and T at Evaluated n_s in Table 1 for INUIT04_08, 1000 nm, HALO06_19, 200 nm, and HALO06_20, 200 nm). This agreement verified the reproducibility of the AIDA chamber experiments, ice nucleation efficiency of hematite particles and size-independence of the n_s calculations. The advantage of using 1000 nm diameter hematite particles was that, due to their comparatively larger surface area, they were efficient in forming ice in cooling expansion experiments at -40 ˚C < T < -36 ˚C (*Hiranuma et al*., 2014).

The temporal profiles of deposition nucleation experiments from HALO campaigns, including N_{ice}, gas T, RH_{ice} and RH_{water} measured by the TDL as well as the polarized light scattering properties in near-backscattering direction measured by SIMONE, are shown in Figure 1. The depolarization ratio, which is sensitive to ice particle nucleation and growth, can be deduced from the latter. During a typical expansion, the air mass in the vessel experiences continuous cooling (for up to 500 s) and an increase in relative humidity (for up to 200 s, Fig. 1 panel i and ii). Figure 1 panel iii shows the temporal plot of the depolarization ratio. At the beginning of the expansion, the depolarization ratio increases because ice is nucleating on the hematite particles. Conversely, repartitioning of gas phase water to ice phase water due to growing ice crystals triggers the declines in both depolarization ratio (i.e., sizing effect,

Schnaiter et al., 2012) and RH, usually after 100 s. The time-delay in our welas ice detection (typically 1 µm is the minimum ice detection diameter for 200 and 500 nm diameter hematite particles) due to slower depositional growth after ice nucleation at lower T is accounted for in our error analyses (Figure 2). We evaluated only up to several hundred seconds of each expansion experiment as the ice nucleating period. Similar experimental profiles for INUIT campaigns are presented in Figure S1.

The initial n_s-isoline curves in the T-RH_{ice} space are illustrated in Figure 2. Constant n_s-isoline curves are obtained by fitting second degree polynomial fit equations to the constant n_s magnitudes calculated at various T and RH_{ice} (see the supplement for more details). Previous AIDA results of two immersion freezing experiments (i.e., INUIT04_13 and INUIT01_28 from *Hiranuma et al*., 2014) are also shown on the water saturation line and used to constrain the fitted curves because immersion freezing is considered part of isolines. Since the n_s values presented in Fig. 3 of *Hiranuma et al*. (2014) only extends up to ~10^9 m^{-2}, the data points of higher n_s values were extrapolated based on the observed values from two measurements. Figure 2 shows several important features of n_s-isoline curves. First, below −60 ˚C, n_s-isolines showed an increase in RH_{ice} required to maintain a constant n_s (i.e., $n_s > 2.5\times10^8$ m^{-2}) with decreasing T (i.e., RH_{ice}-dependent ice nucleation regime). For example, at a RH_{ice} = 120% and T = -75 ˚C, cooling by 1 ˚C corresponds to a 10% decrease in n_s. This observation is interesting because the increase in RH_{ice} required to maintain constant n_s values is consistent with the CNT for deposition nucleation (Eqn. A11 in *Hoose and Möhler*, 2012). Second, the highest sensitivity of RH_{ice} is observed in a region where n_s-isolines are perpendicular to temperature-isolines (~-60 ˚C < T < ~-50 ˚C). Here, n_s is almost independent of T, and solely dependent on RH_{ice}. Finally, we observed strong T-dependent nucleation near water saturation (i.e., while cooling along the water saturation line towards ~-50 ˚C). At a constant RH_{ice} (e.g., 114%), for example, cooling by 1 ˚C from -41 to -42 ˚C corresponds to an increase in n_s of approximately half an order of magnitude (see inset of Fig. 2). This suggests that the n_s values depend on temperature. Interestingly, we observed a continuous increase in n_s during cooling even after the depletion of supersaturation below -40 ˚C (Figure S2). CNT does not explain this predominant T contribution near water saturation (Fig. A1 in *Hoose and Möhler*, 2012). Therefore, other microphysical processes at the particle surface and/or perhaps even within the bulk phase may be responsible for this T -dependent behavior and these results appear to support the existence of a pore or surface freezing

process, as discussed in recent literature (e.g., *Marcolli*, 2014). In particular, we suspect that water condensation on the particle surface plays an important role on subsequent freezing. To support this, the surfaces of our hematite particles are not perfectly smooth and contain some active sites (e.g., pores and steps, *Hiranuma* et al., 2014). Moreover, water vapor may preferably fill the surface cavities due to the reduced saturation pressure in pores or at steps because of negative curvature Kelvin effects (*Marcolli*, 2014), thus leading to namely "surface condensation freezing (SCF)". As described in previously published literatures (*Christenson*, 2013; *Marcolli*, 2014), SCF may be of relevance to homogeneous nucleation (i.e., spontaneous ice nucleation in supercooled aerosol) at relevant T (< -36 ˚C) and/or immersion mode freezing under water subsaturated conditions. Thus, SCF may arise from both homogeneous and heterogeneous nucleation.

3.2. Comparison with previous studies

The n_s-isolines of hematite particles were compared to previous measurements made using different aerosol species. This comparison was performed to (1) confirm that our n_s fit reproduces the overall trend shown by previous studies under certain T-RH_{ice} conditions and (2) to demonstrate that the parameterization with laboratory-synthesized hematite particles quantitatively represents ice nucleation properties of atmospheric dust particles.

Comparison of the hematite n_s-isolines to previous deposition freezing observations are shown in Figure 3. More specifically, previous measurements were performed with natural Saharan desert dust (SD2, *Möhler et al*., 2006), reference Arizona test dust (ATD, *Möhler et al*., 2006; *Welti et al*., 2009), volcanic ash (*Steinke et al*., 2011), soot (*Möhler et al*., 2005), clay minerals (*Welti et al*., 2009; *Koehler et al*., 2010) and organics (*Shilling et al*., 2006; *Wang and Knopf*, 2011). These previous experimental studies used various types of ice nucleation instruments, such as substrate-supported cold stages coupled with an optical microscope (*Shilling et al*., 2006; *Wang and Knopf*, 2011), portable ice nuclei counters (*Koehler et al*., 2010; *Welti et al*., 2009) and the AIDA cloud simulation chamber (*Möhler et al*., 2005; *Möhler et al*., 2006; *Steinke et al*., 2011). They revealed the importance of both RH_{ice} and temperature onto deposition mode ice nucleation of specific particle compositions. In Fig. 3a, previous AIDA results for dusts, ash and soot, are presented. Specifically, we utilized the T-RH_{ice} data at α =

384 0.08 of SD2 and ATD reported in the previous AIDA study (*Möhler et al*., 2006) to define
385 isolines. It is noteworthy that an α of 0.08 corresponds to ~ 10^{11} m^{-2} in n_s when assuming
386 uniform distributions of spherical particles of 0.5 μm diameter ($n_s = (-\ln(1-\alpha))/(\pi(0.5 \times 10^{-6})^2)$),
387 which is in good agreement with the 10^{11} m^{-2} n_s-isoline of hematite particles. For volcanic ash,
388 we adapted n_s values (10^9, 5 x 10^9 and 10^{10} m^{-2}) originally reported in *Steinke et al*., (2011).
389 *Möhler et al*. (2005) found that the ice nucleation of soot starts at the initial increase in polarized
390 light scattering intensity in near-backscattering direction at 488 nm (n_s values are inaccessible).
391 Except for these AIDA studies, other isolines in Fig. 3b and c were defined based on the reported
392 ice nucleation measurements. For instance, *Koehler et al.* (2010) studied the deposition mode
393 nucleation of size-selected (i.e., 200 nm, 300 nm, 400 nm) natural dusts, and reported ice
394 nucleation conditions (T and RH_{ice}) of ATD at α = 0.01 and of Canary Island Dust and Saharan
395 Dust at α = 0.05. *Welti et al*. (2009) also studied the deposition nucleation abilities of size-
396 segregated mineral dusts (i.e., 100 to 800 nm diameter of ATD, illite, kaolinite and
397 montmorillonite) based on α = 0.01. *Shilling et al.* (2006) reported the ice nucleation onsets of
398 ammonium sulfate and maleic acid detected by the decreasing partial pressure of water with
399 FTIR-reflection absorption spectroscopy (e.g., 1 in 10^5 nucleation at about -33 ˚C for a spherical
400 particle size of 1 to 10 μm diameter). *Wang and Knopf.* (2011) investigated deposition freezing
401 of various mineral and organic particles including kaolinite, Suwannee River standard fulvic acid
402 and Leonardite standard humic acid particles. The authors reported the mean size of particles and
403 associated ice-activated fractions at the given T-RH_{ice}.
404 As seen in Fig. 3, the results from previous studies suggest the necessity of increasing
405 RH_{ice} to maintain a constant n_s value below T ~-55°C. They also indicate that nucleation may be
406 triggered by SCF in the region where data and isolines approach water saturation where
407 temperature plays a significant role on ice nucleation. It can also be observed that the contour of
408 our new n_s-isoline parameterization of cubic hematite particles in T-RH_{ice} coordinates generally
409 agrees with the onsets determined by previous studies of other atmospherically relevant aerosols.
410 In particular, the n_s-isolines estimated from ATD and SD2 (~10^{11} m^{-2}, Fig. 3a), which reasonably
411 agree with the hematite n_s-isoline, suggest that atmospheric dust may have similar deposition
412 mode ice nucleation efficiency.
413
414 ***3.3. n_s-isoline-based parameterizations***

Next, the ice nucleation efficiency of hematite particles was parameterized over a wide range of T-RH_{ice}. Three types of parametrical descriptions used in this study are shown in Figure 4. First, based on the AIDA experimental results, a series of constant n_s curves was interpolated to produce isolines in the range of 10^6 m^{-2} < n_s < 10^{12} m^{-2} (Fig. 4a). The lower bound of n_s value (10^6 m^{-2}) was set based on the minimum n_s observed during AIDA expansions. Since the certain regions of n_s-isolines (i.e., n_s < 7.5 x10^{10} m^{-2}; blue lines in Fig. 2) can submerge below ice saturation, the correction was applied to shift them and maintain all isolines above 100% RH_{ice}. The procedure to constrain n_s to >100% RH_{ice} is described in the supplement (Fig. S3). Above the upper bound of 10^{12} m^{-2}, n_s presumably remains constant up to the water saturation line in the T -RH_{ice} space (no experimental data is available in this range). This assumption is valid in the present study because this n_s upper limit was hardly reached in our modeling case. However, more cloud simulation chamber measurements and data points for n_s >> 10^{12} m^{-2} are required to correctly constrain the n_s upper limit. It also has to be noted that the modeled ice crystal number concentration (L^{-1}) derived from ice nucleation of hematite in this study is approximated by multiplying n_s by a simulated total surface of hematite (6.3 x 10^{-10} m^2 L^{-1}).

In the second fit approach (Fig. 4b), the interpolated n_s values were used to formulate the n_s-isoline with a third degree-polynomial fit as a function of T (˚C) and RH_{ice} (%) as

$$n_s^{3d}(T, \mathrm{RH_{ice}}) = -3.777 \times 10^{13} - 7.818 \times 10^{11} \cdot T + 4.252 \times 10^{11} \cdot \mathrm{RH_{ice}} - 4.598 \times 10^{9} \cdot T^2 + 6.952 \times 10^{9} \cdot T \cdot \mathrm{RH_{ice}} - 1.111 \times 10^{9} \cdot \mathrm{RH_{ice}}^2 - 2.966 \times 10^{6} \cdot T^3 + 2.135 \times 10^{7} \cdot T^2 \cdot \mathrm{RH_{ice}} - 1.729 \times 10^{7} \cdot T \cdot \mathrm{RH_{ice}}^2 - 9.438 \times 10^{5} \cdot \mathrm{RH_{ice}}^3$$

for -78 ˚C < T < -36 ˚C and 100 % < RH_{ice} < water saturation (1)

where $n_s^{3d}(T, RH_{ice})$ is the n_s derived from the third degree fit. The resulting spatial plot of isolines for constant n_s is shown in Fig. 4b. Note that the upper temperature boundary of −36 ˚C was assigned as the interface between immersion mode- and deposition mode ice nucleation (*Hiranuma et al*., 2014), and the lower boundary of −78 ˚C is the limit introduced by interpolating the hematite-isoline curves. The third approach (Fig. 4c) consisted in applying the equivalent n_s for deposition nucleation of hematite particles parameterized using the method introduced by *Phillips et al*. (2008 and 2013). In detail, we characterized the nucleation activity

solely of mineral dust through the deposition mode by adapting the Equation (1) from *Phillips et al*. (2008), which accounts for nucleation under water subsaturated conditions, and excluded the contribution at water saturation, i.e., Equation (2) of *Phillips et al*. (2008). AIDA n_s-isoline-based parameterization suggests strong supersaturation dependence of n_s at low *T*. Observed diversity between a new parameterization (Figs. 4a and 4b) and P13 (Fig. 4c) may result in different ice crystal forming propensities and may predict different cloud properties. The potential consequence of observed diversity is demonstrated using conceptual models and discussed in the following section.

3.4. Model simulations

The SCAM5 results for monthly mean profiles of the simulated in-cloud N_{ice} ($Ni \sim N_{ice}$) over the ARM SGP site for five cases are shown in Figure 5. These include (Case 1) the pure homogeneous ice nucleation case, (Case 2-4) cases with contributions from both homogeneous and heterogeneous ice nucleation (hereinafter referred to as the combined case) described in Fig. 4a-c (corresponding to Simulations A, B and C) and (Case 5) the simulation of the different lower boundaries of RH_{ice} (RH_i^*, Simulation D). In addition, the observed profile of ice crystal number concentrations is also shown in comparison to the simulations in Fig. 5. The observational data were collected over the SGP site on eight days of April 2010 during the Small PARTicles In CirrUS (SPARTICUS) campaign (*Zhang et al*., 2013). The results of our simulations suggests that ice crystal formation due to heterogeneous ice nucleation processes inhibits homogeneous ice nucleation and significantly reduces the ice number concentrations for the AIDA parameterizations (Fig. 4a and b). In contrast, due to the much smaller ice crystal production from P13, as shown by the pure heterogeneous case in Figure 5, homogeneous ice nucleation in the P13 case (Fig. 4c) is less affected by heterogeneous nucleation. The observed mean profile of in-cloud ice crystal number concentrations is in agreement with the simulated ones. The differences between the three parameterizations derived from AIDA measurements, corresponding to Simulations A, B and D, are small for both the combined case and the pure heterogeneous ice nucleation case as presented in Fig. 6. This is because the BN scheme used in SCAM5 is based on parcel model theory and uses the predicted maximum ice supersaturation (S_{max}) to calculate deposition ice nucleation rates. S_{max} is determined by assuming that the

supersaturation will reach its maximum where the depletion of water vapor compensates the supersaturation increase from cooling in a cloud parcel (i.e., BN scheme). The three parameterizations (i.e., Simulations A, B and D) have largest differences when RH_{ice} is below 120% while S_{max} calculated in the model is often larger than 115%. This also explains the low sensitivity of N_{ice} to the lower bound of the onset RH_{ice} value (Figs. 5 and 6). We also investigated the impact of different particle size distributions on the calculation (not shown). The impact is small and negligible. The negligible sensitivity to the choice of AIDA parameterizations in SCAM5 simulations (Simulation A and B of Figs. 5 and 6) as well as the negligible sensitivity to the lower bound of the RH_{ice} value for ice nucleation, RH_i^* in Figs. 5 and 6, reflect the limitation of SCAM5 as a large-scale model, which can't explicitly resolve the sub-grid (for the GCM grid box) variability of the supersaturation.

The results of the COSMO model for the vertical profiles of N_{ice} (presumably equivalent to the heterogeneous INP number concentration) are summarized in Figure 7. These results simulate the three different parameterization schemes (corresponding to Fig. 4a-c) in combination with homogeneous freezing. N_{ice} was spatially averaged over all areas of the model domain which in principle allow for deposition nucleation in our simulations, i.e. conditions below -36°C and above 100% RH_{ice}. Because not always n_s is larger than zero (white areas of Fig. 2), also areas without ice formation are contained. It is also noteworthy that only purely heterogeneous ice formation is presented rather than the total ice occurring in the model. As shown in Fig. 7, the mean N_{ice} resulting from the parameterization based on P13 is smaller than that obtained from the AIDA n_s-isoline-based parameterization by more than two orders of magnitude. This large difference results predominantly from the inactivity of P13 at low RH_{ice}. Unlike the SCAM5 results, the COSMO results show the sensitivity to the different lower boundaries of RH_{ice} (i.e., RH_i^* = 105%, Simulation D). For instance, the mean N_{ice} below -36 ˚C with a higher RH_{ice} boundary (105%) is reduced by 12%. This difference is perhaps due to the use of finely resolved grid-scale humidity in COSMO rather than parameterizing S_{max} as done in SCAM5 (*Gettelman et al*., 2010). Figure 8 illustrates the differences between P13 and the AIDA results depending on T and RH_{ice}. Simulated N_{ice} values are segregated in fine T and RH_{ice} spacing (1K and 2% bins, respectively) based on the thermodynamic conditions under which ice crystals were formed in COSMO and summed up over the time of simulation. This segregation allows for an estimation of the relative contribution of different thermodynamic conditions to the

simulated ice formation. Our results show diversity between P13 and the AIDA n_s-isoline-based parameterization. Ice crystal formation was less for P13 and more for the new parameterization. A possible explanation for the observed deviation may be due to the difference in parameterization based on lab- or field data. For instance, atmospheric aging and processing (i.e., surface coating and associated heterogeneous surface reactions) may have altered ice-nucleating propensity and limited deposition nucleation of dust-derived INPs in the P13 parameterization for the field data-derived parameterization as discussed in *Phillips et al*. (2008).

4. Discussions

As described in the previous section (Sect. 3.1), deposition mode freezing cannot solely explain the n_s-isoline observation below water saturation (-50 ˚C < T < -36 ˚C in Fig. 2). Although we presumed that SCF acts as a subset of immersion freezing and plays an important role in this region, further insight and evidence of SCF beyond cloud simulation chamber observations are required to correctly understand the contributions of both homogeneous and heterogeneous nucleation. High-resolution microscopic techniques with an integrated continuous cooling setup are needed to visualize the freezing process of a single particle and to fully understand the complex freezing processes involved in SCF on particle surfaces.

Comparison of the new parameterization to a previous empirical parameterization (P13) showed that the new AIDA n_s-isoline-based scheme predicts more ice (Figs. 4-8). In particular, T-RH_{ice} dependence of N_{ice} and n_s at low T that may coincide in the upper troposphere, and this highlights the need for further investigations. However, it should be noted that there is some evidence for the atmospheric relevance and applicability of the new parameterization. First of all we demonstrated that the new n_s parameterization based on the experiments with hematite particles agrees well with previous literature results for mineral dust aerosol (e.g., *Möhler et al*, 2006; *Welti et al*., 2009; *Köhler et al*., 2010). Second, *Niemand et al*. (2012) demonstrated that different dusts exhibit similar n_s in immersion mode freezing and perhaps such a similarity remains true for the deposition mode ice nucleation of desert dusts. Lastly, the comparison between the observed profile of ice crystal number concentrations and the simulated ones (Figs. 5 and 6) also suggests the validity of the new parameterization. These premises must be further examined in comparing to atmospherically relevant substrates (fresh and aged ones) and their ice nucleation activities in laboratory settings. In situ INP measurements, such as the number concentration and the types of INPs, at the upper troposphere can also help to constrain the parameterization.

Finally, to further develop more atmospherically relevant parameterizations other than the fit-based parameterization with artificial test aerosol, the relationship between $1/T$ and $\ln S_{ice}$ for a constant nucleation rate or n_s based on the CNT can be analyzed (i.e., Eqns. A10-A11 in *Hoose and Möhler*, 2012). In this way, the composition specific $n_s(T\text{-}S_{ice})$ values, where the

transition from SCF to deposition nucleation (or vice versa) occurs, may be better defined and can be then be used as an inexpensive model friendly parameterization.

5. Conclusion

A new heterogeneous ice nucleation parameterization was developed using results obtained from AIDA cloud simulation chamber experiments. The new n_s-isoline-based parameterization is applicable to a wide temperature range from -36 to -78 ˚C and, hence, allows for the examination of ice nucleation spectra in a simple framework for modeling application.

Our experimental results provide a good basis for the T and RH_{ice} dependence of deposition nucleation, and the formulated hematite n_s-isolines are comparable to that of desert dust samples. Consequently, our results with synthesized hematite particles can also be relevant to cirrus applications despite their smaller atmospheric relevance compared to natural hematite. Our isoline formulation suggested three different ice nucleation pathways over the wide range of temperature. In specific, a RH_{ice}-dependent ice nucleation regime was observed at temperatures below ~-60 ˚C, where deposition mode is presumably responsible to trigger ice nucleation. At -60 ˚C < T < -50 ˚C, ice nucleation efficiency was T-independent (i.e., RH_{ice} dependent). Conversely, a predominant influence of T on ice nucleation was observed near the water saturation condition (T > ~-50 ˚C), which may be indicative of nucleation due to condensation of water at the particle surface followed by homogeneous freezing of the condensed water (i.e., SCF). The observed active SCF near water saturation and physical processes at the transitions of nucleation modes still remain to be studied in detail for various types of atmospheric particles.

Our conceptual model examinations also considered the competition between heterogeneous freezing and homogeneous freezing of solution particles to evaluate the relative importance of the different freezing processes in two models (SCAM5 and COSMO). The inhibition of homogeneous nucleation due to heterogeneous freezing was commonly observed in both SCAM5 and COSMO simulations. Our new parameterization revealed a minimum deviation of N_{ice} values estimated by SCAM5 at minimum RH_{ice} values for ice formation (100 or 105%) compared to COSMO. This deviation suggests different sensitivities of the model to the lower bound of the RH_{ice} value owing to the presence of the model-resolved supersaturation to calculate the ice nucleation rate. Overall, our new hematite-based parameterization strongly suggests the role of T and more ice nucleation when compared to the existing empirical parameterization, presumably allowing more ice activation under water subsaturated conditions.

Author Contributions

N. Hiranuma and O. Möhler designed and conceived the experiments. Parameterizations were implemented by N. Hiranuma, I. Steinke and M. Paukert. M. Paukert and K. Zhang carried out modeling studies with input from C. Hoose, N. Hiranuma and G. Kulkarni. M. Schnaiter analyzed SIMONE data. H. Saathiff contributed to TDL measurements and analysis. The manuscript was written by N. Hiranuma. All authors discussed the results and contributed ideas to the manuscript.

Acknowledgements

This work was supported by the German Research Foundation (Deutsche Forschungsgemeinschaft, DfG) under contracts MO 668/4-1 and HO 4612/1-1 within the Research Unit FOR 1525 (INUIT) and by the Helmholtz Association's research programme "Atmosphere and Climate (ATMO)". The authors acknowledge partial financial support by DfG and Open Access Publishing Fund of Karlsruhe Institute of Technology. K. Zhang and G. Kulkarni acknowledge support from the Department of Energy Atmospheric System Research Program. The Pacific Northwest National Laboratory is operated for DOE by Battelle Memorial Institute under contract DE-AC05-76RLO 1830. We would like to thank R. Buschbacher, T. Chudy, E. Kranz, G. Scheurig and S. Vogt for their professional support for the AIDA chamber operation during the INUIT campaigns. We also thank P. Weidler and S. Jaeger for support in preparing the hematite particles. M. Hummel's contribution to the model setup is gratefully acknowledged.

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Table and Figures of "A Comprehensive Parameterization of Heterogeneous Ice Nucleation of Dust Surrogate: Laboratory study with Hematite Particles and Its Application to Atmospheric Models"

October 1, 2014

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Citation:

Hiranuma, N. et al. **A Comprehensive Parameterization of Heterogeneous Ice Nucleation of Dust Surrogate: Laboratory study with Hematite Particles and Its Application to Atmospheric Models**, for *Atmospheric Chemistry and Physics*

Table 1. Summary of aerosol measurements and AIDA ice nucleation experiments. All HALO experiments are from *Skrotzki et al.* (2013).

	Aerosol Measurements			**Ice Nucleation Measurements**				
Experiment ID	Hematite Diameter, nm	Total Number Conc., cm^{-3}	Total Surface Conc., $\mu m^2\ cm^{-3}$	Examined T Range, ˚C	Examined RH_{ice} Range, %	Evaluated n_s, m^{-2}	T(Evaluated n_s), ˚C	RH_{ice}(Evaluated n_s), %
HALO05_24	200	115.0	14.4	-76.1 to -81.9	100.6 to 164.8	10^{11}	-78.2	136.4
HALO04_09	500	112.5	26.9	-75.8 to -80.1	100.3 to 149.8	10^{11}	-77.5	128.3
HALO04_05	500	142.2	30.9	-61.8 to -65.5	100.2 to 135.6	10^{11}	-62.6	111.1
HALO05_18	200	161.9	21.8	-60.3 to -65.2	100.1 to 124.5	10^{11}	-60.8	106.0
HALO06_22	200	145.7	19.2	-50.2 to -53.9	100.3 to 123.4	10^{11}	-50.7	106.7
HALO06_21	200	245.0	32.9	-50.3 to -53.8	100.4 to 115.8	10^{11}	-50.5	102.2
INUIT01_26	1000	342.1	749.0	-41.0 to -47.1	100.2 to 103.9	10^{10}	-41.2	102.2
HALO06_20	200	168.7	22.4	-39.8 to -44.4	100.4 to 128.8	10^{10}	-40.7	111.3
HALO06_19	200	283.0	42.9	-39.7 to -44.5	100.2 to 121.6	10^{10}	-40.6	109.2
INUIT04_08	1000	193.0	647.0	-39.3 to -45.4	100.0 to 113.2	10^{10}	-40.4	110.1
INUIT04_10	1000	161.7	546.6	-37.5 to -43.7	100.0 to 124.1	10^{10}	-40.1	123.3
INUIT01_30	1000	414.5	889.7	-34.6 to -42.0	100.2 to 127.1	2.5×10^{8}	-37.0	122.8

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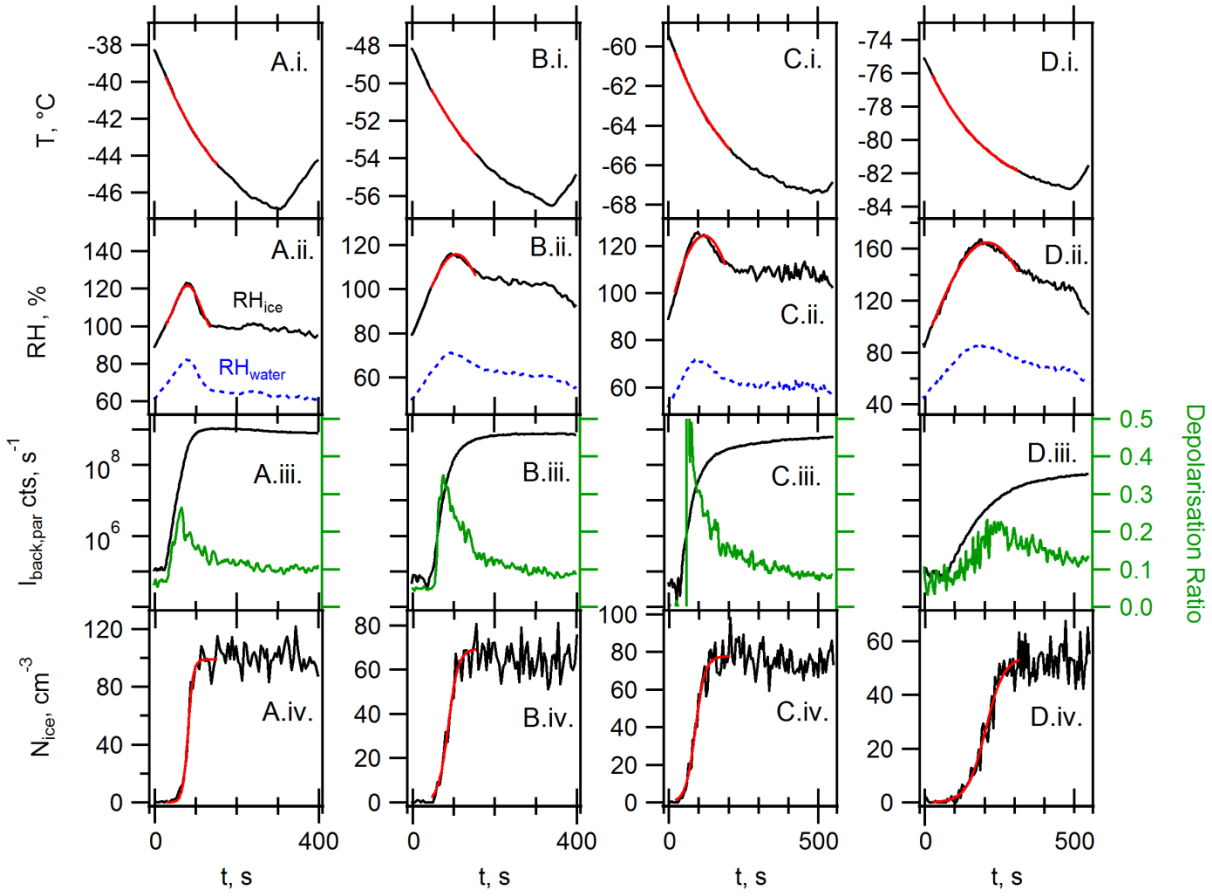
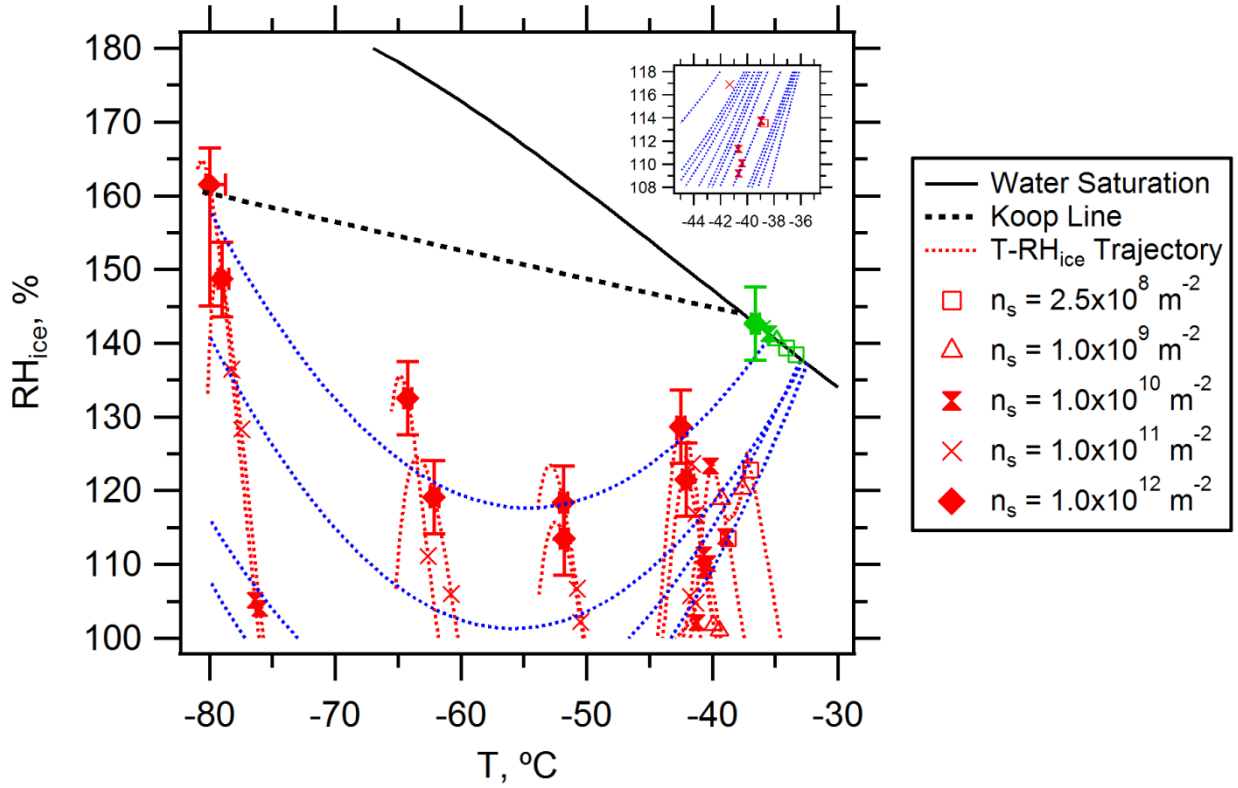

A.i.
B.i.
C.i.
D.i.
A.ii.
B.ii.
C.ii.
D.ii.
A.iii.
B.iii.
C.iii.
D.iii.
A.iv.
B.iv.
C.iv.
D.iv.
T, °C
RH, %
RH_ice
RH_water
I_back,par cts, s^-1
N_ice, cm^-3
Depolarisation Ratio
t, s

Figure 1.



887
888 Figure 2.
889

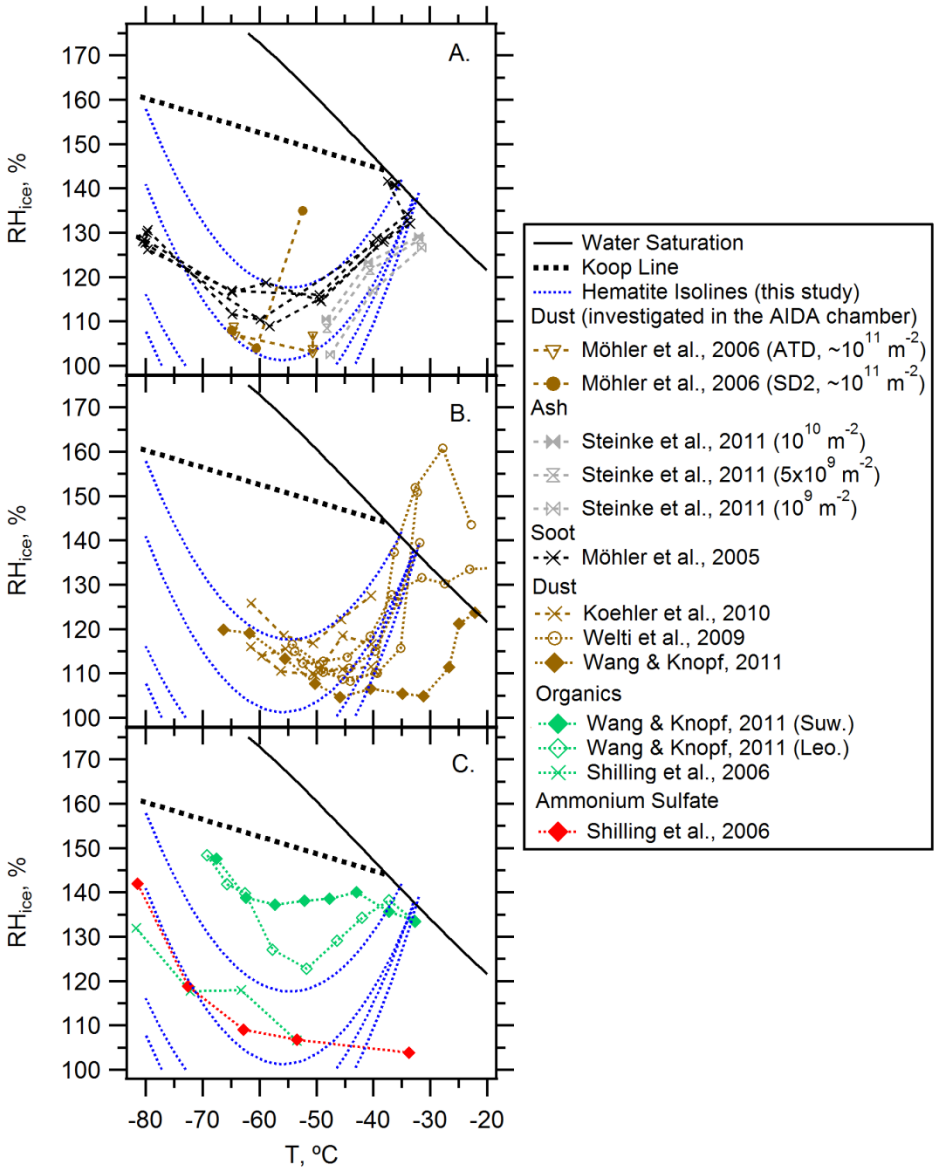

A.
B.
C.
RHice, %
T, ºC
Water Saturation
Koop Line
Hematite Isolines (this study)
Dust (investigated in the AIDA chamber)
Möhler et al., 2006 (ATD, ~10^11 m^-2)
Möhler et al., 2006 (SD2, ~10^11 m^-2)
Ash
Steinke et al., 2011 (10^10 m^-2)
Steinke et al., 2011 (5x10^9 m^-2)
Steinke et al., 2011 (10^9 m^-2)
Soot
Möhler et al., 2005
Dust
Koehler et al., 2010
Welti et al., 2009
Wang & Knopf, 2011
Organics
Wang & Knopf, 2011 (Suw.)
Wang & Knopf, 2011 (Leo.)
Shilling et al., 2006
Ammonium Sulfate
Shilling et al., 2006

Figure 3.

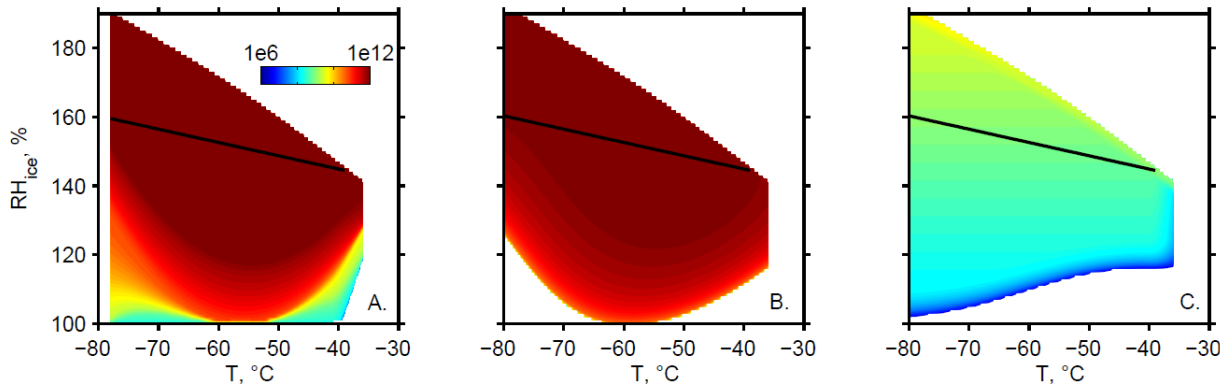
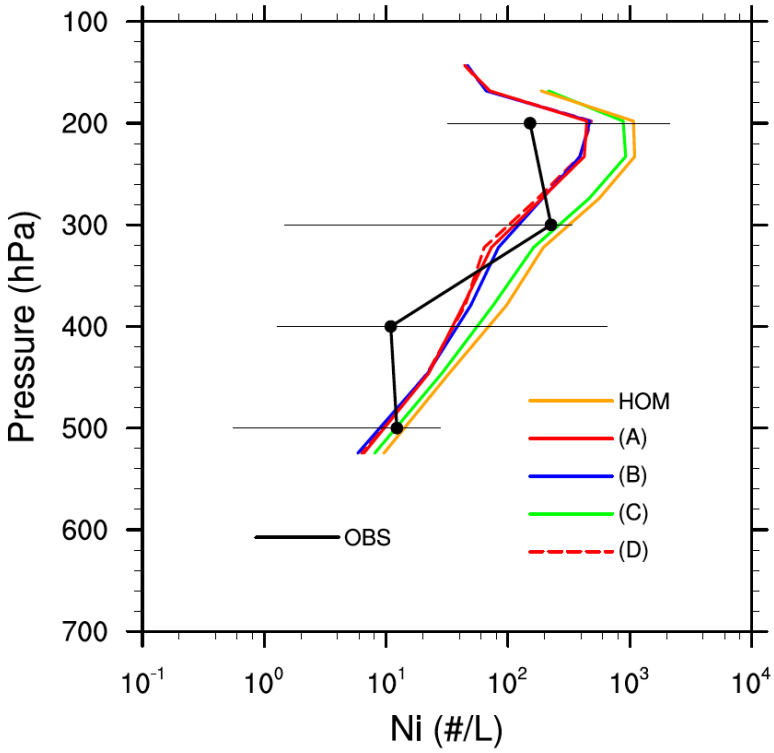


Figure 4.


100
200
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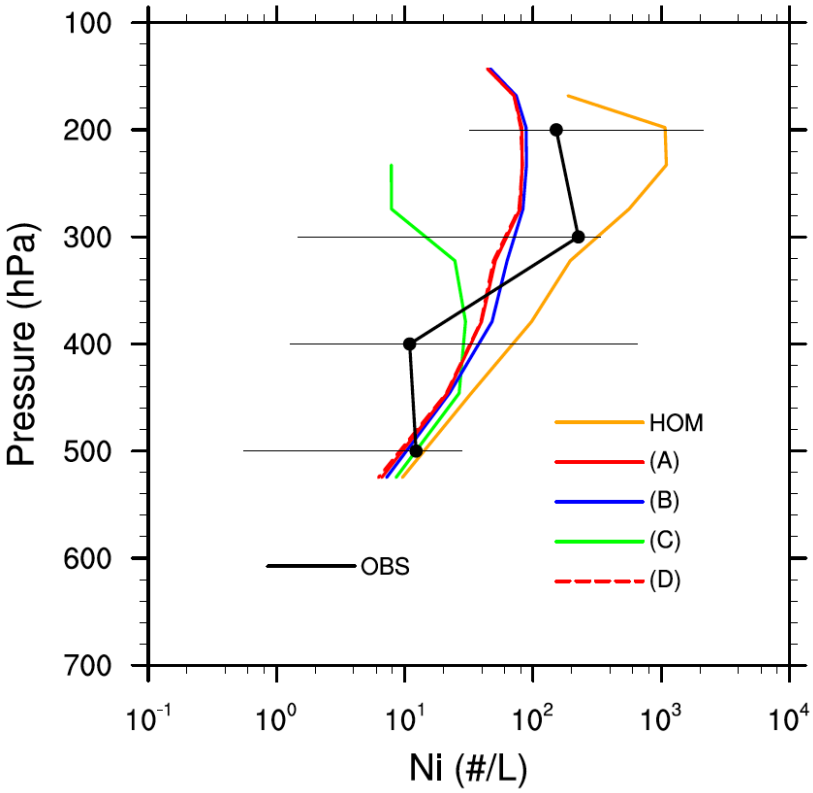
700
Pressure (hPa)
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
Ni (#/L)
HOM
(A)
(B)
(C)
(D)
OBS

Figure 5.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Pressure (hPa)
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10^{0}
10^{1}
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Ni (#/L)
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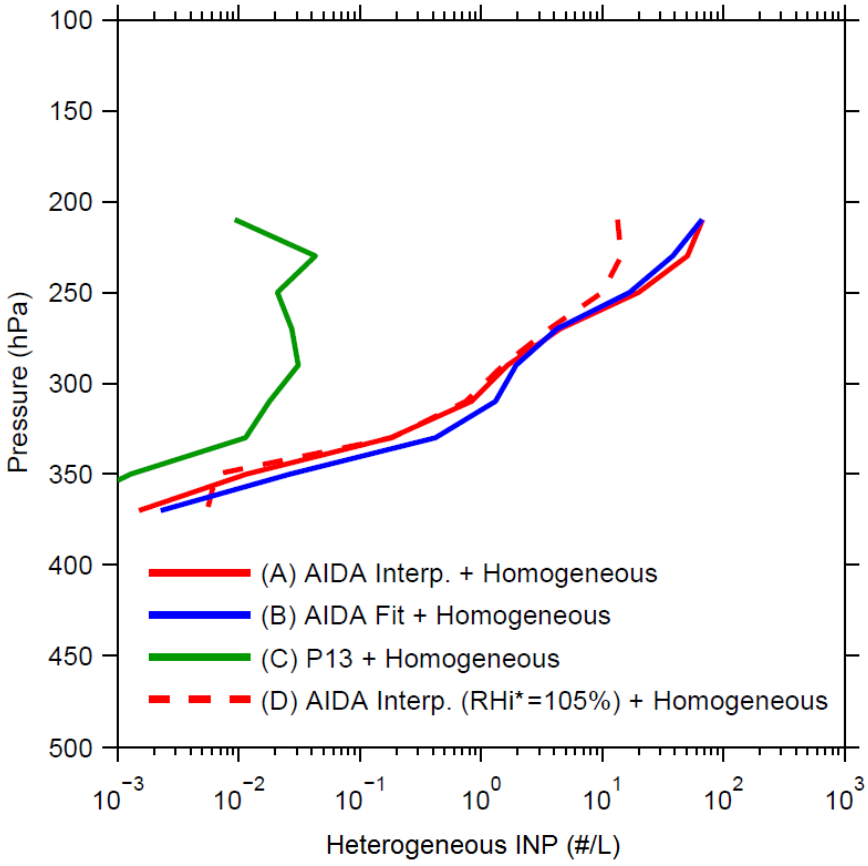
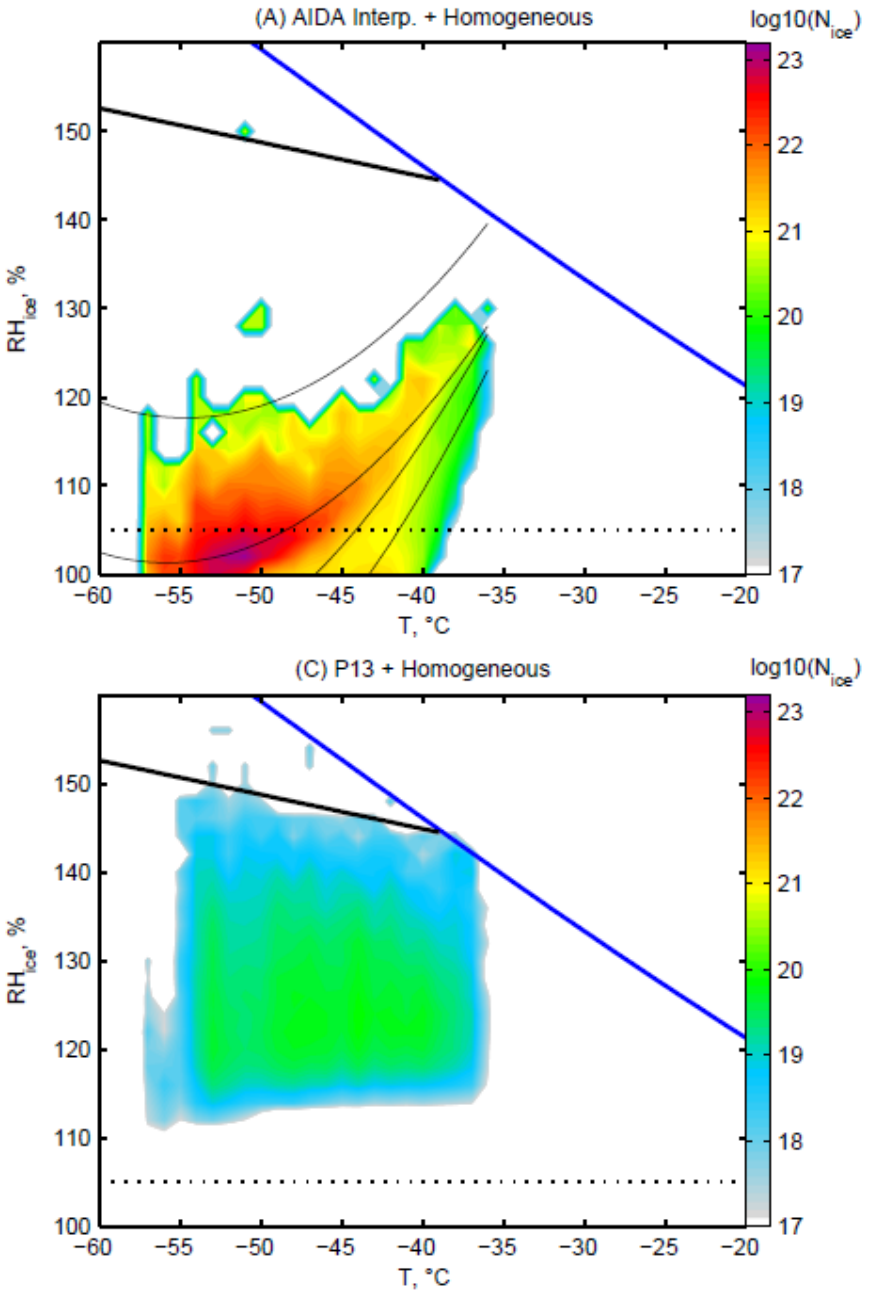
(C)
(D)
OBS

Figure 6.

903



904
905
906 Figure 7.



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908 Figure 8.

Figure Captions

Figure 1. Temporal plots of the representative AIDA deposition mode freezing experiments with various cooling ranges, including A. HALO06_19, B. HALO06_21, C. HALO05_18 and D. HALO05_24. Panels are arranged to show the measurements of i. AIDA mean gas temperature (T), ii. TDL, iii. SIMONE and iv. ice crystal concentration (N_{ice}). Note that the red lines represent interpolated data used for the n_s-isoline formulation. The $I_{back,par}$ in Panel iv axis denotes the backscattered light scattering intensity parallel to the incident polarisation state (log-scaled). An increase in the depolarisation ratio indicates the formation and growth of ice crystals.

Figure 2. The constant n_s magnitudes are joined by lines (blue), representing "isolines" of hematite freezing profiles in the T-RH_{ice} space. The interpolated isolines are equally spaced at every order of magnitude from 10^{12} m^{-2} (top) to 10^{9} m^{-2} (bottom). Experimental trajectories of AIDA expansion-experiments with hematite particles are shown as red dotted lines. The data indicated by green color on the water saturation line represent the previously reported results of immersion freezing (*Hiranuma et al*., 2014). The sub-panel shows a magnified section of T (-35 ºC to -45 ºC) and RH_{ice} (110 to 120 %) space with equi-distant n_s spacing (every quarter magnitude). The error bars at n_s of 10^{12} m^{-2} are from welas.

Figure 3. Ice nucleation onset T-RH_{ice} of previously published data (A. AIDA studies, B. dust, and C. ammonium sulfate and organics) shown together with the isolines of hematite particles from the present study (10^{12} m^{-2}, top, to 10^{9} m^{-2}, bottom).

Figure 4. Spatial plot of isolines for constant n_s derived from A. interpolating AIDA data, B. applying the third degree polynomial fit function to interpolated AIDA data and C. a previously published parameterization (*Phillips et al*., 2013) for hematite particles. The color scale displays log-scaled n_s values in m^{-2}, applicable to all panels. The solid black lines indicate the homogeneous freezing threshold line (i.e., Koop line).

Figure 5. Monthly mean profiles of the simulated in-cloud ice crystal number concentrations ($Ni \sim N_{ice}$) over the ARM SGP site. The four cases shown in the figure include the pure

homogeneous ice nucleation case (HOM) and four combined (heterogeneous + homogeneous) ice nucleation cases: (A) AIDA Interp. + Homogeneous; (B) AIDA Fit + Homogeneous; (C) P13 + Homogeneous; and (D) AIDA Interp. (RH_i^*=105%) + Homogeneous. Black dots show the observed mean profile of *Ni*. Left and right ends of the horizontal bars indicate the 10th and 90th percentiles of the observed *Ni* values at each pressure level.

Figure 6. Monthly mean profiles of the simulated in-cloud ice crystal number concentrations (*Ni* ~ N_{ice}) over the ARM SGP site. The four cases shown in the figure include the pure homogeneous ice nucleation case (HOM) and four pure heterogeneous ice nucleation cases: (A) AIDA Interp.; (B) AIDA Fit; (C) P13; and (D) AIDA Interp. (RH_i^*=105%). Black dots show the observed mean profile of *Ni*. Left and right ends of the horizontal bars indicate the 10th and 90th percentiles of the observed *Ni* values at each pressure level.

Figure 7. The mean heterogeneous INP number concentrations (~N_{ice}) simulated in COSMO. The red dashed line represents the simulation with 105% RH_{ice} as the lower boundary of ice formation, while the others are based on with 100% for the minimum RH_{ice} value.

Figure 8. Accumulated ice crystal concentrations (color scale in total crystals per model domain) as a function of temperature (1˚C bins) and RH_{ice} (2% bins). Heterogeneous nucleation simulated by AIDA parameterization (i.e., Figure 4A) and P13 parameterization (i.e., Figure 4C) was combined with homogeneous nucleation of cloud droplets.