Referee 2

We would like to thank referee 2 for his constructive comments and suggestions. In the following the comments will be addressed and discussed.
The comments of the referee are italicised and marked blue. Our responses are in normal type

General Remarks

The above article presents data on ice nucleation behaviour of chemically, thermally and physically treated Arizona Test Dust particles (ATD). In addition, the ice nucleation behaviour is compared to that of pure ATD particles and further inter-comparisons are made between the ice nucleability of variously treated particles. In particular the paper focuses on immersion freezing results on single particles from continuous flow measurement techniques. The aerosol treatment is characterised and supported from various suite of measurements, in particular from the Aerosol Mass Spectrometry instruments. The work and results presented herein are timely, of interest to the readers of Atmospheric Chemistry and Physics and are important for understanding the effect of chemical ageing of mineral dust ice nuclei in the atmosphere, especially under mixed phase cloud conditions. I recommend this paper for publication after the comments below have been addressed.

Specific Remarks:

Abstract:

***Line 2**: 'influences' should be 'influence'*

The phrase was changed accordingly.

At the end of the abstract, the authors state the results 'are certainly very interesting'. While this may be obvious to a reader whose expertise is in ice nucleation or aerosol-cloud interactions but for the purpose of broad readership I suggest adding a brief statement here (along the lines of atmospheric implications), to suggest why the results are interesting!

We add the following statement to the abstract:
"The strongly enhanced reaction between sulfuric acid and dust in the presence of water vapor and the resulting significant reductions in IN potential are of importance for atmospheric ice cloud formation. Our findings suggest that the IN concentration can decrease by up to one order of magnitude for the conditions investigated."

***Page 18560, Line 9**: The references given here I don't think represent the articles that actually did the science that showed that ice particles (through mineral dust nucleation) can alter microphysical and dynamical properties of clouds, influence precipitation and cloud lifetime. The references given here also used the above as motivation for their*

studies. I expect the references you want to add here would likely be modelling or field observations of earlier studies that investigate the formation of precipitation (via the ice phase), collision-coalescence processes and albedo effects from liquid and/or ice clouds. I suggest, replacing with suitable references or cite a review article with the suitable references therein.

We included the following references:
Martin, *Chem. Rev.*, 2000; Sassen et al., *Geophys. Res. Lett.*, 2003; Lohmann and Diehl, *JAS*, 2006; Lohmann and Hoose, *ACP*, 2009;

Line 15: *insert comma after 'processes'*

The phrase was changed accordingly.

Page 18561, Line 14-16: *the sentence 'With LACIS..... .....in each droplet' is poorly structured. I suggest splitting the sentence into two - something to the effect of: 'In the current work, LACIS was used to investigate the influence of quasi mono-disperse dust particles on immersion freezing. In particular, we note that in this method, only one particle is immersed in a single droplet'.*

We rewrote the sentence as follows: "LACIS was used to investigate the influence of size selected, quasi mono-disperse dust particles on immersion freezing. In particular, we note that in this method, only one particle is immersed in each droplet."

Line 21: *insert 'ATD' between 'coated' and 'particles'*

The phrase was changed accordingly.

Line 25: *replace 'Again' with 'Similar to FROST 1,'*

The phrase was changed accordingly.

Line 26: *should read: '..submicron particles were considered for coating with different amounts...'i.e. continue the sentence.*

The phrase was changed to: "Similar to FROST 1, size selected, quasi monodisperse submicron particles were considered for coating with different amounts of sulfuric acid to explore to what extent the increase of coating amount leads to an increase of surface modifications altering the IN potential of the particles."

Line 28: *insert ‘thus’ after ‘modifications’*

The phrase was changed accordingly.

Line 29: *delete the parentheses and text within and replace text with ‘compared to -34°C for FROST 1).*

The phrase was changed accordingly.

Page 18562, Line 1: *delete the portion of text in parentheses (see comment above). Replace ‘Also’ with ‘In addition’*

The phrase was changed accordingly.

Line 5: *insert ‘sulphuric acid’ before ‘coated’*

In this case also the water vapour and ammonia exposure experiments are included in the word “coated”. Therefore the phrase was rewritten with: “Finally, the sulfuric acid coated (including the additional water vapor and ammonia exposure) and pure ATD particles…”

Line 8-14: *Here the authors say that their work is related to Sullivan et al (2010) and Reitz et al (2011). In addition to describing what these studies are about, perhaps you can also add in a few sentences and describe what the most important findings/results from these papers were, or at least the results that most pertain to the current study.*

The following was included “The CFDC measurements clearly show that for all coatings the ice nucleation ability of the coated ATD particles was lowered compared to pure ATD in both, the deposition and the immersion/condensation mode. However, the deposition mode turned out to be significantly more affected, implying that soluble material on the particle surface goes into solution when particles become activated, and possibly reveals covered surface features (Sullivan et al., 2010a).”

And concerning Reitz et al. (2011): “Reitz et al. (2011) performed the chemical characterization of the differently treated particles using the Compact Time-Of-Flight Aerosol Mass Spectrometer (C-TOF-AMS). They suggest that the different treatments lead to different chemical reactions on the particle surface modifying the ATD particle surface (more details are presented in the results section).”

Line 26: *replace ‘in the course of’ with ‘during’*

The phrase was changed accordingly.

Page 18563, Line 13: *delete '....of all...'*

The phrase was changed accordingly.

Line 21-25: *Can you provide an amount or concentration of how much NH_3 gas was added to the sample line. Was all of this NH_3 consumed by the sulphuric acid coatings? Or did some of this NH_3 contaminate the lines/tubing or get sampled by the mass spectrometers?*

The answer the first part of the question, the following phrase was added to the text:
"Ammonia gas (10 ppm, Air liquide GmbH, Leipzig, Germany) was added to the aerosol flow at a flow rate of 0.50 l/m."

Not all ammonia was consumed by the sulfuric acid coating because ammonia most likely contaminated the tube walls, especially downstream of the point where it was added, i.e. after the water bath. But we cannot determine the degree of contamination. We extended the corresponding paragraph in the results part:
"The missing difference between the experiments with and without ammonia addition could be caused by saturation effects due to the compressed air and/or the tubing downstream of the water bath being contaminated with ammonia, or the ammonia being unimportant in the occurring surface modifications. As will be shown in the discussion section, the latter is most likely the case, because the addition of water vapor leads to an increased reaction between sulfuric acid and particle surface, consuming the available sulfuric acid."
It is therefore responsible for the IN ability reduction.

Page 18564, Line 1-2: *can you give a number of multiply charged particles that could have been sampled by LACIS and the CFDC instruments? Is the doubly charged particle concentration high enough so that perhaps the first freezing branch (low activated fractions) of pure ATD particles (at warmer temperatures), could be explained by the larger particles from multiple charges being active?*

The CCNC measurements show that droplet activation took place in a small supersaturation interval without exhibiting any steps (see Fig. 1) indicating that only a negligible amount of doubly charged particles was present during the experiments. Furthermore, both freezing branches feature different slopes and react differently when sulfuric acid coatings are applied making influences of double charges unlikely.
The following phrase was added to the results part:
"This freezing behavior cannot be explained by doubly charged, i.e. larger particles because the CCNC measurements indicate that droplet activation took place in a small supersaturation interval without exhibiting any steps. That means the number of doubly charged particles was negligible during the experiments. "

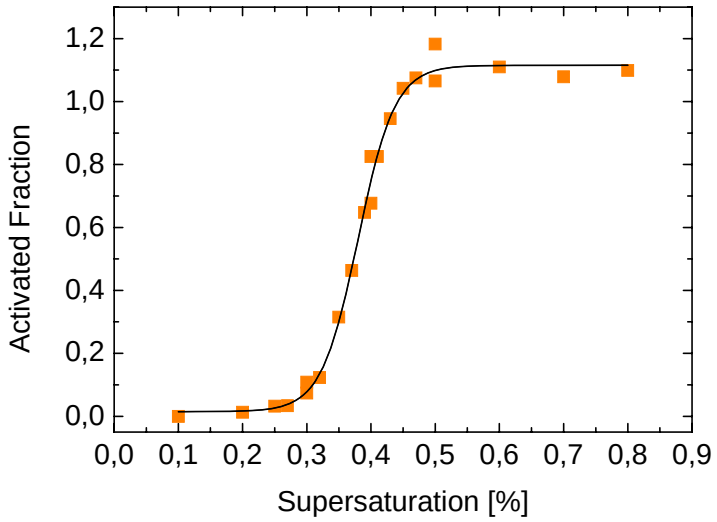

Fig.1: Activated droplet fraction as function of set supersaturation for pure ATD particles.

Page 18565, Line 20: *'6 to 7' should be 6 and 7'*

The phrase was changed accordingly.

Page 18566, Line 5: *here the authors presumably meant that after the walls are cooled down to -40°C, ice in the inner walls of LACIS are generated by passing saturated air through the flow tube? If so, one sentence about how the ice coating is achieved (just a brief mention) is warranted here.*

The corresponding sentence was rewritten: The inner tube walls of the freezing sections were coated with ice by setting the inlet dew-point of the sheath air flow to about - 7°C and cooling the freezing tubes down to -40°C for 5 min prior to the measurements.

Line 12: *replace 'at' with 'coating in' and 'tube' with 'walls'*

"…caused by both the ice coating the inner tube walls…"

Page 18567, Line 20: *replace 'the latter' with 'ammonium sulphate' given that the prior sentence is quite long with multiple objects.*

The phrase was changed accordingly.

Line 20 onwards: *The authors mention the use of compressed air here. I am curious as to what the NH_3 signature is in the compressed air, any indications from background spectra? If the neutralisation of SA by NH_3 under dry conditions is very slow, then how much NH_3 is present in the compressed air such that it should still lead to ammonium sulphate being present on the dry SA processed particles? Doesn't compressed air also have trace contaminants (organics), that could also condense on the particles when they are cooled down to -30°C or so in LACIS? Do you think this influences your results, for example the pure ATD results? i.e. how do the pure ATD results compare to experiments done in high purity air or nitrogen? If there were an effect, then it would be somewhat systematic across all the experiments. Is there any signature of organics from the coated aerosol particle mass spectra?*

The following paragraph is added to the text to answer the question:
"Silicone was found by the C-ToF-AMS on the pure ATD particles. Reitz et al. (2011) suggest the compressed air as source for the silicone. However, test measurements performed during FROST 1, during which the AMS was directly fed from a shaken stainless steel vessel supplied with filtered ambient air, indicated silicone to be part of the dust itself. Furthermore, experiments performed using nitrogen instead of compressed air in the aerosol generation section gave similar freezing behavior of the coated and uncoated dust particles. Besides silicon, also organic compounds were detected on the ATD particles (Reitz et al., 2011). Both the silicon and organic contaminations are likely due to the source and the production method for ATD. However, our experiments show that the small amounts of silicone or other organic contamination did not play a significant role in our measurements."

Page 18568, Line 1: *replace 'most presumably' with 'presumably mostly'*

In our opinion the referee suggestion somewhat changes the meaning of the sentence. Nothing was changed.

Line 11 onwards: *I don't understand how for ATD+SA(70°C)+WB+NH_3 and ATD+SA(70°C)+WB the ammonia signature is similar? Shouldn't the ammonia signature in the former be significantly greater? Is it possible that the reaction of humidified SA with ATD is so fast that by the time the particles 'see' the ammonia, the acid has already been neutralised in forming metal sulphates? From Figure 1 and the text description it looks like the ammonia is added in sequence after the SA coating region.*

The referee is right in saying that the reaction of humidified SA with ATD is so fast that the acid has already been neutralized in forming metal sulfates and that the ammonia is added after the exposure to sulfuric acid and the water vapor. Therefore it had been written and also was added in the results and discussion part:
"The missing difference between the experiments with and without ammonia addition could be caused by saturation effects due to the compressed air and/or the tubing downstream of the water bath being contaminated with ammonia, or the ammonia being unimportant in the occurring surface modifications. As will be shown in the discussion section, the latter is most likely the case, because the addition of water vapor leads to an

increased reaction between sulfuric acid and particle surface, consuming the available sulfuric acid."
"The C-ToF-AMS measurements showed that the neutralization of a part of the sulfuric acid occurred and that the humidification also caused increased surface reactions (Reitz et al., 2011), i.e., both reactions occurred simultaneously. […] it is more likely that the increased reaction of sulfuric acid with the particle surface dominates the IN ability reduction. This is in agreement with Lasaga (1995), who observed that the exposure to water vapor accelerates the reaction of sulfuric acid with mineral dust and indeed in the water vapor experiments a higher fraction of metal sulfate salts was formed compared to the sulfuric acid treatments without water vapor exposure."

Line 13-14: *parentheses should read '(sulphate mass of between 2600 – 2700 ag particle^{-1}).' Is it possible to confirm any of the coating composition data with supporting data from the ATOF-MS that was also used in this study as mentioned in the experimental section (see later comment)?*

Due to low counting statistics and short runtime during FROST 2 not enough data is available from A-TOF-MS to support the coating composition data gained from the C-TOF-AMS.

Page 18570, Line 4: *replace 'any' with 'all'*

The phrase was changed accordingly.

Line 11: *insert 'of' after 'Regardless'*

The phrase was changed accordingly.

Page 18571, Line 20: *insert 'at -30°C' after 'too small'*

The phrase was changed accordingly.

Page 18572, Line 21: *delete 'an'*

'an' was replaced by 'a'

Line 24: *Here the authors provide information Sullivan et al (2010) from the A-TOF-MS about how many particles remained uncoated during these experiments. However, is it possible to give more information about the coatings in support of the C-TOF-AMS results (see earlier comment)?*

Due to low counting statistics and as data from the A-TOF-MS measurements is sparse during FROST 2, not enough data is available to support the C-TOF-AMS findings. The following part was added to the text:
“Reitz et al. (2011) stated that the A-TOF-MS data show that 93 to 100% of the sulfuric acid coated particles contained sulfate (applying the less conservative threshold based on the signal quality of the individual mass spectra). However, sulfate peaks were also detected for pure ATD particles making the quantification of sulfate compounds on the particles somewhat ambiguous. The fraction of pure ATD particles that showed a sulfate peak ranges from 5 to 46% again based on the less conservative threshold. The missing sulfate peak for a small fraction of sulfuric acid coated particles in the A-TOF-MS is presumably related to very low amounts of sulfate on the particle surface so that no significant signal in the A-TOF-MS was produced although sulfate was present. Furthermore the CCNC measurements show that droplet activation took place in a small supersaturation interval without exhibiting any steps indicating that the aerosol was not externally mixed. ”
All in all, this suggests that it is likely that all ATD particles were coated with H_2SO_4.

Page 18573, Line 8: *replace ‘Now we look at’ with ‘Referring to the’ and also replace ‘i.e.’with ‘for’*

The phrase was changed accordingly.

Line 9: *Insert a comma after ‘...ATD + SA(85C)’ and delete ‘For these cases’*

The phrase was changed accordingly.

Line 10-17: *This explanation is suitable i.e. that the SA destroys the active sites for the first freezing branch and could be producing more efficient sites than previously existed for the second freezing branch. However, is there a possible explanation for why more effective sites are not produced on the particles that activate in the first freezing branch? Related to this and to the comment about multiply charged particles: Is it possible that the first freezing branch (small activated fractions) is due the small number of multiply charged particles (larger than 300nm) with larger surface areas and therefore providing more area for surface reaction with SA (which destroys active sites), which would not be the case for the smaller particles (mode of 300 nm) where the surface area is smaller and therefore perhaps a smaller rate of reaction with the surface and thus an increase in the second freezing branch only with the shift towards colder temperatures (T) closer to homogeneous freezing Ts?*

As mentioned above, no doubly charged particles were found which could explain the ice fractions found for T > -35°C.

Page 18574, Line 12: *replace ‘within’ with ‘for’*

The phrase was changed accordingly.

Line 12-13: *insert a comma after 'ammonia'*

The phrase was changed accordingly.

Line 20-21: *insert a comma after 'substance'*

The phrase was changed accordingly.

Line 24: *'...should recover to its condition...' Which condition are the authors referring to here? I find this sentence a little confusing. Some more clarity here would be nice. Also, I thought NH_3 was only added after passing through the water bath? So even in the case ATD+SA+WB+NH_3, the decrease in IN ability comes from the reaction of ATD+SA+WB and therefore I don't understand the clause 'prior to water vapour processing' in line 24.*

The sentence is misleading. What we wanted to say: "Thus, if the neutralization due to the ammonia was the dominating reaction, the resulting ammonium sulfate would most likely dissolve as soon as the particle becomes activated to a cloud droplet inside LACIS. Consequently, the particle surface would then exhibit conditions leading to an IN ability between the pure ATD and the ATD + SA (70°C) case. The sentence was changed accordingly."

Page 18575, Line 1: *replace 'was' with 'were'*

"was" is related to the word fraction, so nothing was changed.

Line 17-18: *replace 'large IN ability reduction' with 'large reduction in IN ability'*

The phrase was changed accordingly.

Page 18576, Line 25: *insert 'we infer from C-TOF-AMS and ice nucleation measurements that' after '...sum up'. I recommend this statement since the conclusions are reached by observing fragments of the reaction products and further supported by the change in ice nucleation properties*.

The phrase was changed accordingly.

Line 29: *replace 'highly active surface features ability' with 'IN ability of the highly active particles'*

replaced with: "…impair the ice nucleating ability of the highly ice active surface features"

Page 18577, Line 2-3: *should read 'nucleating substances and/or surface features which display higher ice nucleation potential might have formed. In general...*'

The phrase was changed accordingly.

Line 11: *insert 'sulphuric acid' after 'water vapour'*

The phrase was changed accordingly.
Line 12: *insert 'to' after 'and'*

The phrase was changed accordingly.

Line 22: *'completely vanished' instead of 'vanished completely'*

The phrase was changed that the ice fraction went below the quantification limit of LACIS (according to Ben Murrays comment.)

Line 28: *replace 'of' with 'in'*

The phrase was changed accordingly.

Page 18578, Line 1: *insert comma after parentheses and delete comma after speculate'*

The phrase was changed accordingly.

Line 2: *replace 'having' with 'that have'*

The phrase was changed accordingly.

Line 1-2: *There is no indication in the paper that the metal cations were also detected in the mass spectrometry of the aerosol particles. So I would rephrase this sentence, to say that the sulphates detected which are likely from metals and possibly* NH_4^+ *rather than saying metal sulphates were detected.*

The phrase was changed accordingly: "sulfates which are likely from metals"

Line 7-9: *Delete last sentence of this paragraph and replace with 'The exposure of sulphuric acid coated particles to the water bath and ammonia seems to be of secondary importance' I feel like it is important to add the water bath here to be clear that ammonia was only added after exposing the SA coated particles to the water vapour.*

Your suggestion changes the meaning of this statement. Therefore we included the following sentence: "The exposure to ammonia after the water vapor exposure seems to be of secondary importance."

Line 12-14: *the sentence that spans these lines is confusing even though I think I know what the authors are trying to say. It is important to be clear here (since it is in the conclusion) and indicate that the water vapour treated particles had SA on them. I suggest something to the effect of: 'Significant reduction in IN ability was observed for SA-coated ATD particles that were passed through the thermodenuder, similar to the IN ability of SA-WB treated ATD particles.'*

The following sentence was included (similar to your suggestion): "Significant reduction in IN ability was observed for sulfuric acid coated ATD particles that were passed through the thermodenuder, similar to the IN ability reduction for the sulfuric acid plus water vapor treated ATD particles.."

Line 15: *replace 'than the' with 'compared to those from'*

The phrase was changed accordingly.

Line 16: *'enhance' should be 'enhanced'*

The phrase was changed accordingly.

Line 23: *replace 'processings' with 'treatment'*

The phrase was changed accordingly.

Final paragraph: *It would be nice if the authors suggested why their results are interesting from an atmospheric implication perspective. Is this study relevant to the atmospheric ice nucleation because most mineral aerosol acting as IN found in the atmosphere is internally mixed with sulphuric acid or ammonium sulphate etc?*

The atmospheric relevance of this work is most directly related to the influence of atmospheric aging on the IN ability of dust particles. The strongly enhanced reaction between sulfuric acid and dust in the presence of water vapor, and the resulting reductions in IN effectiveness suggest that atmospheric IN concentrations could be significantly reduced upon aging (up to one order of magnitude for the conditions

investigated here). Further investigations into the basic mechanisms for modifications in IN effectiveness are needed in order to fully appreciate the extent and magnitude of the atmospheric effects.

Figures:

Figure 1

Would it be possible to include in the caption what 'other instruments' are, relevant to the current study? In the main body of the paper, many instruments are mentioned, but perhaps those most pertinent to the data from this study can be included in the caption. Shouldn't there be a CPC downstream of the WELAS counter? I think this is missing from the schematic.

The CFDC, ATOFMS and C-ToF-AMS were named in the caption, CPC, and DPM were added to the figure (see figure below).

Figure 3

The dark yellow triangles appear to be quite close in colour to the green ones. In panel (a) the difference is colour is clear, but in panel (b) where unfilled symbols are used, it is a little harder on the eye. Perhaps use another colour other than dark yellow.

The color was changed accordingly (see figure below)

Figure 4

I think the order in which the figures are arranged is really good for easy comparison. Would it be possible to put a label on each chart with the respective particle type/treatment? If this is done, then you can also delete the panel descriptions from the text

The labels were put to the figure (see figure below)

Figure 5

This is a nice figure comparing CFDC and LACIS results. However, after reading the experimental section I was expecting results from FINCH and PINC as well, especially PINC, because it is also a laminar flow technique and almost identical to the CFDC. It would be nice to see results from this chamber. Or perhaps the authors can refer readers to where these other data are/will be published.

Due to low counting statistics and runtime during FROST 2, no PINC and FINCH data are available.

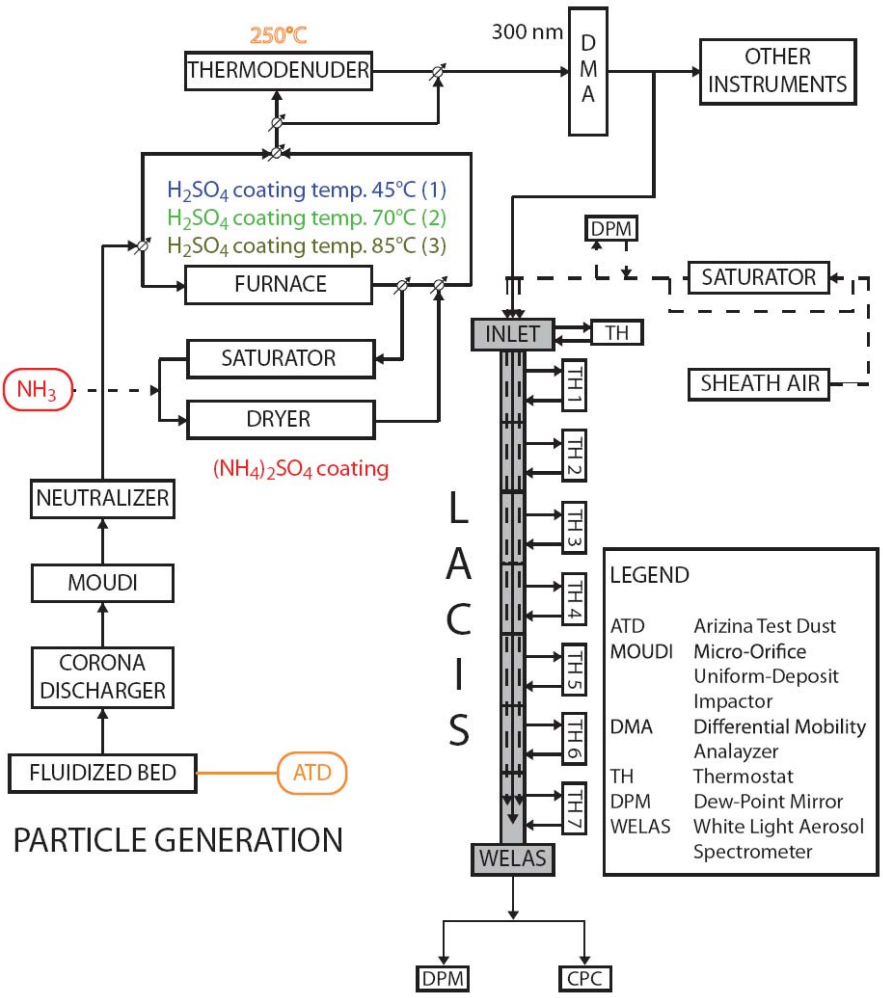

Fig.1 *Sketch of the generation, coating and size selection of the particles. Also included are the setup of particle conditioning and LACIS laminar flow tube. The other instruments box included CFDC, PINC, FINCH, ATOFMS, C-ToF-AMS, CCNC, H-TDMA and the CPC.*

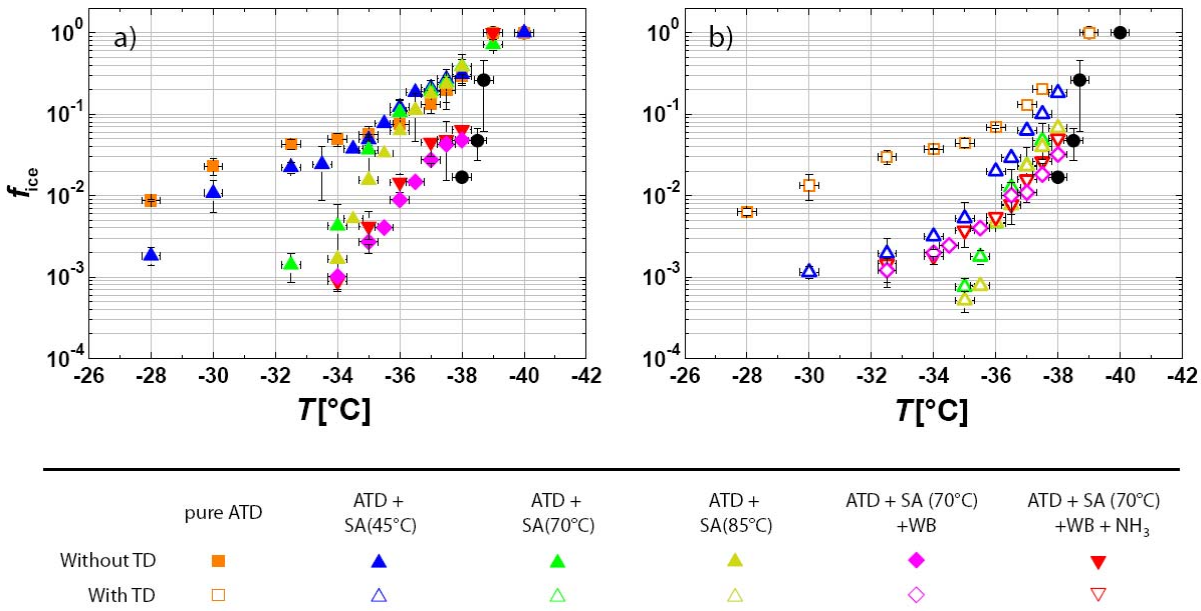
a)
b)
f_{ice}
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
-26 -28 -30 -32 -34 -36 -38 -40 -42
T[°C]
pure ATD
ATD + SA(45°C)
ATD + SA(70°C)
ATD + SA(85°C)
ATD + SA (70°C) +WB
ATD + SA (70°C) +WB + NH_3
Without TD
With TD

Fig.3

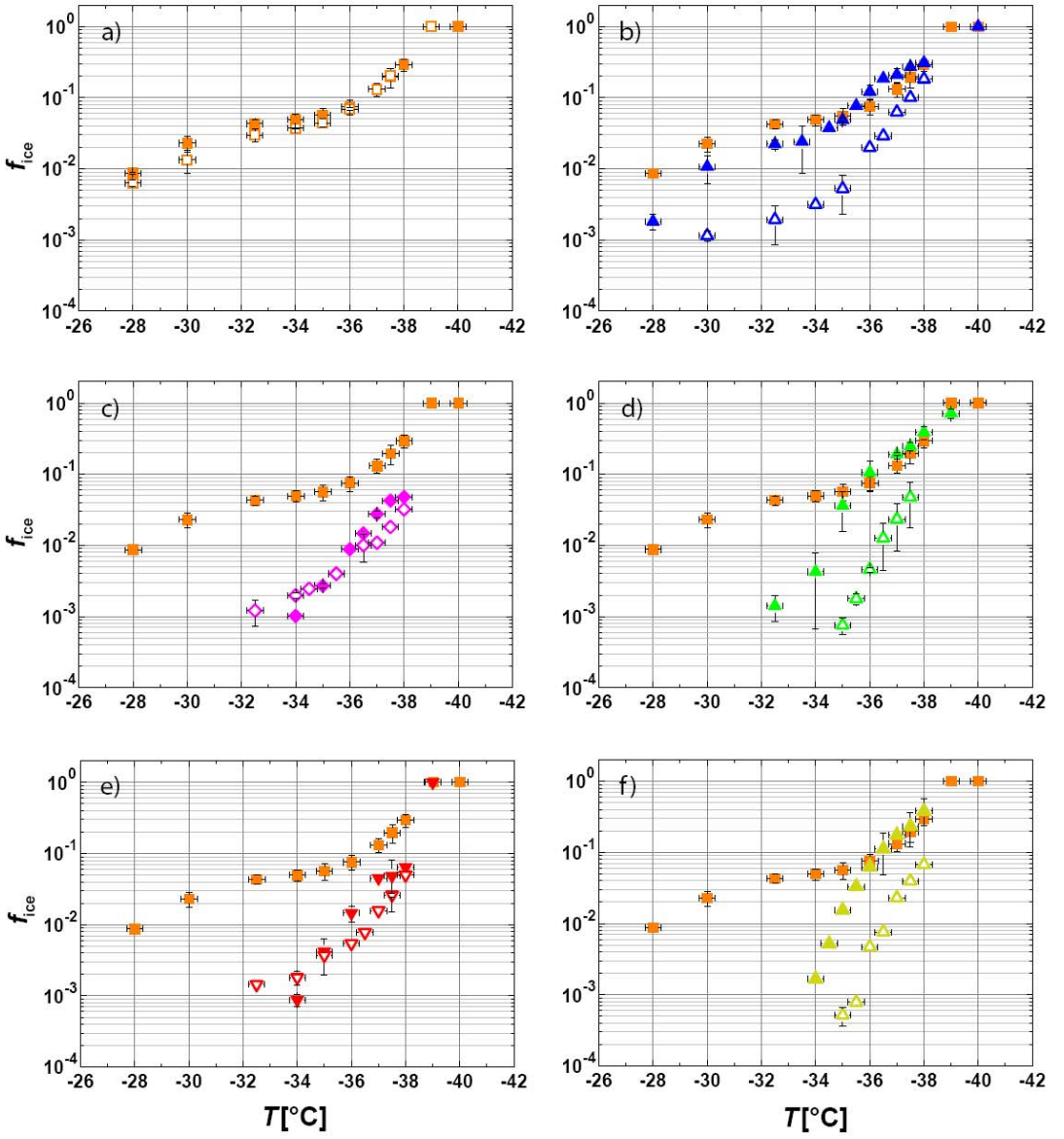
a)
b)
c)
d)
e)
f)
f_{ice}
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
-26 -28 -30 -32 -34 -36 -38 -40 -42
T[°C]
pure ATD
ATD + SA(45°C)
ATD + SA(70°C)
ATD + SA(85°C)
ATD + SA (70°C) +WB
ATD + SA (70°C) +WB + NH_3
Without TD
With TD

Fig.4

References

Cwiertny, D. M., Baltrusaitis, J., Hunter, G. J., Laskin, A., Scherer, M. M., and Grassian, V. H.: Characterization and acid mobilization study of iron containing mineral dust ource materials, J. Geophys. Res., 113, D05202, doi:10.1029/2007JD009332, 2008.

Lasaga, A. C.: Fundamental approaches in describing mineral dissolution and precipitation rates, in: Chemical Weathering Rates of Silicate Minerals, Vol. 31 of Reviews in Mineralogy, Mineralogical Society America, Washington, USA, 23–86, 1995.

Lohmann, U., and Diehl, K.:Sensitivity studies of the importance of dust ice nuclei for the indirect aerosol effect on stratiform mixed-phase clouds, J. Atmos. Sci., 63, 968-982, doi:10.1175/JAS3662.1, 2006.

Lohmann, U. and Hoose, C.: Sensitivity studies of different aerosol indirect effects in mixedphase clouds, Atmos. Chem. Phys., 9, 8917–8934, doi:10.5194/acp-9-8917-2009, 2009.

Martin, S. T.: Phase transitions of aqueous atmospheric particles, Chem. Rev., 100, 3403– 3453, 2000.

Reitz, P., Spindler, C., Mentel, T. F., Poulain, L., Wex, H., Mildenberger, K., Niedermeier, D., Hartmann, S., Clauss, T., Stratmann, F., Sullivan, R. C., DeMott, P. J., Petters, M. D., Sierau, B., and Schneider, J.: Surface modification of mineral dust particles by sulphuric acid processing: implications for ice nucleation abilities, Atmos. Chem. Phys., 11, 7839–7858, doi:10.5194/acp-11-7839-2011, 2011.

Sassen, K., DeMott, P. J., Prospero, J. M., and Poellot, M. R.: Saharan dust storms and indirect aerosol effects on clouds: crystal-face results, Geophys. Res. Lett., 30(12), 1633, doi:10.1029/2003GL017371, 2003.

Sullivan, R. C., Petters, M. D., DeMott, P. J., Kreidenweis, S. M., Wex, H., Niedermeier, D., Hartmann, S., Clauss, T., Stratmann, F., Reitz, P., Schneider, J., and Sierau, B.: Irreversible loss of ice nucleation active sites in mineral dust particles caused by sulphuric acid condensation, Atmos. Chem. Phys., 10, 11471–11487, doi:10.5194/acp-10-11471-2010, 2010a.

Sullivan, R. C., Minambres, L., DeMott, P. J., Prenni, A. J., Carrico, C. M., Levin, E. J. T., and Kreidenweis, S. M.: Chemical processing does not always impair heterogeneous ice nucleation of mineral dust particles, Geophys. Res. Lett., 37, doi:10.1029/2010GL045540, 2010b.