Referee 1 – Benjamin Murray

We would like to thank Benjamin Murray for his valuable comments to improve the manuscript. 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.

This is an interesting experimental investigation of the influence of chemical processing on the ice nucleating ability of Arizona Test Dust (ATD). The authors used the LACIS instrument during a campaign in which other instruments were also used which allows an inter-comparison. They find that ice nucleation by ATD is unaffected by heating to 250 K alone. Addition of sulphuric acid results in less efficient ice nucleation above -35oC, but slightly more efficient nucleation below -35oC. On addition of water or heating, the nucleation efficiency of ATD is substantially reduced over the whole temperature range. This is presumably due to the water and heat facilitating a chemical reaction between components of ATD and sulphuric acid. Ammonia is found to have a second order effect. The subject, quality and novelty of this study make it appropriate for ACP and I recommend publication once the following comments have been addressed.

1) P18561, ln 2-4. *Why should all the ions of a soluble salt go into solution? Could ions not exchange with other ions on or in the solid or perhaps simply adsorb on the surface. I suspect the bulk of the ions are in the aqueous phase at any one time, but they may also reside on the surface too. Also, clays for example (a component of ATD) are used as heterogeneous catalysts and this implies they interact with solute ions in an aqueous medium. This statement and also the one on page 18574 ln 22 need to be modified accordingly.*

We now write that: “…the soluble material should most likely dissolve as the particles become activated to cloud droplets. For example, Sullivan et al. (2010b) observed that nitric acid coatings on ATD particles impaired deposition nucleation below water saturation. In contrast, immersion freezing was not affected leading to the conclusion that nitric acid did not irreversible alter the particle surface. But the question remains whether such a behavior also appears for other acidic coatings like sulfuric acid.”
and:
“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).”

2) P 18563, ln 2. *Some much more detailed data on the mineralogy of ATD was recently published by Broadley et al. (Atmos. Chem. Phys. Discuss., 11, 22801–22856, 2011), which may help with the interpretation of the results.*

Thanks for your suggestion. The data of Broadley et al. has been included.

***3) P 18570, ln 3**. replace ‘first’ with ‘high temperature freezing branch’ – and quantify what range of temperatures are being discussed.*

The phrase was changed accordingly.

***4) P 18570, ln 3.** ‘vanished completely’. This term is not acceptable. The fice value was simply lower than the detection limit. What is the detection limit?*

The phrase was changed accordingly: “For ATD + SA (70°C) and ATD + SA (85°C), f_{ice} was below the quantification limit of about $5*10^{-4}$ for the high temperature freezing branch…”

***5) P 18570, ln 5.** It is very hard to make out the increase in fice due to H2SO4. Maybe quote some values in the text with corresponding uncertainties to clarify this.*

It is a factor of about 1.5 being in part within the uncertainties. A sentence was included in the text.

***6) P 18570, ln 13.** I do not understand what is meant by ‘missing difference’. This needs to be clarified.*

The missing difference in the IN ability is meant. The phrase was changed accordingly

***7) P 18571, ln 15-25.** The agreement between LACIS and the CFDC is very impressive. After studying the figure I would say that this is somewhat understated here. Based on the figure the values agree to within a factor of two and in all but one case the two measurements are within experimental uncertainty.*

The understatement was removed: “…the ice fractions determined with the CFDC and LACIS agree to within a factor of two and in all but one case the measurements are within the experimental uncertainties.”

***8) P 18572, ln7.** Recent work suggests that the pseudo hexagonal lattice match ideas expressed by Pruppacher may not be particularly relevant (at least for kaolinte, which has been described as having a pseudo hexagonal match to ice). Computation work by Hu et al. (Surface Science 601 (2007) 5378–5381) suggests that ice nucleation by kaolinite is probably not due to the pseudo hexagonal lattice of a perfect kaolinite surface. In addition, the idea that amorphous material is a poor ice nucleus has been challenged by recent experiments at the AIDA chamber (Murray, Nature Geoscience, DOI: 10.1038/NGEO817).*

The following sentences were added:

“A recent study by Hu and Michaelides (2007) showed, however, by means of a series of density-functional theory calculations for the adsorption of water on the hydroxylated and siloxane surfaces of kaolinite that the stability of an ice layer formed on the kaolinite surface is not due to the favorable lattice match with ice. Instead it is caused by the substrate being amphoteric with the ability to donate and accept H-bonds.”

“…Not implying that amorphous particles do not initiate ice nucleation in general. E.g., Murray et al. (2011) found that glassy (amorphous, non-crystalline) particles initiated ice nucleation under cirrus conditions.”

9) P 18572, ln18. *‘majority of particles features areas.....’ I do not understand this sentence.*

The sentence was changed to: “However, the majority of particles exhibits surface features with lower nucleation potential (inducing freezing at temperatures below -35°C)”

10) P 18573, ln 11. *I think the use of the term ‘areas’ is unclear. I appreciate that the authors may want to avoid the term ‘active site’, which I think is wise because it has become associated with the time-independent singular model. However, ‘surface area’ implies the physical area of a material in units of cm-2. Broadley et al. used the term nucleation sites and explicitly defined this as either specific active sites (which might be cracks or defects) or crystal faces where a lattice match might be found. The authors also use the term ice active surface features in the abstract, which I think is also much better than ‘areas’.*

We replace areas with ice active surface features.

11) P 18573, ln15. *Why should the reaction between sulphuric acid and ATD be slow without water – reference?*

What we mean is that the reaction between sulfuric acid and ATD surface is slower compared to the reaction if additional water is available. Lasaga (1995) stated that the presence of water vapor increases the reaction between sulfuric acid and mineral dust. Since this statement of slow reaction is placed here without explanation, we removed it.

12) P 18573, ln23. *Destroyed by the thermal treatment as well as sulphuric acid.*

We would say: by the additional thermal treatment after sulfuric acid coating.

13) P 18574, ln11. *‘effective’ doesn’t make sense in this context. How about ‘have a greater influence’.*

The phrase was changed accordingly.

14) P 18576, ln 13. *''not unlikely' = likely ?*

Sure! The phrase was changed accordingly.

15) P 18576, ln 25. *Replace first few words with 'To summarise'*

The phrase was changed accordingly.

16) P 18577, ln 29 and next page, ln 22. *I do not agree with the use of 'destroy' or 'vanished completely'. The number went below the detection limit.*

The phrase was changed accordingly: 'impair' instead of 'destroy', "went below the detection limit' instead of 'vanished completely'

17) P 18578, ln 3. *Are these calcium and magnesium ions. Include word 'ions'. What does interspersed mean in this context. Where exactly are the ions and why are they accessible for reaction? This is very vague.*

"Interspersed" means that Mg- and Fe-ions are substituted into aluminosilicates. (E.g., illite could feature Mg, Fe ions which could substitute Al-ions). Sulfuric acid is a strong acid and will react with the particle materials and therefore with the metals included in the particles. As stated in the text, Cwiertny et al. (2008) showed for example that iron which is predominantly substituted into aluminosilicate minerals of ATD becomes dissolved due to sulfuric acid and the presence of water (pH = 1) forming (soluble) iron(II) and iron(III) sulfate. The phrase was changed accordingly.

18) *I found **Figure 4** quite difficult to see differences between the different experiments when trying to compare different plots. I can think of two possible ways of improving this:*
1) plot the change in fice from the untreated ATD case as a function of temperature.
2) plot the untreated ATD case in each plot for reference.

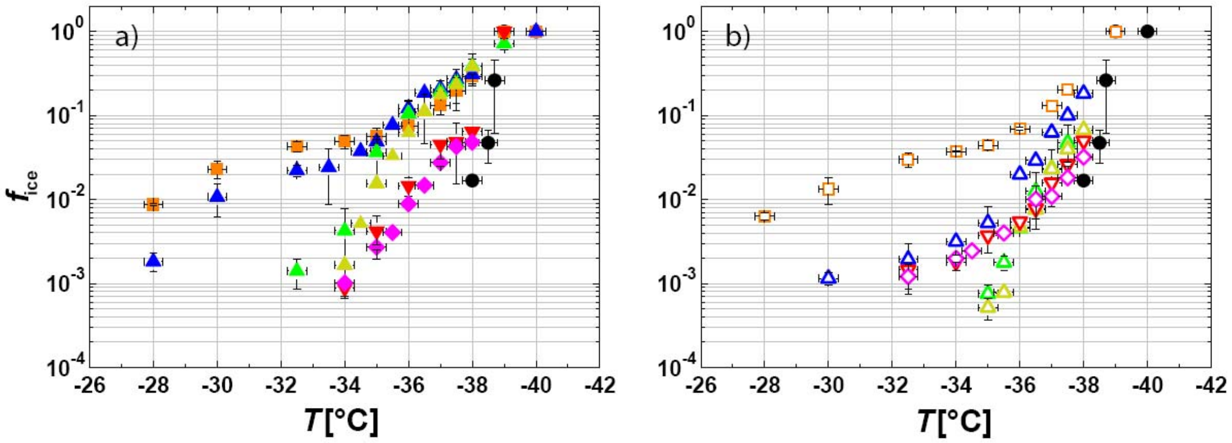
2) untreated ATD case was plotted in each plot for reference

19) *Also, label the plots in **Figure 4** rather than listing it in the caption. I ended up writing on the plots myself. Use the labels in the caption as labels in the figures.*

The labels were added to the plot.

20) Figure 3. *Put a key in the plots. Again, it is very confusing to have to look at the caption to figure out what the symbols mean.*

The labels were added to the plot:



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	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

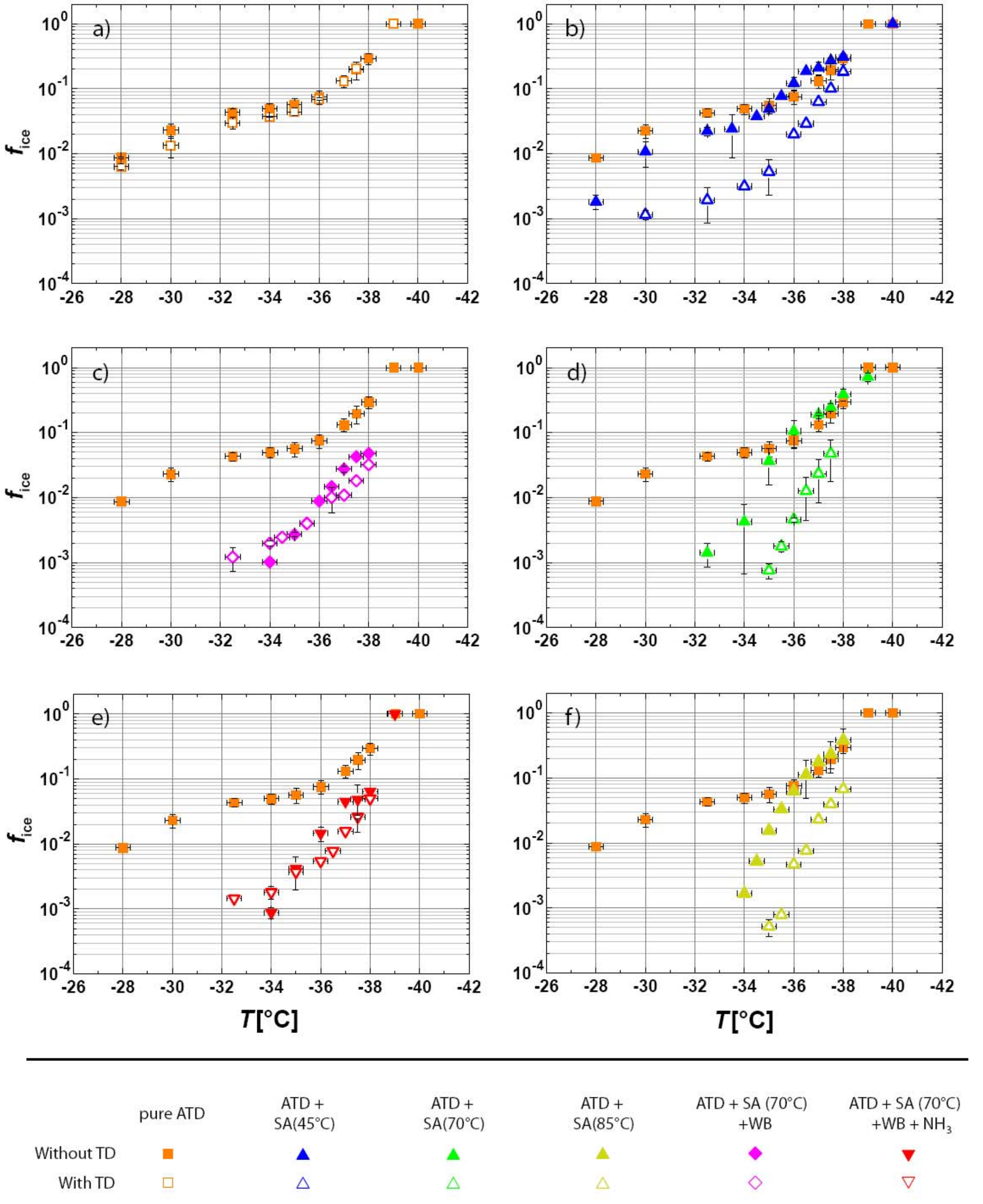
a)
b)
c)
d)
e)
f)
f_{ice}
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
-26
-28
-30
-32
-34
-36
-38
-40
-42
T[°C]
pure ATD
ATD + SA(45°C)
ATD + SA(70°C)
ATD + SA(85°C)
ATD + SA (70°C) +WB
ATD + SA (70°C) +WB + NH_3
Without TD
With TD

Fig.4

References

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