

Our reply to both Referees is below. The Referee's original comments are in italics, and our response below that. We thank both Referees for providing valuable input that helped us improve the revised manuscript.

Anonymous Referee #1

General comments

During the coating process the particles are typically exposed to strongly acidic conditions and heat, both might lead to irreversible destruction of active sites. However, there is one issue, namely the limited timescale of the experiments that has not been given much attention in the discussion of the results. For conditions above water saturation, the particles are exposed to supersaturation for only few seconds. It is not clear whether this is long enough to dissolve the sulfuric acid coating. Active sites might regenerate on longer timescales. Such a discussion should be added to the revised manuscript.

This is a good point, thank you. As we did not study the effect of residence time in the CFDC in these experiments we do not know what effect longer periods of water supersaturation may have had on the active sites. However, we infer sufficient time for dissolution based on analogous studies following nitric acid uptake, as reported separately. We have added some discussion of this topic and the recent related experiments to the revised manuscript:

“The fact that f_{IN} at 105% RH_w was still reduced by the coatings clearly indicates that dissolution during droplet activation does not completely reverse the detrimental effects caused by the sulphuric acid coating. Therefore, some fraction of the ice active sites was irreversibly lost when the sulphuric acid was condensed on the mineral particles. ATD particles exposed to nitric acid vapour at room temperature were recently observed to have reduced deposition nucleation ability, but unaltered immersion/condensation-freezing at the same RH_w values and measured by the same CFDC used here (Sullivan et al., 2010). This suggests that there was enough time in the CFDC for soluble nitric acid coatings to be removed from surface sites by dissolution following the absorption of water above water saturation, thus restoring the ice nucleation ability of ATD particles. The fact that f_{IN} was reduced at 105% RH_w by the sulphuric acid coating in these experiments indicates irreversible modification of surface sites by the coating that is not reversed by dissolution.”

One additional general comment concerns data evaluation: at the beginning of the results section, it is stated that changes in IN fraction do occur until 105%, although above water saturation ice nucleation at the active sites should no longer respond to changes in the gas-phase relative humidity. Therefore, the frozen fraction at this value is taken to characterize immersion/condensation freezing. However, Figure 2 shows a plateau in IN fraction for the pure and the heated ATD at 105% RH_w but not for the SA treated ATD samples. For these samples the freezing onset seems to shift above water saturation. The frozen fraction increases continuously up to the limit for droplet break through, and the discrimination between evaporating droplets and ice crystals is less clear. Reasons for this should be discussed. As a consequence, evaluation at 108% RH_w would increase the frozen fraction significantly and could affect some of the conclusions (e.g. the IN fraction of the sample SA 70C would be similar as the one of

pure ATD). From the discussion of Fig. 2 (page 16913, lines 12-19) it does not become clear whether the authors postulate the presence of a plateau also for the SA treated samples. If yes, they should indicate it in the Figure.

Evaluation of ice nucleation at RH_w higher than 106% is difficult due to interference from droplets that survive the evaporation region for the CFDC evaporation region length and flow rates used in this study. Although we have indicated a region when droplets interfere with our detection of ice in Fig. 2 this is not a hard limit; there is some variability between experiments in the RH_w value where droplet breakthrough occurs, but it was never observed to occur below 106% RH_w during this study. This is why 105% RH_w was selected to evaluate the maximum in the condensation/immersion-freezing fraction. The best indication of droplet breakthrough is observed from a sudden increase in f_{IN} occurring above $\sim 106\%$ RH_w , as observed for the SA and SA + TD treated ATD scans shown in Fig. 2. In all four treatments the response of f_{IN} vs. increasing RH_w approached a plateau in the 102-106% RH_w range, before rising steeply again. We also performed calculations of droplet breakthrough, as indicated by the survival of > 2 micron drops after the evaporation section using the CFDC particle growth/evaporation model of Rogers (1988). These calculations suggest droplet breakthrough at 107% RH_w at -30°C . We therefore conclude that this rise in f_{IN} above 106% RH_w was due to droplets, and not due to the sudden onset of immersion-freezing. While it is possible that the larger droplet sizes produced at higher RH_w values potentially restore active sites by dissolution of the coating, our recent experiments where ATD was exposed to nitric acid vapour suggest that this dissolution and restoration occurs close to water saturation; higher RH_w conditions did not result in a further large increase in f_{IN} (Sullivan et al., 2010). We have added a discussion of the related nitric acid coatings as described above, and have added the following to the discussion of Figure 2: “ATD coated with SA (with or without subsequent heating) also displayed a brief plateau in f_{IN} near 105% RH_w , followed by a sharp rise in f_{IN} as RH_w was increased further. This sharp increase in f_{IN} at these high RH_w conditions is consistent with the appearance of water droplets grown to sizes that survive the evaporation region of the CFDC and interfere with the optical counting of IN grown as ice crystals (Petters et al., 2009). The onset of this behaviour at approximately 107% RH_w at -30°C for this CFDC configuration and flow rate used in this study is quantitatively consistent with the conditions required for water droplets at sizes $> 2 \mu\text{m}$ to survive to the OPC based on calculations using a simple model of particle growth in the CFDC (Rogers 1988). We therefore conclude that the increase in f_{IN} above 106% RH_w was due to droplet breakthrough, and not the sudden onset of immersion/condensation-freezing under high RH_w conditions.”

Several parts of the discussion might improve when results of the ATOFMS results that were also performed during this study were included. E.g. variability of SA coatings between particles, formation of sulfate salts on the particle surface.

We agree and incorporate the ATOFMS results into the discussion. In particular, we added the following to Section 3.2:

“The single-particle measurements obtained by the ATOFMS were queried for various experiments representative of the most common experimental treatment combinations reported here. Using a conservative sulphate peak area threshold of > 1000 , between 84 and 97% of ATD particles contained sulphate for experiments in which ATD particles passed through the sulphuric acid coating tube (and in some cases additional treatments following this). Using a

less conservative peak detection limit (peak height > 50 above baseline) decreases the number of particles that did not produce a sulphate ion signal to approximately 6%. The small fraction of particles that did not produce a sulphate ion signal > 1000 peak area indicates that these particles had no or only small amounts of sulphate, or that the ATOFMS's laser ablated a portion of the particle that did not contain sulphate, even though sulphate was added to the particle (Cziczo et al., 2009). The lack of a step-function in the shape of the CCN activation curve is further evidence against a substantial fraction of externally mixed ATD particles that did not contain sulphuric acid. Finally, SA + TD treated particles had f_{IN} reduced by at least an order of magnitude compared to uncoated ATD (excluding the less reliable measurements at -25 °C and 98% RH_w). As we observed that only particles exposed to sulphuric acid before heating had impaired ice nucleation ability following the thermodenuder, we conclude that the decrease in f_{IN} indicates that ATD particles that did not contain sulphuric acid could only have composed a small fraction no greater than a few percent of the total particle number."

Specific comments

Page 16903, lines 19-20: why should conditions above water saturation be required for immersion freezing? Conditions at water saturation would be sufficient.

Immersion-freezing occurs when activated droplets freeze, while condensation-freezing occurs when a droplet which is still absorbing water during activation freezes. Therefore, conditions above water saturation are required to activate all particles and produce droplet sizes in the CFDC similar to those found in mixed-phase clouds. At water saturation particles will not yet be activated into droplets, especially considering nominal uncertainties in RH_w in the CFDC. As we cannot clearly distinguish between condensation and immersion-freezing using these methods we make no attempt to do so in our discussion. No change was made to the manuscript.

Page 16905, line 20: "The corona discharger did not change the IN ability": Reference to Niedermeier et al. (2010) should be added to this statement.

We added this reference.

Results section and Figure 2: readability of Figure 2 would improve if RH_w for $RH_i = 100%$ at -30C were indicated. Also: RH_i for $RH_w = 98%$ should be mentioned.

At -30 °C and $RH_i = 100%$, $RH_w = 74%$, which is below the range that was typically scanned in these experiments, since f_{IN} is below our quantification limit under those conditions. For $RH_w = 98%$, $RH_i = 131%$ at -30 °C, and $RH_i = 125%$ at -25 °C. This information was added to Figure 2's caption.

Fig. 3b: what is "ag" in "ag/particle"? A change to a mass fraction scale should be considered. This would allow a more direct comparison with the SA volume fraction from CCN shown in Fig. 3a.

ag is attograms ($1 \text{ ag} = 10^{-18} \text{ g}$), which we now define in the text. We changed the x-axis in Fig. 3b to a sulphate particle mass fraction scale, as suggested.

Page 16914, line 21: “. . . responded similarly to all but one of the various physicochemical processing. . .”: It should be specified which one.

With the omission of the water bath exposure experiments from Figs. 4 and 5, this sentence is no longer valid and has been changed to:

“Measurements of f_{IN} at both -30 and -25 °C responded similarly to all the various physicochemical processing combinations described below; however the effect of treatments on f_{IN} at -25 °C and 98% RH_w was difficult to assess due to the small f_{IN} values, only modestly exceeding quantification limits in some cases, for both treated and untreated ATD.”

Pages 16921-22 and conclusions: The discussion of the effect of the water bath is confusing. The authors should be more explicit whether they think that the water bath had a direct effect on the IN fraction or whether the contamination with NH₃ is responsible for the observed increase.

Following comments from both reviewers regarding this we have removed the discussion of the water bath treatments as we do not know what role ammonia contamination may have played. We now focus only on the ammonia gas treatments, which were performed with the water bath in most experiments. We have left the water bath data in Table 1 for completeness but removed the data from the related Figures, as explained in Section 3.3 of the revised manuscript:

“We did not observe different ice nucleation response for SA + WB versus SA + WB + NH₃ treatments. As we suspect the water bath branch was contaminated with ammonia, we cannot conclude whether exposure to water vapour had the same effect as NH₃ exposure, or if there was sufficient NH₃ in the water bath to produce the same result. Therefore, we do not discuss the SA + WB results and focus on the SA + WB + NH₃ experiments.”

Pages 16923-16924: The comparison with previous studies should be extended. In addition to the studies mentioned by the authors, there are additional studies that did not show a decrease in heterogeneous ice nucleation ability by exposing ATD to sulphuric acid, namely Knopf and Koop (2006), who produced the SA coating from a dilute SA solution and Zobrist et al. (B. Zobrist, C. Marcolli, T. Peter, and T. Koop, Heterogeneous Ice Nucleation in Aqueous Solutions: the Role of Water Activity, J. Phys. Chem. A 2008, 112, 3965-3975), who investigated ATD particles immersed in sulfuric acid solutions. The only effect that Zobrist et al. observed was a freezing point depression due to the decreased water activity of the solution. Both studies suggest that sulphuric acid coatings of moderate concentration do not decrease the ice nucleation ability of ATD. Moreover, Niedermeier et al. (2010) only observed an effect of the SA coating on the IN fraction for the highest temperature that they investigated, namely -34C. For lower temperatures coated and uncoated ATD behaved similarly.

We have clarified that Niedermeier et al. only observed an effect from sulphuric acid at -34 °C, which is the closest temperature to our measurements.

Zobrist et al. did not observe an impact from dust particles immersed in sulphuric acid solutions on their immersion-freezing ability beyond those they attributed to solute effects. The

difference from the effect we observed here may be due to the different manner in which sulphuric acid was applied to the dust particles, and the effects of heat. Knopf and Koop atomized dust particles in a very dilute sulphuric acid solution and did not observe a resulting effect on ice nucleation. They reported a large range of RH_i onset values for both types of particles. The dilute (5×10^{-3} % wt) sulphuric acid solution, and polydisperse supermicron dust size distribution used in their experiments could explain the difference from the impairment of deposition nucleation observed here. We added a discussion of these two additional studies: “Knopf and Koop (2006) reported a similarly large range of onset RH_i for ATD particles atomized from a dilute sulphuric acid solution and for atomized ATD and concluded that uncoated and sulphuric acid coated ATD had no significant difference in ice nucleation ability. Similarly, Zobrist et al. (2008) found that ATD particles immersed in dilute sulphuric acid droplets displayed only a freezing point depression for immersion -freezing, that was attributed to the solution’s decreased water activity, and inferred no alteration of active sites by the acid. At 105% RH_w any solute present would be very dilute, and thus our observed reduction in f_{IN} caused by sulphuric acid condensation cannot be explained by solute effects. The different results obtained in this and the previously cited studies could be explained by differences in the particle generation and coating methods used. Further experiments are required to better understand how the concentration of and mechanism by which sulphuric acid and other secondary material becomes mixed with dust particles affects their ice nucleation properties.”

Page 16924, lines 19-23: it is questionable whether the heterogeneous uptake of SO₂ and subsequent oxidation to SA might lead to a concentrated SA coating, since ammonia is all the time available in the troposphere for immediate neutralization.

This is a valid point but would require modeling studies to investigate the timescale under which these processes typically occur. We have revised this discussion as follows: “Based on these results, dilute sulphuric acid that is produced during cloud processing in non-evaporating cloud droplets would be expected to have a lesser impact on the dust’s freezing ability than concentrated sulphuric acid that is produced through heterogeneous uptake of SO₂(g) and subsequent oxidation to H₂SO₄ in non-activated particles. H₂SO₄ produced in this manner may also be quickly neutralized by the uptake of ammonia gas.”

Page 16924, lines 26-28: Zobrist et al. (2008) have shown that ATD immersed in ammonium sulfate solutions showed no decrease in ice nucleation ability other than the freezing point depression expected due to the decreased water activity. This should be considered when discussing the effect of ammonium sulfate on immersion mode freezing of ATD.

Although this is true, other studies have observed an effect of ammonium sulphate on deposition nucleation of mineral dust, and here we have observed an effect on both deposition and immersion-freezing. Solute effects would not explain the observed decrease in f_{IN} at 105% RH_w as the particles were immersed in droplets and the solute would be very dilute. Therefore, the role of ammonium sulphate on ice nucleation is not yet clear, and differences in particle coating methods may be responsible for the different observed effects. We have added this discussion to our comparison to other related experiments, as follows:

“Similarly, Zobrist et al. (2008) found that ATD particles immersed in dilute sulphuric acid droplets displayed only a freezing point depression for immersion-freezing, that was attributed to the solution’s decreased water activity, and inferred no alteration of active sites by the acid. At 105% RH_w any solute present would be very dilute, and thus our observed reduction in f_{IN} caused by sulphuric acid condensation cannot be explained by solute effects. The different results obtained in this and the previously cited studies could be explained by differences in the particle generation and coating methods used.”

And in the final paragraph of the discussion:

“ATD particles immersed in an ammonium sulphate solution had reduced immersion-freezing ability attributed to solute effects alone, implying no alteration of active sites (Zobrist et al., 2008).”

Anonymous Referee #2

I suggest that the authors consider removing the data and discuss on the experiments with the H₂SO₄ coatings followed by the water bath (3rd panel in Figures 4 and 5).

The authors cannot rule out contamination by NH₃, and as a result, the discussion is speculative. I suggest that this discussion be left for another paper when contamination can be ruled out.

Following comments from both reviewers regarding this we have removed the discussion of the water bath treatments as we do not know what role ammonia contamination may have played. We now focus only on the ammonia gas treatments, which were performed with the water bath in all but one case. We have left the water bath data in Table 1 for completeness but removed the data from the related Figures, and explain the rationale behind this in Section 3.3 of the revised manuscript as follows:

“We did not observe different ice nucleation response for SA + WB versus SA + WB + NH₃ treatments. As we suspect the water bath branch was contaminated with ammonia, we cannot conclude whether exposure to water vapour had the same effect as NH₃ exposure, or if there was sufficient NH₃ in the water bath to produce the same result. Therefore, we do not present the SA + WB results and focus on the SA + WB + NH₃ experiments.”

Page 16903, line 2-3. Replace “ice vapour pressures” with “h₂O vapour pressures” or “ice supersaturations”? The same comment applies to line 11.

We changed this to “ice supersaturations” in both instances.

A discussion on the kinetics of water uptake into the acid coated particles would be beneficial. Do the acid coatings come into equilibrium with the RH on the time scale of the experiments?

Although such a discussion would certainly be beneficial we don't believe that the required information on the kinetics of water uptake into these systems is available. The condensation of water occurs on the timescale of fractions of a second (Snider and Petters, 2008). The residence time over the water bath was about 70 s, while that of the CFDC was 5 s. We do not suspect kinetic limitations due to the absorption of water over the water bath. Although the residence time in the CFDC is much shorter, recent experiments using HNO₃ suggest that there was sufficient time in the CFDC for particles to absorb water and for surface material to be removed by dissolution. This is discussed further below.

Page 16919, line 21-22. Could the results also suggest that only a fraction of the particles were coated with sulphuric acid? The results from the single particle mass spectrometer would be useful here.

Yes, this is possible. However, the fact that f_{IN} at -30 °C and 105% RH_w was not appreciably reduced after coating with SA at 45 °C, but f_{IN} was then reduced after the coated particles were sent through the thermodenuder at 250 °C suggests that the particles did contain sulphuric acid, but the coating only impaired immersion-freezing after exposure to heat above 45 °C.

Regarding the ATOFMS measurements, we have added the following to Section 3.2:
“The single-particle measurements obtained by the ATOFMS were queried for various experiments representative of the most common experimental treatment combinations reported here. Using a conservative sulphate peak area threshold of > 1000, between 84 and 97% of ATD particles contained sulphate for experiments in which ATD particles passed through the sulphuric acid coating tube (and in some cases additional treatments following this). Using a less conservative peak detection limit (peak height > 50 above baseline) decreases the number of particles that did not produce a sulphate ion signal to approximately 6%. The small fraction of particles that did not produce a sulphate ion signal > 1000 peak area indicates that these particles had no or only small amounts of sulphate, or that the ATOFMS’s laser ablated a portion of the particle that did not contain sulphate, even though sulphate was added to the particle (Cziczko et al., 2009). The lack of a step-function in the shape of the CCN activation curve is further evidence against a substantial fraction of externally mixed ATD particles that did not contain sulphuric acid. Finally, SA + TD treated particles had f_{IN} reduced by at least an order of magnitude compared to uncoated ATD (excluding the less reliable measurements at $-25\text{ }^{\circ}\text{C}$ and $98\% RH_w$). As we observed that only particles exposed to sulphuric acid before heating had impaired ice nucleation ability following the thermodenuder, we conclude that the decrease in f_{IN} indicates that ATD particles that did not contain sulphuric acid could only have composed a small fraction no greater than a few percent of the total particle number.”

Page 16920, line 20-23. Here I assume that “irreversibly” implies a chemical reaction. Could it also be the case that even at very low concentrations of sulphuric acid, sulphate still blocks active sites. Please discuss. I agree that the heat processing experiments show a chemical reaction.

It is possible that sulphuric acid that is physically adsorbed to an active site renders the active site inaccessible. However, we would expect the acid to be reversibly dissolved off the active site above water saturation in this case, but the observed impairment of immersion-freezing suggests against this for these experiments. This is why we conclude that irreversible chemical reactions were responsible. Recent experiments in which ATD was exposed to HNO_3 vapour revealed that while deposition nucleation was impaired, immersion-freezing was not (Sullivan et al., 2010). This suggests that the dissolution of surface coatings after droplet activation can restore ice nucleation ability provided no irreversible modification of active sites has occurred. We have added a brief discussion of this to the revised manuscript:

“ATD particles exposed to nitric acid vapour at room temperature were recently observed to have reduced deposition nucleation ability, but unaltered immersion/condensation-freezing at the same RH_w values and measured by the same CFDC used here (Sullivan et al., 2010). This suggests that there was enough time in the CFDC for soluble nitric acid coatings to be removed from surface sites by dissolution following the absorption of water above water saturation, thus restoring their ice nucleation ability. The fact that f_{IN} was reduced at $105\% RH_w$ by the sulphuric acid coating in these experiments indicates irreversible modification of surface sites by the coating that is not reversed by dissolution.”

I don't completely understand how the authors are deciding if a result is statistically different when comparing results from different processing. See for example:

We have re-analyzed data from experiments that produced mean values notably different from other replicates. In some cases, particularly in the first few experiments, the RH_w scan rate was much higher than the desired 1% per minute. A fast scan rate increases the uncertainty in the calculated RH_w the aerosol lamina experiences because the wall temperatures do not reach a steady state. For the few experiments where the RH_w scan rate was $> 2\%$ /minute around the 98% or 105% RH_w measurement values, we have rejected these data points. The points thus rejected are:

Expt. 1.1, Pure ATD at -30 C and 98% RH_w

Expt. 2.1, ATD + TD at -30 C and 98% RH_w

Expt. 12.2, Pure ATD at -25 C and 105% RH_w

Page 16914, line 25-26. "Coating with sulphuric acid at 70 or 85 C caused large decreases in f_{IN} of at least one order of magnitude both below and above water saturation." The results for $T=-25C$, $RH_w=105\%$, and coating with $SA=70C$ does not appear to be consistent with this conclusion.

With the rejection of Expt. 12.2 discussed above, there is now a factor of 10 difference between untreated ATD and ATD + SA 70 C at these conditions.

Page 16916, line 1-2. "The additional humidification step caused a larger decrease in f_{IN} for the immersion/condensation-freezing regime compared to the SA coated reference treatment." But, for $T=-30C$, $RH_w=105\%$, and $SA=70C$ it looks like the error bars overlap.

This is true. As we have removed discussion of the water bath following both reviewers' suggestions this statement has been removed.

Page 16917, line 25. "Sulphuric acid coated dust particles always had reduced f_{IN} compared to uncoated dust, except for the 45 C coating in the immersion/condensation-freezing." Is this statement consistent with the $T=-25C$, $RH_w=105\%$, and $SA=70C$ data? The data appear to overlap, at least for one measurement.

With the rejection of Expt. 12.2 discussed above, there is now a factor of 10 difference between untreated ATD and ATD + SA 70 C at these conditions. Therefore, this statement is now valid.

Page 16918, line 4. "Heating coated dust reduced f_{IN} further in the immersion/condensation-freezing regime." Is this true for $SA=70C$? Again, I am not sure what error bars to consider here.

For experiments in which f_{IN} was not already below our quantification limit, heating coated dust further reduced f_{IN} by at least a factor of 10 at both 98% and 105% RH_w at -30 °C. The response is difficult to evaluate at -25 °C and 98% RH_w due to the small number of treatments tested under these conditions, and small f_{IN} values for both untreated and treated ATD. At -25 °C and 105% RH_w heating SA 70 treated ATD (i.e. SA 70 + TD) only slightly reduced f_{IN} and it cannot be distinguished from the SA 70 treatment. In general, we based our conclusions regarding the effects of treatments from the -30 °C data as f_{IN} is initially larger for untreated ATD, allowing us

to observe a greater range of response, and many more measurements were made at this temperature than at -25 °C. We have clarified this, and the specific cases that were different at -25 C as discussed above, in the revised manuscript.

How are the authors judging whether or not a result is statistically different? I realize that repeating a measurement several times may be impractical during a campaign. Please expand on the method used to determine if a result is statistically different and ensure the conclusions and specific statements are in agreement with the statistics.

We acknowledge the issue raised by the reviewer concerning the evaluation of results from the different treatments. We performed non-parametric statistical tests as appropriate for non-normally distributed populations of data such as our 1 Hz measurements of f_{IN} obtained here. Both the Mann-Whitney and Kolmogorov-Smirnov tests were used to determine if the means from two different treatments were statistically different, using the OriginPro 8.0 analysis software. Unfortunately, both tests concluded that replicates from the same treatment, such as untreated ATD, were statistically different at the 50% and 99% confidence levels. It is clear from the mean and standard deviations (Table 1) that the replicate measurements of untreated ATD at, for example, -30 C and 105% RH_w were quite similar (e.g. Expts. 16 a & 16i). A one-way repeated measured ANOVA test was attempted and also concluded that replicates from the same experiment had statistically different mean values, at a range of confidence levels. These tests are therefore not appropriate to determine if different treatments produced different mean values of f_{IN} , since they conclude that replicates from the same treatment had statistically different means of f_{IN} . This failure is likely caused by the noise inherent to the 1 Hz measurements, and the frequent zero counts recorded. Although we did not perform enough replicates to characterize the distribution and variability in the f_{IN} population of replicate measurements for the same treatment, we did use the Student's t-test to provide some insight into the statistical significance of the results. This is explained in the revised Methods section:

“As there was not enough time during the campaign to perform enough replicate experiments to characterize the distribution and variability in populations of measured f_{IN} for the same treatment, it is difficult to properly determine the statistical significance in differences in f_{IN} determined following different treatment combinations. We did perform student t-tests for a subset of exemplary treatments in which more than one replicate was performed, to provide a sense of what degree of difference in f_{IN} is necessary to conclude that different treatments produced statistically different mean values of f_{IN} . The results of these tests are described along with the experimental results below. In our discussion, we focus on treatments that produced changes in f_{IN} of an order of magnitude or more, which is typically greater than the uncertainty limits and produced significantly different f_{IN} values at the 99% confidence level according to the t-test. We also focus on the -30 °C measurements, as we were better able to detect changes in f_{IN} at this lower temperature and performed more measurements there.”

And in the revised Results section:

“The student's t-test was used to evaluate the statistical significance in differences of mean f_{IN} values for various thermochemical treatments. This test was used to compare pooled f_{IN} values for exemplary treatment combinations only when more than one replicate was performed, and not assuming equal variance between the two treatment populations. As a guide to the degree

of change in f_{IN} required to produce significantly different f_{IN} values, untreated vs. heated ATD (TD) was significantly different at the 94% confidence level, unheated ATD vs. SA 45 was different at the 97% confidence level, and both unheated ATD vs. SA 45 TD and unheated ATD vs. SA 70 were different at the 99% confidence level. The latter two comparisons where the results were significantly different at a high confidence level had differences in f_{IN} greater than one order of magnitude. We therefore use a one order of magnitude difference in f_{IN} as a benchmark to determine if treatments produced statistically different results, particularly when only one replicate was performed."

With the rejection of some data points following reanalysis as discussed above, many of the ambivalent cases raised by the reviewer have been clarified. We now focus on treatments that produced large changes in f_{IN} of one order of magnitude or more to conclude that a particular treatment had a notable effect on ice nucleation. When f_{IN} was observed to be small the signal-to-noise ratio was also reduced, resulting in the larger error bars for $f_{IN} < 10^{-3}$. This makes it more difficult to distinguish between treatments that produced small f_{IN} values. It makes it especially difficult to evaluate the effects of treatments on f_{IN} at $-25\text{ }^{\circ}\text{C}$ and $98\% RH_w$, since untreated ATD had a low $f_{IN} < 10^{-3}$ to begin with. Thus, we derive most of our conclusions from the $-30\text{ }^{\circ}\text{C}$ and $105\% RH_w$ measurements.

Cited References

- Knopf, D. A., and Koop, T.: Heterogeneous nucleation of ice on surrogates of mineral dust, *J. Geophys. Res.*, 111, D12201, doi:10.1029/2005JD006894, 2006.
- Snider, J. R., and Petters, M. D.: Optical particle counter measurement of marine aerosol hygroscopic growth, *Atmos. Chem. Phys.*, 8, 1949-1962, 2008.
- 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.*, In press, doi:10.1029/2010GL045540, 2010.
- Zobrist, B., Marcolli, C., Peter, T., and Koop, T.: Heterogeneous ice nucleation in aqueous solutions: the role of water activity, *J. Phys. Chem. A*, 112, 3965-3975, 2008.