<u>**Response to comments from Referee 1. Referee comments in *italics***</u>
Current version of manuscript – ACPD version
LE – low exposure
HE – high exposure
Ka – Kaolinite
ATD – Arizona Test Dust
Revised manuscript page/line references in **bold text**.

Interactive comment on "Laboratory studies of immersion and deposition mode ice nucleation of ozone aged mineral dust particles" by Z. A. Kanji et al.
Anonymous Referee #1, Received and published: 5 June 2013
Kanji et al. report the measured ice nucleation properties of two types of mineral dust, in both the deposition and immersion regimes, and the effect of high levels of ozone exposure in a tank reactor on the ice nucleation properties. There is only one previous report that studied the effect of ozone on ice nucleation by mineral dust, so this study is worthwhile. Though it needs to be pointed out that as ozone is a secondary pollutant formed by photochemical reactions of other pollutants, that it is unlikely that dust particles would be exposed only to appreciable levels of ozone during atmospheric transport and not also be exposed to other pollutants. The authors used appropriate methods to determine the results, and present a detailed analysis of their results. Unfortunately, the data analysis performed is often quite lacking, and the results are very over interpreted. It is hard to distinguish a significant difference between the ice nucleation properties of many of the systems, and thus many of the rather strong claims made by the authors are not in fact supported by the data. The mechanistic interpretation of the observations is also not justified in many cases. Given these serious deficiencies, this manuscript requires major revisions before it might be acceptable for publication in ACP. I think the data measured in these experiments is of high quality and is valuable, but its value is hampered by the manner in which the data is currently analyzed and interpreted.

We thank Referee 1 for the positive comments regarding the valuable and high quality nature of the data. In the following comments we aim to alleviate the Referee's concerns regarding the interpretation of the data presented by responding to the individual comments below.

The most critical issue is in how similar the ice nucleation response appears to be from different systems. For example, Kaolinite (Ka) and Ka with low-exposure ozone overlap each other in Figs. 7A and somewhat in Figs. 8A and 10A. All the 3 ATD systems overlap extensively in Fig. 7B, 8B, and ATD and LE-ATD overlap extensively in Figs 9B and 10B. Yet when the authors describe these different systems they present the data as if there are real and significant differences between them. I.e. that ozone (and different levels of ozone) have clear effects on the ice nucleation properties. This is just not supported by the data they present in many cases. The discussion of the results requires major revision to present the data in a more honest manner. It would also help if error bars were provided for all three datasets in Figs. 7A&B.

We would like to preface this response by saying, we take the Referee's point and carefully examine the manuscript to correct any unintended claims throughout the manuscript that arise from over interpretation of our results regarding the effects of ozone aging on the IN properties of Ka and ATD.

We point the Referee to the current version of the manuscript on page 8722, line 18-19 where we already state that only a subtle enhancement of LE-Ka IN activity is reported in Fig. 7a. We also point out that at 238K, the LE-Ka has the same activity as Ka. We only report a clear suppression of IN activity from Fig. 7a for the HE-Ka particles, thus we are not claiming significant effects for both exposures. We utilise Fig. 8a (in current manuscript), to confirm the subtle trend observed in Figure 7a and this is stated in the current manuscript on page 8723 line 28-29. We note that for the deposition regime, we do not observe any overlap in the data between LE-Ka, Ka and HE-Ka in Fig. 8. In Fig. 10a, only data at one temperature overlap (at 238 K, LE-Ka and Ka), with the rest of the data points showing clear differences between the systems investigated. For immersion mode we report HE-Ka particles **do not** show different IN activity compared to Ka based on n_s(T) on Page 8730 line 19-20. The reported changes are based on the fits of the data which have been fit using error weighting. In addition, when fits plotted with 95% confidence interval bands, do not overlap. We considered the fits to be significantly different from one another. Similarly for ATD referring to Fig. 7b, we report in the current version of the manuscript on page 8723 line 14-16 that there isn't a difference of IN activity between the ATD and aged-ATD. We also state that the data points are within the measurement uncertainties.

However, we agree with the Referee that we may have overstated the ageing effect based on Figure 7b on page 8723 lines 16-19, which we now remove. In reference to Fig. 8b, we have now re-phrased the paragraph on page 8724, lines 8-19 **(page 20 line 11-18)** to reflect the scattered ageing effect inferred from Fig. 8b. In addition we add to the conclusions section of the revised manuscript **page 32, line 11** that the LE-ATD showed insignificant changes in IN activity compared to ATD.

The overlap of IN activity of ATD and LE-ATD as seen in Figs. 9b and 10b is acknowledged in the current version of the manuscript in section 3.3, but we have modified this section to be more concise and explicitly state (**page 21 line 27-28**) that no difference was observed between the IN activity of ATD and LE-ATD (immersion mode). Lastly, for Fig. 10b we have already in the current version of the manuscript on page 8730 lines 26-29 and page 8731 lines 1-4 stated that no difference is observed in the IN activity (deposition mode) between ATD and LE-ATD, however we take the Referees suggestion and state this concisely and explicitly in the revised manuscript (**page 24 line 18-19**).

Lastly, we prefer to include error bars for just one set of data points in both Figs. 7a and 7b, since the error bars are based on average RH uncertainty and not precisions – therefore carry the same value for all data points shown in Fig. 7.

The plots of ice active fraction at 95% RH versus temperature (or for immersion freezing) are the most meaningful ways to plot the results that require the fewest assumptions to be made (Figs. 8 and 9). So I would base the assessment of the effect of ozone primarily on these figures (as well as full RHw scans, as I discuss below).

We agree, and now include exemplary full RH scans as **Figure 6** in revised manuscript (see comment below)
For ATD there is a pretty clear loss of ice nucleation ability from ozone exposure in the deposition regime, but this is one order of magnitude loss at most. In the immersion regime the

effect is only clear with high O3 exposure. For Kaolinite, there may be an enhancement of deposition ice nucleation ability with lower O3 exposure, but the data is quite scattered so this effect is not clear. The loss of IN ability at higher O3 exposure is more clear. In the immersion mode the loss of ice nucleation ability after Ka was exposed to O3 is pretty clear.

We agree, and have made changes in interpretation/wording (see responses above) to the manuscript to better reflect the changes observed due to ozone ageing.

Why low exposure would increase IN ability of Ka in the deposition mode but decrease it in the immersion mode is a mystery.

Low O_3 exposure increases the IN ability of Ka in **both** the deposition and immersion modes (see Figs 8a and 9a in current manuscript).

Based on the data presented, I really do not think the authors can conclude much more from their data. They should be very careful to not over-interpret or over-sell their results. The effects of ozone are just not clear enough in many cases to support many of the conclusions the authors state. Even the largest observed effects on IN ability are limited to one order of magnitude change at most – these are not hugely significant changes, though the authors state that they are.

We now state the factor by which we observe enhancement or suppression from one system to another (in various parts of the revised manuscript). We use the term significant to refer to the relative difference in IN activity between two systems rather than an absolute enhancement or reduction in ice nucleation.

When discussing results from other groups, it is very important to keep in mind the temperature range and ice nucleation regime the measurements were made at. For example, for the ambient measurements of aged/coated particles in Mexico City and Los Angeles, these measurements were made at cold cirrus temperatures of 233- 205 K. The effects of aging/coatings might be very different at cirrus temperatures compared to mixed-phase cloud temperatures, as are studied here. (Page 8707, line5)

On page 8707 following line 5, in lines 7-9 in the current version of the manuscript we already specify the RH and the temperature range of the Mexico City and Los Angeles study. In this introduction section we are not proposing that the effects of ageing are expected to be the same at mixed-phase cloud temperatures. We merely present a brief survey of ageing IN experiments in the literature.

Prompted by this comment however, we now include the T and RH conditions of the work from Baustian et al. (2012) conducted in Storm Peak in the revised version of the manuscript on **page 6 lines 15-16**.

The stated discrepancy between the effects of coatings on ice nucleation from laboratory versus field measurements is also inaccurate. The recent understanding seems to be that coatings impair deposition ice nucleation, but may not impair immersion freezing. It is critical to distinguish between these two modes when discussing any effect of aging/coating on ice

nucleation. It is also important to state in what mode the ice nucleation measurements were made. (page 8707, line 15)

We now state that the contrast between laboratory and field studies is specifically for deposition mode ice nucleation in the revised manuscript **page 6 lines 17-18**. The contrast comes from the suppressed IN activity of aged particles observed in deposition mode in the laboratory versus the IN activity of field collected samples that show efficient IN activity despite being highly aged or internally mixed with organics and sulphate. We also clarify that previous work has found suppressed IN activity for deposition mode in section 4.5 (comparison to previous work) on page 8736 line 9 (**page 29, line 24**)

The paper is rather long and wordy, considering the amount of data that is actually presented. This makes the paper difficult to follow. The authors do present a detailed summary of related work throughout the paper, which is appreciated, but they may want to trim this as it does add a lot of length.

We agree, and have now shortened various sections of the paper to be more concise and achieve better flow thus shortening the manuscript length. In addition, we remove Figures 2 and 3 based on Referee 1's suggestion. In particular, we shorten sections 3, 4 and 5 in various parts.

Abstract, lines 19-22: An enhancement is discussed in one sentence, and then immediately after a suppression of IN ability. This is confusing.

We modify the sentence in the Abstract on line 20 to better emphasize the break between the two sentences (**page 2 line 18-19**).

Section 2. The experimental overview/summary is not necessary.

In section 2 we provide information about the aerosol particles, temperature range of the studies and provide references for the instruments used. We think it is better to keep it in the paper.

Section 3. The summary at the beginning is also not necessary.

We agree, and remove Section 3.0. In addition we also remove a similar section 4.3.0

Section 3.1. It would help if the motivation behind deriving the ozone update kinetics was stated upfront.

We agree, done! We now state the motivation at beginning of section 3.1 (**page 14, lines 16-19**)

3.1. No references are given to the composition of ATD.

We have now refer readers to the nice work of Vlasenko et al. (2005) for a full compositional analysis of ATD in section 3.1 on **page 16, lines 5-6** of the revised manuscript.

Ozone uptake on mineral dust typically exhibits a fast initial decal, and then a slower constant decay, as observed here. How were the initial (fast) uptake kinetics determined?

The initial kinetics were determined from the initial rapid loss of ozone to the dust surface when particles were continuously added to the tank (see Fig. 6 and page 8718 lines 16-23 in current manuscript) while monitoring O_3 concentrations. To determine the uptake coefficients and surface coverage, the maximum surface area was used (at the peak of the particle concentration).

And why were the initial kinetics used here, when the dust is exposed to ozone for 2 hours? The slower kinetics that persist seem more relevant to this work.

The initial kinetics were used because most of the ozone loss occurs in the initial period of adding particles to the tank. This is likely when any modifications to the surface of the dust occur. The decay time series in the 2 hours after the initial rapid loss of O_3 has a very similar slope to the background loss of O_3 to the stainless steel tank, we therefore believe that the O_3 loss in the two hours after the initial rapid loss is in fact background wall loss (see Fig. 6 of current manuscript) and that in this period the dust particles were already saturated with respect to O_3 loss

Ozone decay kinetics on dust are inversely related to the concentration of ozone used. The authors state this, yet seem to ignore this important fact by linearly extrapolating from their ozone exposures to other conditions to compare with those results,

We assume Referee 1 is referring to the comparison of the uptake coefficients obtained in this work to those of Karagulian and Rossi (2006)(KR06) on page 8719 line 8 of the current manuscript. In this comparison we in fact make use of the inverse relationship to demonstrate agreement between our work and that KR06, i.e. by reporting that in our work we used higher O_3 concentrations than those of KR06 and obtained lower uptake coefficients for ATD than that of KR06.

or to extrapolate from their high O3 concentrations to atmospheric conditions. This is not justified, the kinetics are not first order with [O3]!

We now remove the extrapolation of our high O_3 concentrations to atmospheric conditions in the revised manuscript in section 3.1 on **page 16 line 29 to page 17 line 10** and we have caveated our low O_3 concentration extrapolation to the atmosphere on **page 17 lines 11-17**. In addition we have also removed the extrapolation of the high exposure experiments to the atmosphere in the conclusion section for example by deleting the phrase '...corresponding to ~3 days of atmospheric exposure at 45 ppbv..'

I do not see how dust will be exposed to significant levels of ozone and no other pollutants that might age/coat the surface.

We agree and acknowledge this on page 8720 line 18 of the current version of the manuscript (**page 17 lines 5-10**)

NOx is required for ozone production, as the authors discuss (page 8719, line 23). In fact, the de Reus et al. (2000) study cited here concluded that half of the ozone loss observed was due to direct uptake of ozone on dust, while the other half was an indirect loss caused by the uptake of nitrogen oxides to the dust. There is no way for dust to be exposed only to ozone and to no other pollutants in the troposphere. The surface sites can also regenerate after reacting with ozone, this is what allows mineral dust surfaces to catalytically destroy ozone.

We further agree with Referee 1. In the revised manuscript we remove any extrapolations to suggest that high exposure will be equivalent to longer ageing times in the atmosphere (see comment above).

This work aims to present a first step towards investigating the effects of trace gas ageing on ice nucleation properties of dust. The natural next step for future studies would be to include other pollutants such as NO_x, which we already acknowledge this the conclusions section of the current manuscript on page 8741 line 5-10 **(page 33 line 7-12).**

Not all dust surfaces exhibit catalytic behaviour towards ozone uptake, in some cases the saturation of the surface is observed as is indicated by the surface coverage for Ka in the current work. There is some (ATD) to no (Ka) catalytic activity inferred from our work and is discussed on page 8718 line 10-15 of the current manuscript (**page 15, lines 11-17**).

The Fine mode (A2?) of Arizona Test Dust was used here. The authors should be aware that many other reports have used the Ultrafine (A1) fraction of ATD for ice nucleation work. These fractions have different particle size, and are also processed differently. I believe A2 is washed while A1 is not.

In the study of Niedermeier et al. (2010), the Ultrafine fraction (A1) was used, we now report in section 3.3 on **page 21 lines 16-19** that in addition to the particle size differences, the dust sample we use is washed and that of Niedermeier et al. (2010) is not to further explain the differences in the results obtained.

More details regarding how the dust size distribution (did not) changed over the several hours of the experiment should be described. If the size distribution was changing this could greatly affect the IN activity. The particle concentrations did decrease substantially during the experiment.

We acknowledge that changing size distributions or change in particles sizes can definitely affect the IN activity. Because the size distribution did not change significantly over the course of the we did not show time series of the size distributions, however, we attach below exemplary size distributions at three different times of the day to show that for both Ka and ATD the number of particles reduced over the course of the experiments, however, the size range remained roughly the same.
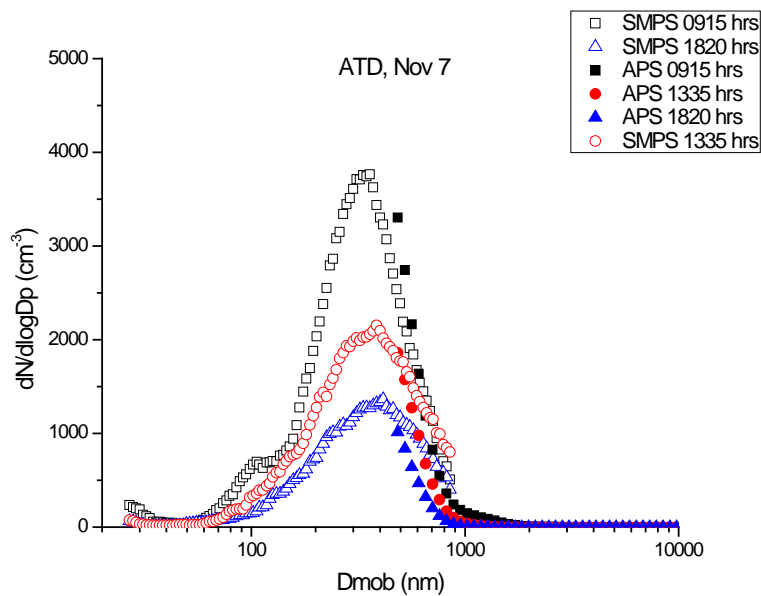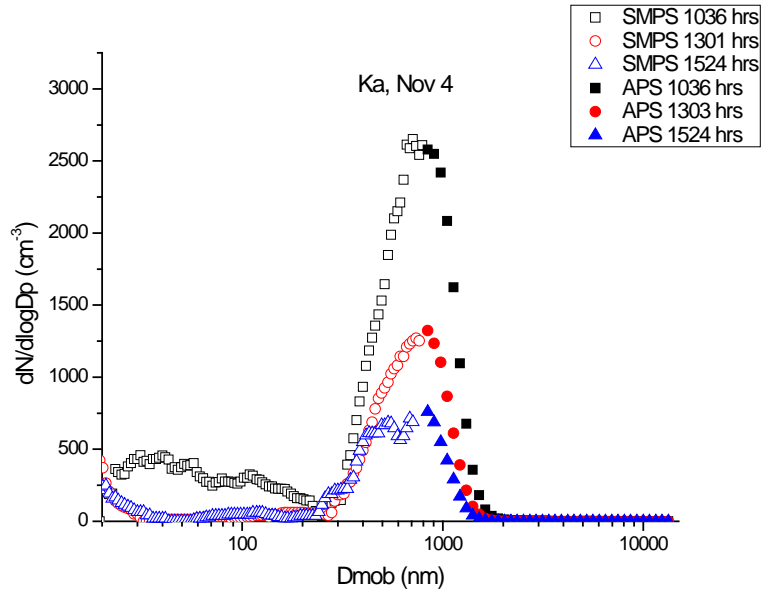
Merging SMPS and APS size distributions is not straight-forward, since two different diameters are being measured (mobility and aerodynamic), and only one depends on particle density. There are published methods for doing this merging that the authors should implement.

We agree with Referee 1. We did in fact use published methods to convert our aerodynamic diameters to mobility diameters in order to merge our APS data with SMPS data. We used particle densities and slip correction factors based on aerodynamic and mobility diameter for this conversion. The methods/formula we used are described in detail in DeCarlo et al. (2004) while we used Jennings (1988) to calculate the Knudsen number and mean free path of air used for merging the two data sets. We add these references in the revised manuscript in section 2.1 on **page 9, lines 21-23**.

The authors should also be cautious in relying solely on the mode diameter to describe the polydisperse size distribution.

We use the surface area mode diameter only for the immersion freezing experiments since we cannot use the $n_s(T)$ approximation, we can't use the surface area of the ensemble, we must use that of an average representative particle (see equations 3 and 4, current manuscript). The frozen fractions reported for immersion freezing in this work are between 10-100% and implying that that majority of surface area mode diameter particles partake in freezing thus using the mode diameter is a reasonable assumption. If most of the freezing we reported were taking place at one extreme end of the size distribution, the mode diameter not be a reasonable assumption, we agree.

I assume that the relative humidity of the IN chamber was scanned at a fixed temperature, though this is not discussed. How were these scans performed? At what scan rate?

In the revised manuscript we now include the information on how the scans were performed, including the scan rate in section 2.2.1 (**page 11, lines 11-15**). The scan rate was between 2.5 – 4% RH_w/min. Given the residence time of particles in PINC (~7 seconds in growth section), even at the highest scan rate the particles are exposed to only a small change (0.67%) in RH_w within the chamber which is much less than the RH uncertainty in PINC ($\pm$2%).

It is very important that the full scans be shown.

We now show exemplary full scans in the revised manuscript (**Fig. 6**). (see response to comment below).

No discussion of the quantification of the instrument's background IN counts is presented. This is a critical issue for all CFDC-like instruments. The IN background must be measured regularly by filtering the sample air. How was this done, and what were the typical background IN concentrations? A properly performing CFDC should have background IN of just a few per L.

Quantification of the background is reported in previous papers that use the same instrument (Chou et al., 2011). For this work we did conduct regular background measurements by sampling filtered particle free air for 5-10 minutes before and after an RH scan was completed, so approximately every 25 minutes. We have added a description about background quantification to section 2.2.1 in the revised manuscript. Briefly, the average background was 3.7/L (between 0.6/L to 6/L) and we now report this in section 2.3 (instrument measurements and uncertainties) **page 13, lines 28-29**.

Along with this the authors should discuss if any large dust particles caused a false IN signal in the OPC or IODE detectors. This can easily be determined by operating the ice chamber at room temperature, for example. There was supermicron dust present in their samples, and the impactor may not effectively remove all supermicron particles.

False counts from the OPC were minimized by using the 3µm threshold for counting ice. This has been added to the revised manuscript in section 2.2.1 on **page 11, line 18**. However, before every RH scan was initiated we also were able to quantify the false counts in the OPC ice counting bins (as part of the 10 min background scan) by sampling particles at $RH_i = 100\%$ for a few minutes at every temperature reported. While supermicron particles are not completely removed by the impactor, we believe that by greasing the impactor surface we achieve pretty effective removal (this has been reported in Chou et al. 2011, Figure 3). False counts in the IODE detector are have been characterised in detail which results in our conservative estimate of IODE's detection limit of 10% AF. In addition the false counts are taken into account while computing the error bars for frozen fractions obtained from IODE. We allude to this in the current version of the manuscript on page 8716 line 20 (**page 14, lines 3-6**). In addition we refer readers to Lüönd et al. (2010) for more detail on the false counts from IODE.

The restriction of the IMCA instrument to measuring immersion freezing only for IN fractions > 0.1 is quite concerning. This is a high level of IN activity, only exhibited by large particles from very active mineral dust samples and at low temperatures. Size selected submicron dust rarely exhibits such high activity. Important immersion freezing that occurs below this high threshold will be missed. This must be discussed.

We agree with the Referee with regard to measuring immersion freezing frozen fractions greater than 10%. This limitation results in us not being able to resolve the IN activity between 0-10%. We already acknowledge this explicitly with regards to Ka in the current manuscript on page 8725 line 3-5 and for ATD on the same page line 20-22. Furthermore, to the same line (**page 21, lines 22-23**) in the revised manuscript we add the following ' .. and thus we would not be sensitive to any differences in IN activity below the 10% frozen fraction level'.

With regards to size selected submicron dusts rarely exhibiting immersion freezing activity above 0.1 frozen fractions, there is plenty of evidence to the contrary from the literature. For example in the work of Welti et al.(2009) and Lüönd et al.(2010) it is shown that submicron size selected Ka (Fluka) particles (200, 400 and 800 nm) exhibit immersion freezing fractions of much higher than 10% (up to 90%) at T > 236 K. In addition, in the work of Niedermeier et al. (2011) immersion frozen fractions of up to 30% relevant to the heterogeneous freezing regime for 300 nm ATD particles were observed. In the work of Sullivan et al. (2010), it was also shown that 200 nm ATD particles showed maximum IN fractions of greater than 20% above water saturation and this maximum was not because of the IN activity but rather due to instrument limitations (approaching the water droplet survival region). Lastly, in the current work majority of the particles are in the submicron fraction and we have shown that these particles do freeze heterogeneously for both Ka and ATD.

While it is commonly used, reporting conditions for ice nucleation at some arbitrarily chosen activated fraction is not a useful way to analyze ice nucleation experiments. This reduces the complexity of the ice nucleation behavior over a range of T and RHw to just one number, at some arbitrary condition. In fact even the same research group cannot agree on what activated fraction to use. 0.1% is used here, but this group has previously used 1%. What is the justification for the choice of AF used here? The best justification would be in full scans of the IN fraction versus RHw at fixed T were shown. Then the full ice nucleation response will be

revealed. It is much more meaningful to instead report the IN fraction observed at a chosen RHw that represents an ice nucleation mode, such as was done using RHw = 95%. This is a much more meaningful analysis.

We agree with Referee 1 that choosing an arbitrary activated fraction limits the behaviour observed and therefore we have now based on the Referee's suggestion removed Figs. 2 and 3 and added exemplary full scans RH scans (**Fig. 6**) for both Ka and ATD particles for both low and high O_3 exposures at 236 K. We now discuss this in section 3.2 **page 19, lines 22-28** of the revised manuscript. We fully agree with the referee regarding the deposition mode plots at RH_w 95%, and the same reasons motivated us to include such plots in the current version of the manuscript (Fig 8).

The other important problem with using AF to analyze the data is that depending on the activity of the dust, the AF will cause you to report the ice nucleation response in different modes. An active dust will have AF = 0.1% in the deposition regime, while a less active dust will not achieve the same AF until the immersion mode is reached. As we know that the ice nucleation properties of dust particles respond differently to aging in the different modes, one must be careful that they are comparing measurements from the same modes. The authors should focus their analysis on the measurements at 95% RHw for the deposition mode (Fig. 8), and the immersion mode data using IMCA. Activated fraction is poorly constrained and not meaningful. Again, some exemplary full RHw scans should be presented. The authors appear to realize this important issue, yet continue to analyze the data in this confusing manner: "The representation of data in Fig. 8 and the observations made thereof are an indication that the crosssection of data at AF = 0.1 % (as presented in Fig. 7) can be limiting and not fully representative of the ice activation spectra obtained for deposition mode nucleation, especially given the onset RHw for both LE-ATD and ATD data were mostly within the instrument uncertainty in Fig. 7." (Page 8724, line 15)

We agree with Referee 1(see comment above) and as the Referee has pointed out, we also acknowledge this in the current manuscript. We choose to leave Fig. 7 (**Fig. 5**) in the revised version for the reason that this type of a figure does indeed show that for the sampled particle there exists a transition temperature where the dust transition's from nucleating ice in the condensation freezing to deposition mode. Furthermore as pointed out by the Referee, the arbitrary choice of plotting 1% and 0.1% is a common practice and in this paper we explicitly show the limitations of this type of representation by directly comparing Figs 7(**5**) and 8(**7**).

In many instances the authors could be more clear what they are referring to. For example, they state that another paper agrees with their conclusions, yet do not state their conclusions (Page 8724, line 1).

In the revised manuscript we consider this statement redundant and remove it completely.

Or they state that other data agrees with their observations, but do not state their actual numbers to facilitate this comparison (page 8725, line 9).

We have now edited this part to be more specific and report exact temperatures to show agreement between our work and that from the literature. This has been modified in the revised manuscript on **page 20, lines 23-26**.

Section 3.3. The immersion freezing properties of the dust without ozone exposure should be discussed first, and compared to other published results, before the effect of ozone is discussed. This section jumps around a lot and is hard to follow.

We agree and re-organised section 3.3 to follow the above suggestion and to be more ordered and concise.

Page 8725, line 23: "The immersion freezing of 300 nm ATD particles has been reported by Niedermeier at al. (2010), however T50 % occurred at T < 236 K in the homogeneous freezing regime, suggesting that the particles did not freeze heterogeneously in contrast to the current work." This faulty analysis is based on the notion that only if particles have an extremely high ice active fraction of 50% are they considered to freeze heterogeneously. This is completely incorrect, and is a good example of the problems with the IODE's very high detection limit of AF > 0.1. Niedermeier et al. did observe 300 nm ATD particles to be good immersion freezing nuclei, just not at the very high AF required by these authors.

We agree, in the manner currently reported in our manuscript, it appears that the ATD particles did not freeze heterogeneously in the work of Niedermeier et al. (2011), whereas 30% of the particles did in fact freeze heterogeneously. We modified this section to present an accurate comparison in the revised manuscript (**page 21, lines 10-13**).

Page 8726: These are all still very high levels of immersion freezing activity, yet the authors discuss the data as if a decrease in AF of 33% is a hugely significant change. A very large fraction of the dust can still nucleate ice even after ozone exposure. Again, the effect of ozone is overstated here.

We re-phrased the sentence on page 8726 line 11-13 (**page 22 line 2-3**) to report that 33% of the particles were not able to act as Het. IN due to O_3 ageing rather than claiming a significant reduction in IN activity.

Section 4.2. The brief discussion of stochastic versus deterministic models of heterogeneous ice nucleation was nicely done and appropriate. The authors might also cite the recent sensitivity analysis of (Ervens & Feingold, 2013) that concluded that ice nucleation is least sensitive to time compared to temperature, particle size, and contact angle.

We thank the reviewer for the comment and add the relevant reference and its description in section 4.2 on **page 22, lines 2-3** in the revised manuscript.

n_s(t) needs to be better explained to be clear to the readers. What does it describe?

After the first sentence in section 4.2, we have added the following sentence "$n_s(T)$ is therefore the number of sites on a particle surface that can be responsible for initiating ice nucleation at a

given temperature, assuming that one active site gives rise to a single ice crystal" to further describe n_s(T) (**page 23, lines 19-21**).

Page 8733, line 3: "ATD responded differently to the O3 exposure in both deposition and immersion mode, i.e. no significant enhancement in ice formation was observed. This is not surprising however given that the BET surface area of ATD is 50 % that of Ka and thus presents a smaller surface area that can be altered due to heterogeneous oxidation of O3." Wouldn't the smaller BET surface area suggest a smaller effect of O3 on ATD versus Ka, as opposed to no effect that the authors suggest here? This interpretation does not seem justified.

We agree. We meant here is that the smaller BET surface area has resulted in a change that is not quantifiable by the ice nucleation methods used here. Either the change (due to ozone ageing) is very small or the change occurring does not impact the ice forming abilities of the particle. In addition, it is also possible that no change to the surface of the ATD is occurring for the low exposure experiments thus no enhancement is observed. We have now made this more explicit by modifying the entire last paragraph of section 4.3.1 in the revised manuscript (**page 27, lines 4-12**).

Page 8733: Surface oxides do not only form by reaction with aluminum minerals. The observed different response for ATD vs. Ka is not at all well explained here by referring to their different compositions. I do not think the authors can really say much about what is actually happening at the mineral surface of the two systems when ozone reacts with it. Also, given the long exposure times and high [O3] used here, I think all the surface sites will be saturated by O2 or other oxygen species, for both dust systems. This is supported by the fact that the ozone kinetics were observed to be in the slow and constant regime for most of the 2 hours of exposure, following the short rapid loss period.

We agree, we have removed such arguments based on composition on page 8733 and now present a modified paragraph for this section in the revised version of the manuscript (see comment above).

Page 8734: "For immersion freezing HE-ATD showed a larger suppression in ns than HE-Ka. A reason could be due blocked reactive sites on the surface if ATD that are likely ice nucleation active sites arsing[sic] from the physisorption of O3 that occurs on silica. . ." In the preceding paragraph you stated that less surface oxides would form on ATD due to the lower Al content, and that surface-bound O2 would be released from ATD, regenerating the surface sites. That contradicts what you have proposed here. None of this is adding up.

We may have confused the potential reader and Referee by this statement. In the preceding section we mean smaller amounts of **reactively-formed** surface oxide species would result from the lower alumina content in ATD (from low O_3 exposure), whereas in this section we refer to non-reactively bound O_3 (physisorption) on the surface mostly observed to happen with silica (from high O_3 exposure). We have now removed the part that states less surface oxides would form on ATD due to the lower alumina content from section 4.3.1 (preceding paragraph) see comment above. In addition we now clarify 'reactively formed' in section 4.3.1 **page 26 line 20** of the revised manuscript.

However, we point out that the argument presented in this section 4.3.2 is not meant to corroborate that of section 4.3.1. The behaviour of O_3 uptake is reported to be different at high concentrations versus low concentrations of O_3 exposure. The blocking of the reactive sites by O_3 (physisorption) is a mechanism reported to occur, particularly for high O_3 concentration exposure. We have now clarified this explanation in the last paragraph of section 4.3.2. (**page 27 line 30 to page 28 line 4**).

Also, the statement about regeneration of the surface sites pertained to the low exposure experiments. We do not imply this for our high exposure experiments. There has been evidence from previous work that dust surfaces are known to passivate and lose their ability to take up O_3 from increased exposure to O_3 (Sullivan et al., 2004).

Section 4.5. I do not see how the conditions used here (high [O3] for 2 hours) are "atmospherically relevant conditions".
We agree, and have now removed 'atmospherically relevant conditions' from this statement and replaced it with 'from ozone exposure' (**page 29, line 2-3**). In addition we also remove the phrase 'atmospherically relevant' and replace it with 'from ozone exposure' on page 8726 line 15-16 in the current manuscript (**page 22, line 5**).

The authors also seem to focus on comparing their work to the others that have shown an enhancement or impairment of IN ability due to aging. It would be more appropriate to discuss all effects that have been observed from aging. Many studies have show that aging does not impair immersion freezing. Again, it is important to distinguish the effects on deposition vs. immersion ice nucleation.

To section 4.5 we now add two more studies (Sullivan et al., 2010;Niedermeier et al., 2011a, b) on **page 27 line 7 -13** that have shown ageing from coatings of nitric and sulphuric acid did not inhibit freezing above water saturation/immersion freezing. For the comparisons already presented in the current manuscript, we refer to the specific modes (deposition vs. immersion) when making the comparisons to our work, see section 4.5 page 8735 line 17 and line 23 in current manuscript. (**page 28, line 5 and 12**).

However, we understand that Referee 1's comments about distinguishing between ice formation modes could be motivated by lines 9-12 on page 8736 – which we now remove from the revised version of the manuscript because we consider it to be repetition of what is discussed in earlier sections of the paper. In addition we specify deposition mode nucleation for the comparison presented on **page 29, line 21**.

Page 8736, line 1: Montmorillonite is an aluminosilicate clay, and much more similar to Ka than ATD. This comparison doesn't make sense.

We have removed this comparison from the revised manuscript.

Page 8712, line 24: "The IN counters have been extensively described in previous work." These works should be cited.

We have now added the relevant citations in the revised manuscript (**page 10 lines 29-30)**

Page 8716, line 24: What is IASSD? There is an overuse of acronyms in this paper, and it becomes confusing.

IASSD: ice active surface site densities. We now exclusively use $n_s(T)$ in the revised manuscript to refer to this concept and have removed the acronym from the paper.

Page 9738, line 2: Is "50-0.1 particles cm-3" a typo?

These are the upper and lower estimates of dust concentrations in the atmosphere taken from Murray et al. (2012).

I don't think Figures 1-3 are necessary. Figs. 2 & 3 are available in other papers that describe these methods.

We agree, we have removed Figures 2 and 3. We prefer to leave Figure 1 in the revised manuscript as it is not available in previously published work from our group.

Table 2. Uncertainty ranges should be given for individual values.

We have now added to Table 2 in the revised manuscript the range of temperature for each $T_{50\%}$ that takes into account the individual uncertainty values in temperature measurement.

Table 5. A Lot of significant figures are used here.

We have reduced the number of significant digits to keep it consistent within the fit equations in Table 5.

Figure 11. The agreement of this data with the fit from Niemand et al. looks quite poor to me. While their fit does go through the center of your data, the slope is very different. The text presents this as good agreement – this is not justified. It is interesting that all the fits converge at low T for the ATD but not for Ka. Discuss this?

We have modified the text in the last paragraph of section 4.5 (**page 30, lines 204**) to specifically state that agreement between the Niemand et al. (2012) fit and ours is only for T > 240 K. In addition we remove the statement that suggests based on this agreement that Ka is a good proxy for natural dust, but rather we state the IN activity of Ka is closer to that of natural dusts compared to ATD.

The Ka fits do not converge at low temperature, in particular for the HE-Ka, because the AF for the HE-Ka at low temperature does not reach 1. Thus we do not expect the $n_s(T)$ to converge. For ATD, we reach AF of 1, at the low T end of our data. In addition, the slope of the HE-Ka curve in Figure 9 (current manuscript) is different compared to Ka and LE-Ka thus we do not expect the $n_s(T)$ to converge. The slopes for the ATD curves in Figure 9 are all similar, therefore resulting in $n_s(T)$ converging at low T end of our data set.

Ervens, B., & Feingold, G. (2013). Sensitivities of immersion freezing: Reconciling classical nucleation theory and deterministic expressions. Geophysical Research Letters. doi:10.1002/grl.50580

References

Baustian, K. J., Cziczo, D. J., Wise, M. E., Pratt, K. A., Kulkarni, G., Hallar, A. G., and Tolbert, M. A.: Importance of aerosol composition, mixing state, and morphology for heterogeneous ice nucleation: A combined field and laboratory approach, J. Geophys. Res.-Atmos., 117, doi:10.1029/2011jd016784, 2012.

Chou, C., Stetzer, O., Weingartner, E., Juranyi, Z., Kanji, Z. A., and Lohmann, U.: Ice nuclei properties within a Saharan dust event at the Jungfraujoch in the Swiss Alps, Atmos. Chem. Phys., 11, 4725-4738, doi:10.5194/acp-11-4725-2011, 2011.

DeCarlo, P. F., Slowik, J. G., Worsnop, D. R., Davidovits, P., and Jimenez, J. L.: Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part 1: Theory, Aerosol Sci. Technol., 38, 1185-1205, doi:10.1080/027868290903907, 2004.

Jennings, S. G.: THE MEAN FREE-PATH IN AIR, J. Aerosol. Sci., 19, 159-166, doi:10.1016/0021-8502(88)90219-4, 1988.

Karagulian, F., and Rossi, M. J.: The heterogeneous decomposition of ozone on atmospheric mineral dust surrogates at ambient temperature, Int. J. Chem. Kinet., 38, 407-419, doi:10.1002/kin.20175, 2006.

Lüönd, F., Stetzer, O., Welti, A., and Lohmann, U.: Experimental study on the ice nucleation ability of size-selected kaolinite particles in the immersion mode, J. Geophys. Res.-Atmos., 115, DOI:10.1029/2009jd012959, 2010.

Murray, B. J., O'Sullivan, D., Atkinson, J. D., and Webb, M. E.: Ice nucleation by particles immersed in supercooled cloud droplets, Chem. Soc. Rev., 41, 6519-6554, doi:10.1039/c2cs35200a, 2012.

Niedermeier, D., Hartmann, S., Shaw, R. A., Covert, D., Mentel, T. F., Schneider, J., Poulain, L., Reitz, P., Spindler, C., Clauss, T., Kiselev, A., Hallbauer, E., Wex, H., Mildenberger, K., and Stratmann, F.: Heterogeneous freezing of droplets with immersed mineral dust particles – measurements and parameterization, Atmos. Chem. Phys., 10, 3601-3614, doi:10.5194/acp-10-3601-2010, 2010.

Niedermeier, D., Hartmann, S., Clauss, T., Wex, H., Kiselev, A., Sullivan, R. C., DeMott, P. J., Petters, M. D., Reitz, P., Schneider, J., Mikhailov, E., Sierau, B., Stetzer, O., Reimann, B., Bundke, U., Shaw, R. A., Buchholz, A., Mentel, T. F., and Stratmann, F.: Experimental study of the role of physicochemical surface processing on the IN ability of mineral dust particles, Atmos. Chem. Phys., 11, 11131-11144, doi:10.5194/acp-11-11131-2011, 2011a.

Niedermeier, D., Hartmann, S., Clauss, T., Wex, H., Kiselev, A., Sullivan, R. C., DeMott, P. J., Petters, M. D., Reitz, P., Schneider, J., Mikhailov, E., Sierau, B., Stetzer, O., Reimann, B., Bundke, U., Shaw, R. A., Buchholz, A., Mentel, T. F., and Stratmann, F.: Experimental study of the role of physicochemical surface processing on the IN ability of mineral dust particles (vol 11, pg 11131, 2011), Atmos. Chem. Phys., 11, 11919-11919, doi:10.5194/acp-11-11919-2011, 2011b.

Niemand, M., Mohler, O., Vogel, B., Vogel, H., Hoose, C., Connolly, P., Klein, H., Bingemer, H., DeMott, P., Skrotzki, J., and Leisner, T.: A Particle-Surface-Area-Based Parameterization of Immersion Freezing on Desert Dust Particles, J. Atmos. Sci., 69, 3077-3092, doi:10.1175/jas-d-11-0249.1, 2012.

Sullivan, R. C., Thornberry, T., and Abbatt, J. P. D.: Ozone decomposition kinetics on alumina: effects of ozone partial pressure, relative humidity and repeated oxidation cycles, Atmos. Chem. Phys., 4, 1301-1310, 2004.

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, L24805, doi:10.1029/2010gl045540, 2010.

Vlasenko, A., Sjogren, S., Weingartner, E., Gaggeler, H. W., and Ammann, M.: Generation of submicron Arizona test dust aerosol: Chemical and hygroscopic properties, Aerosol Sci. Technol., 39, 452-460, doi:10.1080/027868290959870, 2005.

Welti, A., Lüönd, F., Stetzer, O., and Lohmann, U.: Influence of particle size on the ice nucleating ability of mineral dusts, Atmos. Chem. Phys., 9, 6705-6715, 2009.