Response to ACP 2013-839 Referee and Short Comments

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Response to Referee Comment #1

The authors would like to thank Anonymous Referee #1 for the suggestions and insights provided in this review. After careful consideration of the information provided, we would like to offer the following responses.

Specific Comments

- *Please add to the text or to supplementary material a figure such as Fig. 3 from Kumar et al. (2011a) (activated fraction vs. dry diameter with sigmoidal fit) to more directly show the effects of charge and/or shape correction on the determination of the critical diameter.*

  A new figure that shows activation curves and critical supersaturations for the ammonium sulfate (AS) calibration has been included as validation for this method (New Figure 1). A figure that shows examples of the raw activation curves of the dry dusts and the effects that charge correction have on these curves has also been included (New Figure 2). The shape corrections use the distribution of surface area-equivalent sizes as observed using the electron microscopy (EM) data. The effects of this correction are shown already in Figure 3, but the accompanying text has been clarified to explain how this correction is made. The text now reads:

  "...since the larger particles will activate first, the fraction of multiply charged particles for a given size is subtracted from the activation curve, and the curve is then rescaled to include only singly-charged particles (Fig. 3). The fraction of larger, multiply charged particles are observed with EM and are compared to the calculated values."

  "Mineral dust particles are approximated as elliptical cylinders with major axis, d_{M}, and minor axis, d_{m}, and maximum thickness, h_{max}, which is constrained by mobility sizing... Electron micrographs provide a means to determine the dimensions of the cylindrical face, and the particles mobility diameter provides an upper bound on the height by bounding its volume."

- *31042:14-16 "κ-Köhler is a suitable framework, less complex than FHH theory, to describe clay mineral nucleation activity despite apparent differences in with respect to size." This sentence must more clearly reflect its basis on the ~300nm threshold above which the two approaches are known to give similar results. It seems the intent is to also suggest that if the proper corrections could be applied, then κ-Köhler theory would be suitable down to lower sizes, but this is not readily apparent.*

This sentence has been replaced in order to clarify the unclear wording in the initial version by "κ-Köhler is a suitable framework to describe clay mineral nucleation activity. Apparent differences in κ with respect to size arise from an artifact introduced by improper size-selection methodology. For dust particles with mobility sizes larger than ~ 300 nm, i.e. ones that are in an atmospherically relevant size range, both κ-Köhler and FHH theory yield similar critical supersaturations. However, the former requires a single hygroscopicity parameter instead of the two adjustable parameters required by the latter."

- *Section 3.3.1 The application of charge correction is fairly standard, though this work, through electron microscopy results, shows limitations based on the shape of the particle size distribution. References to Moore et al. 2010, Kumar 2011a, Kumar 2011b would be appropriate, and if there are differences in the method of calculation, they should be noted.*

  We note the charge correction equations in this work as well as in Moore et al. (2010), Kumar et al. (2011a), Kumar et al. (2011b) are from Wiedensohler (1988) and the original reference is made. These calculated fractions match (within measurement uncertainty) those observed using EM. Both of these points have been stated more clearly in Section 3.3.1. Since we use the same original reference we do not believe that Moore et al. (2010), Kumar et al. (2011a), Kumar et al. (2011b) – already referenced in other locations – should be re-referenced here.

- *31057:22-23 "Using cyclone impaction efficiently removes the larger particles before they enter the DMA". This would more accurately be stated as: "Using cyclone impaction efficiently removes the larger particles before applying a Boltzmann charge distribution."*

  This change has been made.

- *31058:4-5 "There is agreement in the charge- and shape-corrected activation results in this study and those found in Kumar et al. (2011a) and Kumar et al. (2011b) (Figs. 4 and 9)." This agreement is fairly clear in Fig. 4, but less so in Fig. 9, particularly for dry ATD. The fact that the data at Dp < 300nm is suggested to be questionable and most of the Kumar data is in this region makes the issue of agreement (both lying along the same line of constant κ) somewhat murky. It seems that the general sentiment of this paper is in disagreement with these previous results in terms of relevance (due to the size-range), and stating agreement, without conditions, blurs the arguments you seem to be making. This should be more clearly addressed. It might help to more directly compare results if FHH fits were made for your data, though that would involve fitting to data in the size region unlikely to be correctly sized, as displayed in Fig. 6.*

  Figure 9 has been replaced by New Figure 3. The new version of the figure includes κ lines fitted to the data larger than 300 nm and makes the comparison of results easier. The comparison between studies have been clarified to include the caveats. The

new version will read, "For sizes larger than 300 nm where correctly sized particles are expected to be found, there is agreement in the charge- and shape-corrected activation results in this study and those found in Kumar et al. (2011a) and Kumar et al. (2011b) (Figs. 4 and 9)."

- *31058:5-7 "The exception is an inability to reproduce the Kumar et al. (2011b) 100 % activation of the larger mode of wet-generated ATD." Please clarify this statement, because this detail is not mentioned previously in the text.*

Section 4.2.1 of Kumar et al. (2011b) states, "While performing CCN activation measurements on wet generated ATD aerosol, almost all particles of the second peak activated (with an activation fraction ~1.0)." In this study, the larger mode of wet-generated particles were observed to activate with critical supersaturations ~ 0.15-0.2%. This extra information has been included in the text for clarity. It now reads:

"The only exception is for the activation of the larger mode of wet-generated ATD. Kumar et al. (2011b) reports that the activated fraction of this larger wet-generated mode is ~ 1, but in this study, the larger mode of wet-generated particles is observed to activate with critical supersaturations ~ 0.15 - 0.2%."

- *31059:26-27 "This change in nucleation behavior using wet-generation is not observed when the dust is simply wetted and re-dried." This observation seems significant for interpretation of the conclusion regarding wet-generation of dust aerosols, because it speaks to the issue of atmospheric relevance in terms of the humidity-exposure during a particles lifetime. It should be expanded upon earlier in the text. The data supporting this statement could be added as supplementary material.*

The re-dried dust data are now included in Table 1. This sentence has been moved to the Results section and now reads, "This change in nucleation behavior using wet generation is not observed when the dust is simply wetted and re-dried. Nucleation experiments were repeated with wetted and re-dried dust, and the results were identical (within measurement uncertainty) to those of the original dry dusts (Table 1)."

The implications of this statement are discussed in the Conclusions and atmospheric implications section, "The wet-generated ATD results show that the critical supersaturation of atomized dust can be different than that of the dry dust (a change that is not observed when the dust is simply wetted and re-dried). No known atmospheric processes lead to the redistribution of soluble material among large numbers of particles (100's or more), as is the case in atomization of a slurry."

Our preference is to not include a supplementary material section for this single point. All relevant material for this response are included in the text.

- *Fig 4: Caption. "n-lets" should be specifically mentioned and defined in the caption.*
  Fig 4: Caption. "results form this study" should read: results from this study.

Occurrences of "n-lets" have been replaced by "no singlets." "Form" is now "from."

- ***Fig 6. It would be much clearer to have the ordering of elements the same for between the left (dry) and wet (right) columns. Then the "additional" elements found in the wet generation case would be segregated to the right side, and a clear line could be drawn to separate the consistent and "additional" elements. Trying to see the different elemental compositions from reading the bar labels makes the differences less obvious.***

  Figure 6 has been replaced by New Figure 4, which is organized in the requested way for clarity.

- ***Fig. 5: Caption. Please make the caption clearer, such as: "Results from ion chromatography analysis for filtered supernatants of ground (magenta) and unground (black) samples of the three mineral dusts. In bottom right, unfiltered (black) and filtered (green) DI water control." Fig. 5: Caption. "The filtered slurry supernatants show higher concentrations of soluble material." It seems this refers to the control DI water, since all the mineral slurries were filtered. Please clarify this statement.***

  This caption now reads "Results from IC analysis for filtered supernatants of ground (magenta) and unground (black) samples of the three mineral dusts. Bottom right panel shows unfiltered (black) and filtered (green) DI water control. The filtered slurry supernatants show significantly higher concentrations of soluble material than the DI water control."

- ***Fig 6: Caption. "(red boxes on x- axis)" It does not appear that the red boxes represent the additional elements but rather the 400nm particle results.***

  This caption has been replaced by the one for New Figure 4.

Response to Referee Comment #2

The authors would like to thank Anonymous Referee #2 for the suggestions and insights provided in this review. After careful consideration of the information provided, we would like to offer the following responses.

General Comments

- ***Garimella et al. present CCN-derived hygroscopicity measurements of dry and wet-generated mineral dust aerosol particles. They combine electron microscopy, single-particle mass spectrometry, and ion chromatography to gain deeper insights into the physical and chemical properties of the aerosol produced, and how this is affected by the generation method used. The effects that particle shape and charge have on CCN-derived measurements of hygroscopicity are significant for mineral dust aerosol, and are certainly worth exploring to better constrain these artifacts, and produce more accurate measurements. While the overall experiments and results presented are ok, major revisions are required to improve the clarity and quality of this work before this***

manuscript should be accepted for publication. These revisions center upon the collection and analysis of the CCN data, and also the particle shape and charge corrections performed. Neither of these is explained in enough detail, or enough supporting data, to evaluate properly. This work is also highly similar to some previously published work that is not cited or discussed here, and this needs to be addressed... This paper seems to try to serve two purposes: 1) To provide a more accurate method for the measurement of the hygroscopicity of mineral dust particles that better constrains the effects of particle shape and charge (i.e. particle size), and 2) To report measurements of the hygroscopicity of mineral dust particles and compare the effect of wet versus dry-generation methods. By trying to meet these two different though related goals, I find the paper was not as clear or strong as it could be. It seems like the focus, and the more novel aspect, is the development of improved hygroscopicity measurements, by constraining particle shape and charge artifacts. Unfortunately not nearly enough details regarding this method and the results obtained are provided to allow a proper evaluation of the success of the method.

This response concerns the previous paragraph which is an overview of Reviewer 2's concerns: The main critique presented in this comment is the lack of supporting detail and clarity, especially in the collection and analysis of the CCN data, and also the particle shape and charge corrections performed. Per Reviewer #2's suggestions the paper has been revised to include more information about the collection and analysis of the CCN data and the corrections applied to this data. The references suggested by the reviewer have been cited in the indicated places. The paper has been revised for clarity throughout, especially in the indicated sections. There are now more details about the methodology and quantitative comparisons to allow for proper evaluation. These additions have been made to the existing text and figure captions and by including additional figures. Specific points made by Reviewer 2 are described in sequence below.

- *Another general criticism is that many of the figures are barely discussed in the actual text. For example, I couldn't find any mention or discussion of the actually hygroscopicity parameter values (kappa) determined in this work. It seems like the reader is just expected to find the results in the figures alone. Please discuss the results presented in each figure. Both the Results and Discussion sections are strikingly brief.*

More information and interpretation concerning the figures have been included in the text to increase clarity. The Results section has been expanded to include more thorough explanations of the findings, especially the data in the figures. The Discussion section now contains more supporting details and quantitative comparisons to help interpret the results.

- *As the authors explain, particle shape and particle charge issues can lead to significant inaccuracies in the measurement of the hygroscopicity of mineral dust particles. The authors use electron microscopy measurements to better constrain this. This is a good idea, but not enough details are provided to demonstrate the methods success. Central to this issue are the particle counting statistics. How many particles were examined using SEM for each mineral dust type, selected size, and generation method studied*

here? Was a large enough sample analyzed by SEM to produce a statistically significant sample population (e.g. based on Poisson statistics)? Was the SEM analysis randomized in any way so a representative (unbiased) sample of individual particles was analyzed?

The Methods section 3.2.5 has been expanded to address these questions. $n \sim 50$ particles per size per species per generation method are used to perform the shape and charge corrections. Particle concentrations during experiments are $\sim$ 30-90 particles per cc, so the number of particles measured by the CCNC for a given data point (1 minute of data) so $N \sim 15000\text{-}45000$. Using a typical standard deviation of a lognormal fit to the EM data of $\sigma = 35$, the sampling error at the 95% confidence level after population size correction is:

$$e(\%) = Z_{\alpha=0.05}\frac{\sigma}{\sqrt{n}}\sqrt{\frac{N-n}{N-1}} = 1.96\frac{35}{\sqrt{50}}\sqrt{\frac{45000-50}{45000-1}} \simeq 10\%$$

which is the level of sampling error. The sampling was randomized by choosing a subsection of the microscope grid at low magnification and then proceeding to measure the particles in that section.

- *On a similar note, as fitting the measured CCN curves properly is critical to the accurate determination of the hygroscopicity parameter, it is very surprising than zero CCN activation curves are presented here. Especially when you consider the large contribution from multiply-charged particles typically present in size-selected dust aerosol that makes fitting these curves additionally challenging - which is exactly what the authors are trying to address. Some activation curves must be shown, so it is clear how these are fit, and how the contribution from multiply-charged particles is dealt with. I.e. does the multiply-charged particle fraction determined from the SEM measurements agree with the multiply-charged plateau in the activation curve? See for example (Rose et al., 2008; Sullivan et al., 2010)... I am also concerned that the CCN/CN ratio was only measured at 5 different supersaturation values for each activation curve. It can be quite difficult to accurately fit the activation curve and find the critical supersaturation with so few data points, especially for complex activation curves with a large contribution from multiply charged particles as experienced with mineral dust aerosol. Again, some CCN activation curves and their fits must be shown to properly evaluate this method and the accuracy of the results. This manuscript should not be accepted for publication until this large omission is corrected.*

A new figure that shows activation curves and critical supersaturations for the ammonium sulfate (AS) calibration has been included as validation for the CCNC method (New Figure 1). A figure that shows examples of the raw activation curves of the dry dusts and the effects that charge correction have on these curves have also been included (New Figure 2). Multiply charged fractions calculated using the method in Wiedensohler (1988) are equivalent (within measurement and sampling uncertainties) to those observed in the EM data. This statement has been included in the Results section, "For correctly-sized particles, the fraction of multiply charged particles as calculated using the equations

in Wiedensohler (1988) matches (within measurement uncertainty) the fraction observed using EM even with a sheath to sample flow ratio less than 10:1."

- ***There was also no mention of how the CCNcs supersaturation was calibrated. This is an important detail as the specific method and thermodynamics used can have an important effect on the measured critical supersaturations (Rose et al., 2008). Please add these details.***

  Along with New Figure 1, the following text is now included in Section 3.2.3, "The CCNC chambers are validated with 50, 80, and 100 nm ammonium sulfate particles to verify that they can reproduce literature values of critical supersaturation and a κ for ammonium sulfate of 0.61 (Petters and Kreidenweis, 2007). The results of this validation is shown..." in New Figure 1.

- ***Many of the methods used here (CCN analysis, electron microscopy, single-particle mass spectrometry, and ion chromatography) were previously used to perform a similarly detailed analysis of the effects of wet versus dry-generation methods on the hygroscopicity of calcium carbonate particles (Sullivan et al., 2010). Considering how similar this previous work is, it should certainly be cited and discussed here.***

  References to Sullivan et al., (2010) have been included in the Introduction, Results, and Conclusions and atmospheric implications sections.

- ***It is difficult to evaluate whether the hygroscopicity data is most accurately described by K-Koehler theory, or by the FHH adsorption isotherm, from the way the results are presented. E.g. Figure 9 is busy and it is hard to see the trends and agreement with the Kappa lines. If the data does match well with lines of constant-Kappa, the Kappa line for the best-fit value of Kappa could be plotted for each mineral dust system to show how well the data does or does not agree.***

  Figure 9 has been replaced by New Figure 3. The κ lines of 0.001 and 0.01 are provided to illustrate the bracketing range of values to be used in models. Also, κ fits to the data from this study and Kumar et al. (2011a) are shown for each dust.

- ***Since you have a measurement of the soluble material present in the initial mineral dust from the ion chromatography, you could estimate the hygroscopicity this soluble material would impart to the dust aerosol, and compare that to the hygroscopicity actually measured for the dry generated aerosol. It would be very useful to test whether the observed aerosol hygroscopicity can be mostly explained by the soluble material measured in the bulk dust.***

  We thank Reviewer 2 for bringing up this point on a way to 'double check' the presented data.

  Soluble material on the surface of a mineral dust particle would increase the hygroscopicity of the particle. For the samples in this study, the soluble mass fraction

obtained from the IC results is $\varepsilon_s = 0.23\%\text{-}0.45\%$. Assuming that the soluble material has a $\kappa_s = 0.61$ (that of ammonium sulfate) and the insoluble dust has a $\kappa_{is} = 0$, the overall hygroscopicity of the dust particle can be estimated by the mixing rule used to determine κ for a multicomponent particle (Petters and Kreidenweis, 2007). The resulting hygroscopicity of the dust particle imparted by the soluble component is then

$$\kappa_{dust} = (1 - \varepsilon_s)\kappa_{is} + \varepsilon_s\kappa_s = 0.0014 - 0.0027$$

This estimate falls within the range of CCNC-derived values for κ_{dust} values of 0.001 - 0.01. The IC-derived can also be compared to the one estimated using the method from Kumar et al. (2009). Again assuming that the soluble material has a $\kappa_s = 0.61$ and taking the CCNC-derived κ_{dust} values of 0.001 - 0.01 observed in this study,

$$\varepsilon_s = \frac{\kappa_{dust}}{\kappa s} = 0.16\% - 1.64\%$$

This range is comparable to both the $\varepsilon_s = 0.23\%\text{-}0.45\%$ soluble mass fraction obtained from the IC results and the 2% soluble mass fraction of ATD reported by Vlasenko et al. (2005).

This analysis is now included in the text.

Specific Comments

- *Introduction: Should also cite some field measurement papers where dust particles were found to have nucleated cloud droplets. The cited papers (Page 30144, line 25) all seem to be laboratory studies.*

  Citations for Lee et al., (2010), Furutani et al., (2008), and Ma et al., (2004) have been included to show field measurements of dust as CCN.

- *A nice review of dust as a nutrient to the ocean is provided by (Jickells et al., 2005).*

  This reference has been included.

- *Page 31045, line 20: (Sullivan et al., 2010) also explored the effect of wet-generation on the hygroscopicity of mineral particles.*

  This reference has been included.

- *Page 31047, line 1: A Kappa value of zero corresponds to a non-hygroscopic but wettable surface (water can condense). Referring to "hydrophobic species" is not strictly correct.*

  The text now reads, "and approach zero for non-hygroscopic species..."

- *Page 31048, line 3: Should cite some more recent actual field-based measurements of the range of ambient aerosol hygroscopicity observed.*

  The text now reads, "Observational studies have shown that typical atmospheric aerosols have κ between 0.1 and 0.4 (Andreae and Rosenfeld, 2008; Juranyi et al., 2010; Moore et al., 2011; Friedman et al., 2013; Lathem et al., 2013)."

- *Section 3.2.1: How stable over time is the aerosol populations size distribution produced by dry generation?*

  The size distributions in show the averaged results from before and after the activation experiments. In all cases, the size distributions were equivalent within measurement uncertainty. This is now mentioned in Section 3.2.1.

- *The similarities and differences between Kappa-Koehler theory and FHH adsorption theory should be made more clear. What effects (e.g. hygroscopic growth, Kelvin effect, adsorption) does each include or not include? I.e. The adsorption isotherm appears to not include a hygroscopicity/Raoult term.*

  At the end of Section 2.2, the text now reads, "In this treatment of FHH theory, the water activity is related to the of thickness of the adsorbed water via the BET multilayer equation of state for the adsorbed water layer (Henson et al. 2007, Kumar et al., 2009b). Therefore, the equilibrium saturation ratio for a droplet depends on the thickness of the adsorbed water layer via the activity of water. In κ-KT, however, the water activity in a solution instead depends on solute hygroscopicity."

- *Page 30148, line 1: It is important to compare what size fraction of ATD was used here versus in other studies. The A1 Ultrafine or A2 Fine size fraction has been used in most ATD studies I am aware of. I believe the A2 fraction is washed in water while the A1 is not. Obviously this could affect the resulting hygroscopicity. What fraction is the "Nominal 0-3 um" ATD used here? Similarly, the fact that the samples were ground in ethanol is somewhat concerning, as this could also alter the hygroscopicity and distribution of compounds between particles/grains. It is good that ground ATD was compared to unground ATD. A similar comparison needs to be performed for both the MON and Illite samples - should not assume that they are also unaffected by the grinding in ethanol method.*

  After speaking with a Powder Technologies representative, there is no difference in the treatment of the different dust fractions with respect to washing. The A1 Ultrafine fraction is the same as Nominal 0-10 micron dust, and the A2 Fine fraction is coarser. The Nominal 0-3 micron fraction is the smallest fraction sold by PTI and is the one used in this study.

  Regarding the grinding process, the hygroscopicity and distribution of compounds between particles/grains do have the potential to change. However, as demonstrated by the ground/unground comparison of ATD activation and the IC experiments indicating

similar soluble material concentrations in ground and unground samples, the grinding method does not noticeably change activation behavior or leaching of solutes. Furthermore, Cicel and Kranz (1981) show that wet grinding of phyllosilicates clays leads chiefly to delamination of the clay layers rather than degradation of clay crystallinity. A similar comparison with NaMon and Illite is not readily possible since the unground powder of the former is quite coarse and the latter consists of solid chips before grinding. These issues are discussed in Section 3.1.

• *Section 3.2.2: What is the DMA sample flow rate? It appears to be 1.36 lpm, with a sheath flow of 5 lpm. This results in a quite low sheath:sample flow ratio well below the desired 10:1 ratio, thus broadening the DMA transfer function. I did not see this discussed - it should be.*

The DMA flow rate is indeed 1.36 Lpm, which does lead to a broader transfer function than if the ratio were 10:1. One of the main conclusions of this work is to verify the shape and size of the size-selected aerosol, which is accomplished in this study with EM and aerodynamic sizing. Section 3.2.2 now includes the statement " The DMA sheath flow is set to 5 L min^{-1} to maintain a fixed ratio with the sample flow rate. Though this sheath flow to sample flow ratio is smaller than the typically desired 10:1 ratio, the presence of undesired effects on the resulting size distributions are checked using EM and PALMS."

The Results section now includes the statements "For correctly-sized particles, the fraction of multiply charged particles as calculated using the equations in Wiedensohler (1988) matches (within measurement uncertainty) the fraction observed using EM even with a sheath to sample flow ratio less than 10:1." and "The PALMS results indicate that the distributions peak at the desired size and that the majority of doublets and triplets are removed even with a sheath to sample flow ratio less than 10:1."

• *Section 3.3: It is very surprising that the data processing section contains zero information on how the CCN activation curves were fit to derive the critical supersaturation. This needs to be discussed, with example activation curves and fits shown. The correction for particle multiple-charge and shape are central to this papers results, but I found the explanations of exactly how these corrections were performed to be overly vague. Please provide more details explaining the process used, any underlying assumptions, and resulting uncertainties. For example, how accurate is the estimate of the multiple-charge correction obtained from the charge distribution inferred from the polydisperse aerosols size distribution? This could be compared to the empirical multiply-charged fraction that can often be observed in the CCN activation curve by the height of the lower CCN activation curve on the CCN/CN axis (Rose et al., 2008; Sullivan et al., 2010).*

As discussed above in the general comments section, New Figures 1 and 3 have been included to clarify the CCNC methodology. For charge correction, section 3.3.1 now says "since the larger particles will activate first, the fraction of multiply charged particles for a given size is subtracted from the activation curve, and the curve is then rescaled to

include only singly-charged particles (Fig. 3). The fraction of larger, multiply charged particles are observed with EM and are compared to the calculated values."

Shape correction is used to determine the surface area equivalent diameters, and as Section 3.3.2 explains, "Mineral dust particles are approximated as elliptical cylinders with major axis, d_M, and minor axis, d_m, and maximum thickness, h_{max}, which is constrained by mobility sizing... Electron micrographs provide a means to determine the dimensions of the cylindrical face, and the particles mobility diameter provides an upper bound on the height by bounding its volume."

- ***The Results section was strikingly brief. The figures presented were barely discussed. This is the meat of the paper and really needs to be significantly expanded. The text of the Introduction (which could be trimmed some) is longer than the Results.***

The original aim of the Results section was to provide a brief summary of the experimental findings without significant discussion or interpretation. Per the request of the reviewer, the section has been expanded to include discussion of the results figures and the captions.

- ***Page 31058, line 1: The "agreement" between these results and those of Kumar et al. described is extremely vague. Please be specific and quantitative in drawing these comparisons.***

Figure 9 has been replaced by New Figure 3. The new version of the figure includes κ lines fitted to the data larger than 300 nm and makes the comparison of results easier. The Discussion section now begins "For sizes larger than 300 nm where correctly sized particles are expected to be found, there is agreement in the charge- and shape-corrected activation results in this study and those found in Kumar et al. (2011a) and Kumar et al. (2011b) (Figs. 4 and 9)."

- ***Page 30158, line 18: Please explain how not accounting for this size artifact would bias the results of Kumar et al. How large an effect could this artifact have had?***

The deviation of the FHH fits from κ lines occurs only when data smaller than 300 nm is included. Otherwise, Kumar would report κ values similar to those in this study. The text now reads "The FHH fits from Kumar et al. (2011a) include data from smaller-sized particles, but these data may be biased by the size artifact observed in this study. No direct observational evidence is provided to ensure that these smaller particles are correctly sized. Since both FHH and κ-KT agree at the larger sizes, the data from these sizes exhibit a narrow range of κ, and appropriate amounts of soluble material are found using IC results (see next paragraph), κ-KT is a found to be the suitable framework to describe clay mineral dust nucleation activity."

- ***Page 30158, line 25: "In the case of ATD there is an apparent discontinuity in κ at the smallest sizes considered even when size is corrected." This is also vague. Please expand upon this and describe more fully.***

This paragraph has been revised to say "The κ value for 200 nm ATD is higher than that for larger sizes even after shape correction. Because ATD is an industrially derived sample that is mechanically ground more than in either nature or in the laboratory, results for particles smaller than 300 nm are not representative of atmospheric particles. They may be subject to unknown artifacts, possibly compositional, which are responsible for the discontinuity. The data are provided here for reference but are omitted when determining κ."

- ***Discussion: Please be quantitative when discussing the effect that wet-generation has on the hygroscopicity of mineral dust particles. The Discussion was also overly brief, and much too qualitative. I did not see actual values for Kappa discussed in the text.***

  The Discussion section paragraph on wet generation now includes the following, "Especially in the smaller (< 100 nm) mode of particles, wet generation increases the range measured κ's dramatically from 0.001 - 0.01 to 0.01 - 0.45. At these smaller sizes, wet generation liberates soluble material with a much higher hygroscopicity than the original dust."

- ***Fig. 2: Why is the DMAs size cutoff perfectly sharp? If this is supposed to represent the DMAs transfer function, this is not correct. It is not clear what is being presented in this figure.***

  This figure shows a theoretical step function size distribution (in blue) and how it would be "seen" by a DMA (in green) as a result of doubly and triply charged particles. The figure is intended to caution the reader against sampling from the lower-size tail of this type of size distribution since there would be a disproportionately large number of doubly and triply charged particles in this tail. The caption now reads, "Artifact introduced into a idealized step function size distribution due to SMPS charge corrections. The "actual" idealized size distribution is shown in blue, and the size distribution reported by a DMA (after charge correction) is shown in dashed green. The difference between the two distribution arises from miss-assigning correctly-sized particles to smaller size bins, as would be done for multiply charged particles. The two sloped regions in the green curve correspond to the singly charged particles mis-assigned as doubly or triply charged."

Response to Referee Comment #3

The authors would like to thank Anonymous Referee #3 for the suggestions and insights provided in this review. After careful consideration of the information provided, we would like to offer the following responses.

Specific Comments

- ***Page 3, line 30. The sentence is either incomplete or "e.g." refers to citations. In a later case citations should be used without parentheses.***

  "E.g." refers to the citations, so the parentheses have been removed.

- *Page 4, lines 28-30. Arizona test dust is "an industrially derived sample" (as noted in the discussion part of this manuscript) rather than a "mineral dust sample . . . commonly observed in the atmosphere".*

  The Abstract now reads, "Droplet formation conditions are investigated for two common clay minerals, illite and sodium-rich montmorillonite, and an industrially derived sample, Arizona Test Dust." The Introduction now reads, "This study investigates the activation potential of two common clay minerals, illite and sodium-rich montmorillonite (NaMon), and an industrially derived sample, Arizona Test Dust (ATD), commonly used in aerosol and CCN studies."

- *Page 5. Lines 5-7. Sullivan et al. (2010) should be cited here as well, since they discuss the same issues. They also discuss possible processes responsible for the observed discrepancy between CCN activity of dry- and wet-generated mineral dust aerosol so I recommend mentioning how results of this manuscript agree with results published by Sullivan et al. (2010).*

  This reference has been included.

- *Page 5, line 23. Replace ρ by ρ_w to be consistent with equation (1).*

  This change has been made.

- *Page 6, line 10-11. Since this manuscript involves discussion of wet vs dry particle generation methods and its effect on CCN activity it is worth to mention here if dry or wet generation method was used in Herich et al. (2009).*

  The last paragraph of the Introduction section now reads "Though many studies in the literature, e.g. Herich et al. (2009) and Koehler et al. (2009), have used both dry and wet particle generation, more recent work (Sullivan et al., 2009; Sullivan et al., 2010; Kumar et al., 2011b) has indicated that wet atomization of mineral dust particles leads to anomalous results in their activation."

- *Page 7, line 7-8. Please make a comment either here or in introduction why 100-1000 nm is the desired size range.*

  The text now reads, "In order to increase the number of particles in the size range corresponding to the accumulation mode in the atmosphere (100–1000 nm, in all cases diameter)..."

- *Part 3.2.2 Particle Sizing and Counting. It is noted here that inlet DMA flow is 1 L/min while DMA sheath flow is 5 L/min. It is recommended to maintain DMA sheath to inlet flow ratio = 10:1 for the best size accuracy. Is there a specific reason that this ratio is 5:1 here? What is the impact of this setting on the size measurement?*

The DMA flow rate is indeed 1.36 Lpm, which does lead to a broader transfer function than if the ratio were 10:1. One of the main conclusions of this work is to verify the shape and size of the size-selected aerosol, which is accomplished in this study with EM and aerodynamic sizing. Section 3.2.2 now includes the statement " The DMA sheath flow is set to 5 L min^{-1} to maintain a fixed ratio with the sample flow rate. Though this sheath flow to sample flow ratio is smaller than the typically desired 10:1 ratio, the presence of undesired effects on the resulting size distributions are checked using EM and PALMS."

The Results section now includes the statements "For correctly-sized particles, the fraction of multiply charged particles as calculated using the equations in Wiedensohler (1988) matches (within measurement uncertainty) the fraction observed using EM even with a sheath to sample flow ratio less than 10:1." and "The PALMS results indicate that the distributions peak at the desired size and that the majority of doublets and triplets are removed even with a sheath to sample flow ratio less than 10:1."

- *Page 9. Line 11. Remove "America".*

This change has been made.

- *Page 12, line 8. The ratio between the mobility and the volume equivalent diameters according to DeCarlo et al. (2004) is $D_m/(C_c(D_m e)) = (D_{ve}\chi)/(C_c(D_{ve}))$ where C_c is the Cunningham slip correction factor.*

The text now reads "A spherical particle has $\chi = 1$. D_m and D_{ve} can be related by $D_m/C_c(D_m) = \chi D_{ve}/C_c(D_{ve})$, with $\chi \geq 1$. Since C_c monotonically decreases with increasing particle size, D_m is always lager than D_{ve} for non-spherical particles. Therefore, knowing a particle's electrical mobility diameter provides an upper bound for the volume of a non-spherical particle."

- *Page 14, line 21. Insert space between "400" and "nm".*

This change has been made.

- *Page 30, line 6. I recommend indicating how many measurements were performed to determine standard deviation of measured supersaturation.*

Section 3.2.3 now includes, "Each of the last three minutes at a given supersaturation is taken as a single data point, leading to three measurements per supersaturation."

Response to Short Comment by Dr. P. Kumar

The authors would like to thank Dr. Kumar for the short comment on this manuscript. A number of points are highly insightful and we have used them to improve the quality and clarity of the manuscript.

We take this comment seriously and there are 3+ pages of point-by-point response below. However, we are compelled to note several irregularities with this "Short Comment" both for the Editor, Reviewers 1-3, and for Dr. Kumar:

1. Per ACPD rules "Short Comments" are 10 pages or less. The initial comment was over 14 pages and this was cut to 11 upon our request (none the less we note that this comment is still in excess of ACPD policy despite our request for clarity).
2. Our experience is that "Short Comments" directly concern issues with the paper and do not act as an unsolicited review. Thus, while we appreciate the first page of the comment, we stress that this is not a 4th Review and should directly concentrate on issues with the manuscript. Our point by point response therefore addresses new points by Dr. Kumar and does not repeat points or editorial notes raised by Reviewers 1-3.
3. We note there are also requests for detail far beyond that voiced by the reviewers – e.g. details on the inline dryer (already described), the Teflon beads used for particle generations, for figure structure / line weight / symbols. We in all cases defer to the Reviewer suggestions and limit responses to what should be Reviewer editorial points, not Dr. Kumar's requests.
4. Finally, we note that this "Short Comment" largely concerns the direct comparison of our manuscript to Dr. Kumar's papers of 2009 (a – a paper on parameterizations for models and b) and 2011 (a and b): there are 45+ calls for comparison in this "Short Comment" : *we do not believe short comments should be used to so excessively call to attention the work of the commenter*. Nonetheless, we have added references to the 2009 papers and we note that the 2011 papers were highly referenced in the original manuscript and these references have increased in the revised version.

General Comments

• *The main conclusion of the study is that κ-KT is preferred over FHH-AT, especially since the former is deemed "simpler". The suggestion seems at first logical and practical, given that κ-KT is a standard approach to parameterize CCN activity. The important consequences of adopting fundamentally different activation physics for mineral dust in calculations of cloud droplet number (CDN) are however overlooked...*

 ...Therefore, using KT to parameterize CCN activity of dust/mineral aerosol can get the CCN number correctly, but will by design bias the CDN and its sensitivity to aerosol, and hence the Aerosol Indirect Effect in regions of freshly emitted dust. I strongly recommend the authors to revise their manuscript to caution the readership of these issues.

 This study does conclude that κ-KT is preferred over FFH-AT for describing the CCN activity of mineral dust. One reason for this conclusion is that the size-dependent critical supersaturation for dry-generated mineral dust particles is described well by lines of constant κ once data from the smaller sizes—a region of the size distribution where large numbers of doubly and triply charged are sampled—is removed.

Studies earlier than Kumar et al. (2011a) report dry dust data for particles sized smaller than 300 nm dry diameter. In this size range, sampling large numbers of doublets and triplets will lead to misleading results. The main arguments for including adsorption in CCN activity and hygroscopic growth (Kumar et al., 2009) are based on these data.

Specifically, Kumar et al. (2009) suggests that κ-KT is inappropriate for dust activation (and thereby promotes using FHH theory) because of 1) a higher than expected soluble fraction of dust using κ-KT and 2) differences in dust hygroscopicity under sub- and supersaturated conditions (Herich et al., 2009). However, both of these concerns are rectified if the correct range for κ (0.001-0.01) is used and the size distribution artifact is considered. Using the assumptions and calculation in Kumar et al. (2009), κ_{dust} values of 0.001-0.01 observed in this study indicate soluble fractions of $\varepsilon_s = 0.16\%$-1.64%. This range is comparable to both the 0.23% - 0.45% soluble mass fraction obtained from the IC results and the 2% soluble mass fraction of ATD reported by Vlasenko et al. (2005). These numbers are more reasonable amounts than those suggested in Kumar et al. (2009).

Also, despite difficulties comparing such values to HTDMA results so close to the detection limit, this range of κ values matches the range of results ($\kappa = 0.001 - 0.007$) from the HTDMA analysis of ATD, illite, and NaMon in (Herich et al., 2009). Overall, based on the results from this and previous works, the authors of this study suggest that the small amounts of soluble material that is present on mineral dust particles allows both the hygroscopic growth and CCN activation of mineral dust particles to be described adequately with κ-KT.

The consequences of using one framework over the other with respect to CDN and indirect effects have been discussed in the Conclusions and atmospheric implications section.

- *κ-KT is not simpler than FHH-AT. Both follow a simple power law of sc vs. Ddry (with different exponent). I can argue they exhibit the same degree of complexity when applied to dust: κ-KT requires two parameters, the kappa of the soluble fraction, and, its virtual variability with size; FHH-AT requires AFHH and BFHH (which can be approximated with one set of values). Given this and that a CDN parameterization to account for the correct theory has been developed and used in GCMs (and available to the community for general use) for dust aerosol, I strongly recommend the authors to revise these statements accordingly.*

Places where κ-KT is called simpler or less complex than FHH-AT have been revised.

Specific/Technical concerns:

- *The κ lines shown in Figs 3, 4, and 9 by Garimella et al. (2013) for $\kappa = 0.1, 0.2, 0.02$, and 0.01 seem to be incorrect. $\kappa = 0.1$ should read $\kappa = 0.01$, etc. The κ lines upon which the results of Kumar et al. (2011a,b) and Herich et al. (2009) plotted also seem incorrect. This impacts the comparisons and discussions made by authors...*

κ values shown in Figures 3, 4, and 9 were indeed mislabeled. These values and those in the abstract and conclusions should instead range from 0.001 to 0.01. The text has been changed accordingly.

- ***Page 31058, Line 18: The authors claim that the FHH fits from Kumar et al. (2011a) may be biased by the size artifact, and no evidence is provided to indicate that the smaller particle were corrected in Kumar et al., 2011a. This is incorrect. An example of the impact of multiple charging is shown in Fig. 3 of Kumar et al. (2011a), where one can clearly see that the multiple charge correction in this case increased Ddry from 170 nm to 247 nm. Kumar et al. (2011a) also conclude that the effect due to multiple charge correction is further pronounced at lower critical supersaturations (equal to 0.15% and 0.20%). Further, Kumar et al. (2011a) describe the procedure utilized for correcting the Ddry due to multiple charges as well as reference the procedure of Moore et al. (2010) to account for the uncertainty in the activation efficiency due to counting statistics uncertainty and flow rate variability. Please revise this incorrect statement used by the authors in this study regarding Kumar et al. (2011a).***

The data from smaller particle sizes are included in the FHH fits from Kumar et al., 2011a. These smaller sizes are subject to the sizing artifact and were not removed to calculate the fits. Since this size range contains few to no correctly-sized particles, the standard charge-correction procedure is no longer sufficient, and it becomes difficult to compare data from this range to those from sizes larger than 300 nm.

Editorial Comments:

The suggested changes in this section have been made to improve clarity.

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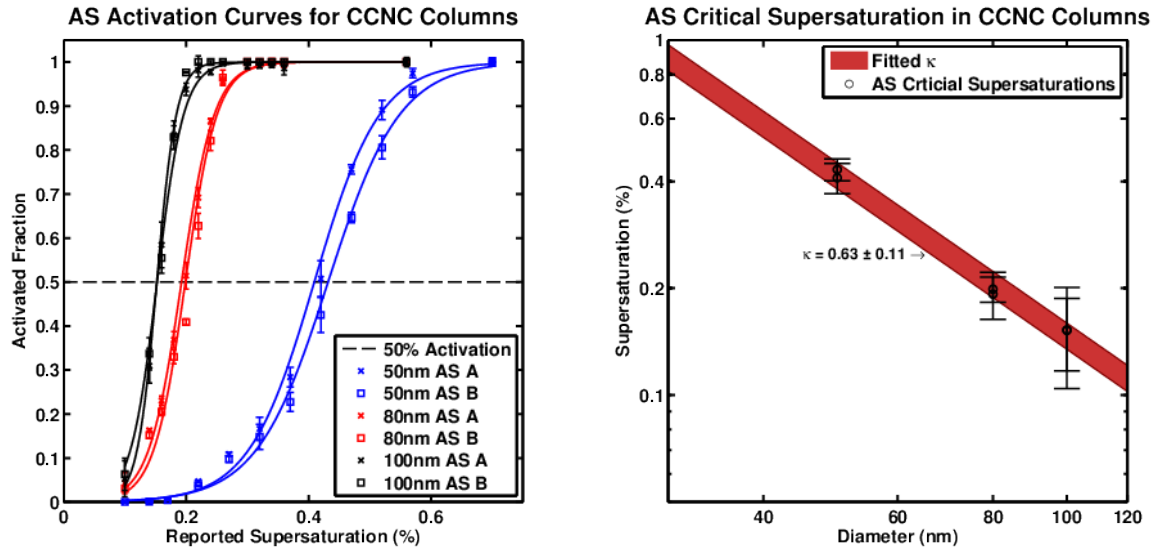
New Figure 1: Left: AS Activation Curves for 50, 80, and 100 nm particles in the A and B columns of the CCNC. Right: Critical supersaturation as a function of mobility diameter from the interpolated 50% activation points from the curves on the left. A κ value of 0.63 ± 0.11 corresponds well with literature values (Petters and Kreidenweis, 2007) and provides validation of the CCNC setup.
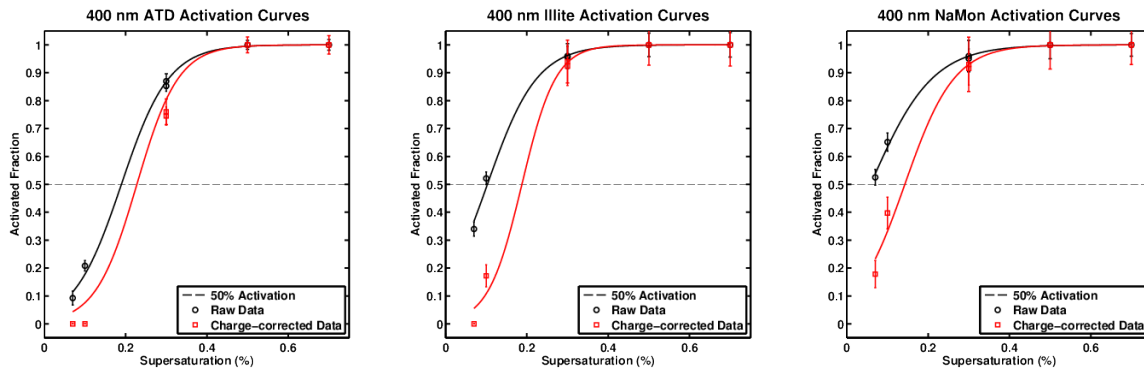
New Figure 2: Activation curves for the three dusts, size-selected at 400nm. In black are uncorrected results, with sigmoid fits, and in red are charge-corrected results with sigmoid fits. The calculations in Wiedensohler (1988) and EM observations both indicate that fraction of multiply charged particles at this size is ~0.4. The uncertainty associated with this charge correction technique is shown by the y-error bars in all critical supersaturation vs. diameter plots in this work.
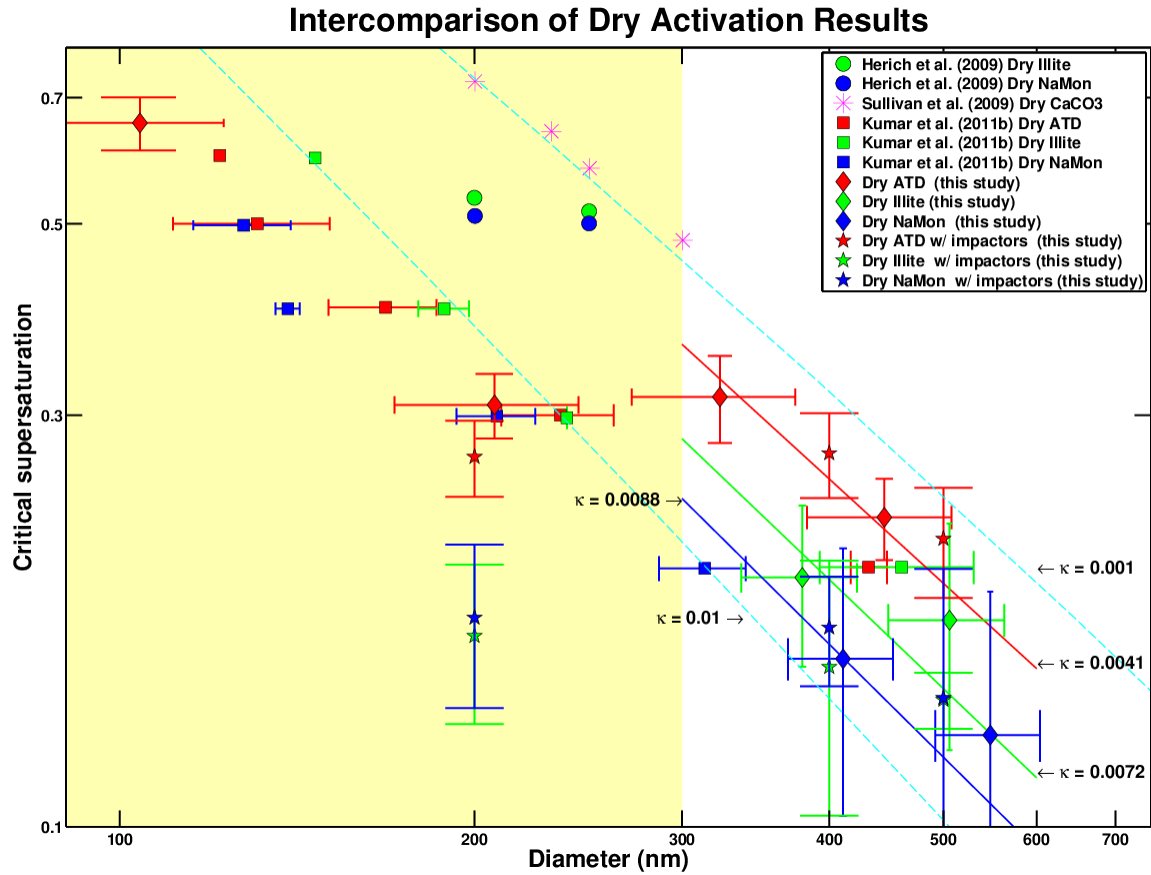
New Figure 3: Critical supersaturation vs. diameter of dry-generated particles from this study compared to results from previous studies. The solid lines show fitted κ lines for particles larger than 300 nm. The dashed cyan lines show that data fall between κ = 0.001 and κ = 0.01. The data in the yellow shaded region (< 300 nm) are unlikely to be correctly sized, as indicated by the EM results.
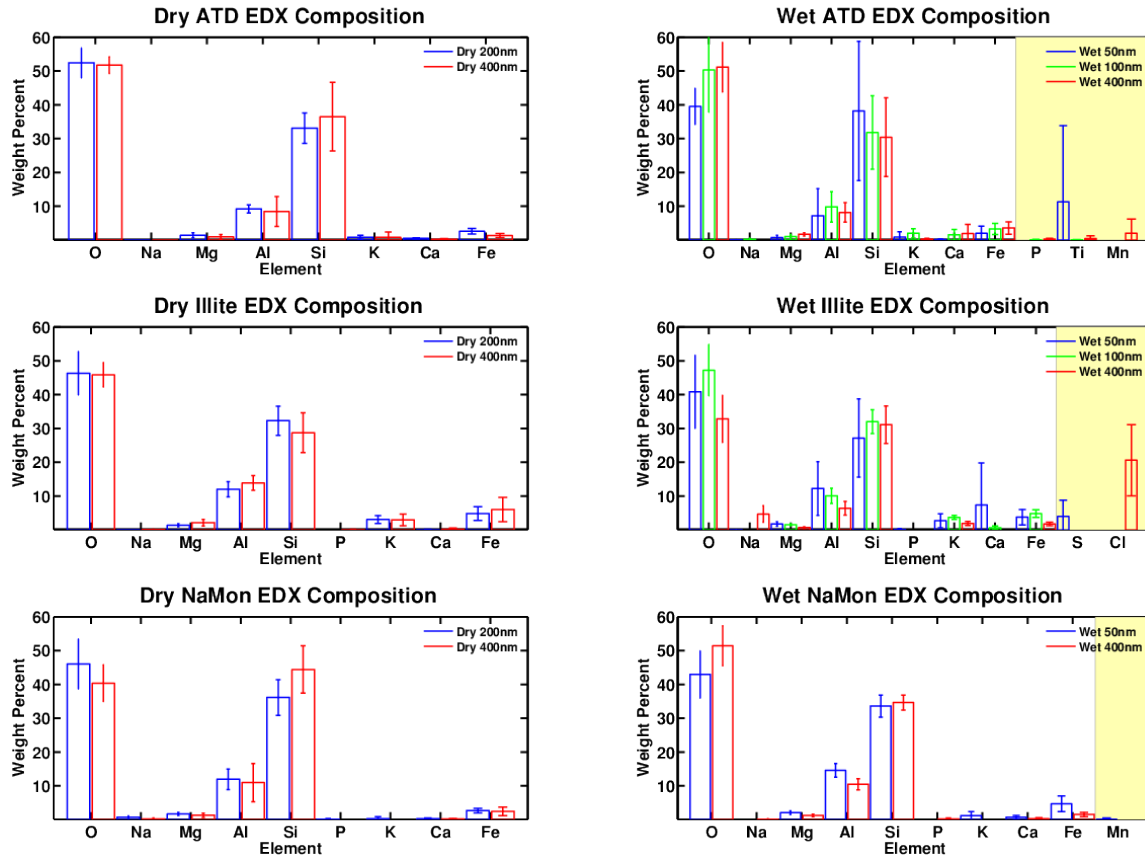
New Figure 4: Elemental abundances measured using EDX indicating minimal size dependence in the composition. The wet-generated particles (right) exhibit additional elements (shaded in yellow) compared to dry particles (left), which may correspond to soluble material repartitioning. Color bars indicate size according to the legend.