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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Cloud condensation nucleus activity comparison of dry- and wet-generated mineral dust aerosol: the significance of soluble material" *by* S. Garimella et al.

Anonymous Referee #2

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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 move 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.

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 along. Please discuss the results presented in each figure. Both the Results and Discussion sections are strikingly brief.

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 method's 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 signif-

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icant 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?

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.

There was also no mention of how the CCNc's 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.

Many of the methods used here (CCN analysis, electron microscopy, single-particle mass spectrometry, and ion chromatography) were previously used to perform a sim-

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ilarly 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.

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.

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.

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.

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

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

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.

Page 31048, line 3: Should cite some more recent actual field-based measurements

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of the range of ambient aerosol hygroscopicity observed.

Section 3.2.1: How stable over time is the aerosol population's size distribution produced by dry generation?

The similarities and differences between Kappa-Koehler theory and FHH absorption 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.

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.

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.

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 paper's results, but I found the explanations of exactly how these corrections were performed to be

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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 aerosol's 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).

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.

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.

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?

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

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.

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

Cited References

Jickells, T. D., An, Z. S., Andersen, K. K., Baker, A. R., Bergametti, G., Brooks, N., ...

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Torres, R. (2005). Global iron connections between desert dust, ocean biogeochemistry, and climate. Science, 308(5718), 67–71.

Rose, D., Gunthe, S. S., Mikhailov, E., Frank, G. P., Dusek, U., Andreae, M. O., & Pöschl, U. (2008). Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment. Atmospheric Chemistry and Physics, 8(5), 1153–1179.

Sullivan, R. C., Moore, M. J. K., Petters, M. D., Kreidenweis, S. M., Roberts, G. C., Laskin, A., & Prather, K. A. (2010). Impact of particle generation method on the apparent hygroscopicity of insoluble calcium minerals. Aerosol Science and Technology, 44(10), 830–846.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 31041, 2013.