Responses to Anonymous Referee #1

1. The shape effect observed in this study seems to be nearly an upper limit since the experiments focus on the flaming regime, and also evaporation during TEM analysis (leaving behind fractal-like backbones) can enhance shape factor as mentioned in section 4.2. This point needs to be more clearly mentioned. Since aged particles are reasonably spherical, the focus of this study is biomass burning aerosol "near source". It appears that the relevance to "near source" is mentioned only in conclusion. This clarification should be a part of introduction or another early part of the paper.

We thank the reviewer for this comment and have included this comment at the end of the introduction.

2. The results and discussion on dark (fresh) and aging experiment should be more clearly separated. If I understood correctly, the TEM was operated during the beginning and the end of the experiment (Page 12565, Line 2), but only results during the beginning was used (Page 12568, Line 5: "The TEM was not used in this section because saturation of the TEM grids required extensive time. . ."). Since the shape factor, χ, was only available for the dark condition, relevance of sections 4.3 and 4.4 are limited to fresh aerosol. Currently, sections 4.1, 4.3, and 4.4 are about fresh aerosol; section 4.2 is about aged aerosol. In my opinion, this organization makes the discussion hard to follow.

We thank the reviewer for this comment. We tried reorganizing the paper but feel that the paper best flows when the data is presented first and the sensitivity analysis is presented at the end.

3. A very relevant paper, Martin et al. (2013) is not cited. Martin et al. carried out chamber experiments of biomass burning aerosol and observed collapsing of non-spherical aerosol when exposed to a high relative humidity, resulting in underestimation of κ. Similarities and differences between this study and Martin et al. should be discussed.

We thank the reviewer for this comment and have included Martin et al. (2013) and a discussion of what we think is the biggest difference between our studies. That is, that we were able to measure the degree of nonsphericity of our particles.

4. Petters et al. (2009a) is cited as an example of in-situ sampling of possibly non-spherical CCN. However, Petters et al. preconditioned particles by humidifying the sample flow to >95% RH and then drying to RH < 5%, in order to collapse particles prior to the size-resolved CCN measurement (section 2.3 in Petters et al.). This point must be clarified.

This point has been clarified in multiple places in the text and a short discussion of the

consequences (and our reasons for using Petters' values) has been included in S4.4.

5. Section 4.4: Sensitivity of κ to χ is shown by applying χ = 1 ~ 1.5 to two biomass burning aerosol (Black Spruce and Sage Brush) observed by Petters et al. (2009a). However, as mentioned above, it is very unlikely that χ of particles observed by Petters et al. is as high as 1.5 because of the particle preconditioning step. Therefore, the calculated maximum κ of 1.1 (even higher than pure KCl) (Carrico et al., 2010) is not reasonable. For the purpose of sensitivity analysis, I think a systematic analysis of synthetic data would be better than using Petters et al. with an unreasonable assumption (χ ~ 1.5). When slip correction factors are ignored, the impact of (constant) χ on κ is simply χ^3 (1.50^3 = 3.38), which reasonably explains the reported change of κ from 0.07 to 0.24 and 0.33 to 1.1 (factor of 3.3 ~ 3.4). I believe it would be much more informative to illustrate to what extent slip correction matters in the impact of constant χ on κ.

We have left the aforementioned section in the manuscript for a complete discussion of the topic but have added the requested discussion on slip correction after it. We agree that this helps put into perspective the extreme κ value.

6. Page 12572, Line 18: Are you suggesting BC may be sparingly soluble? That seems unreasonable. Please add more description. You could just say sparingly soluble species could contribute to deviation from Köhler theory. Size-dependent chemical composition can also contribute to changing κ as a function of size (or sc).

We thank the reviewer for this comment and the recommended wording has been implemented in the text.

7. Conclusions: "SOA condenses on the fractal particle and the volume changes (measured through electrical mobility) are small compared to changes in particle mass." The data is not shown in this paper. Please provide relevant data such as time-series of effective density and particle volume (possibly as supplement).

Fig 5 shows the changes in fractal-like dimension that occur with biomass burning photochemical ageing. The increasing Df' is indicative of an increasing effective density; thus the ratio of mass to volume changes as described above. Supplemental Materials Figure S1 have been included to support these facts.

8. Page 12573 Line 25-28: How can you make this statement about the impact of chemical and physical transformation on non-ideality since χ is only available for fresh aerosol?

We would like to point out that the fractal-like dimension from the APM-SMPS system is available for aged aerosol and points towards an increase in the sphericity of the aerosol with time (Fig. 5). Furthermore we have taken care to distinguish differences between the fresh and aged biomass burning data sets. Additional information has been provided in supplemental materials to show the changes in both electrical mobility and particle mass during photochemical ageing.

9. I think it is important to emphasize that when material density (rho_m) is known (e.g.,

pure inorganic salt), measurements of mobility diameter (Dm) and the effective density (rho_eff) using the APM system is enough for acquiring accurate Dve, from theollowing equation: mp=π/6* rho_m * Dveˆ3=π/6 * rho_eff * Dmˆ3 which was utilized by Kuwata and Kondo (2009). The uniqueness of this study is experimental observation of χ (as a function of size) to compensate for the unknown rho_m of biomass burning aerosol.

We thank the reviewer for this comment and have included this point in section 2.2.

Minor comments:

Page 12556, Line 9: "microscopy" should be "microscope" to be consistent with aerosol particle mass analyzer and scanning mobility particle sizer (instrument, not technique)

Microscopy has been changed to microscope.

Page 12557, Line 14: "Particles formed . . . non-uniform" is an unnecessarily repetitive sentence.

The sentence has been removed.

Eq. (1), Page 12558, Line 21: sc and Sc are mistaken (sc = Sc – 1). It can be lnSc or sc. Note lnSc = ln(1+sc) ~ sc

"s_c" has been changed to "S_c" to correctly reflect the equation as presented in Petters and Kreidenweiss, 2007.

Page. 12559, Line 10: κ-Köhler theory does not necessarily assume ideal solution. κ includes the effect of non-ideality typically in the form of osmotic coefficient (Φ) or van't Hoff factor (i) (e.g., Rose et al., 2008). When ideality is assumed, κ simply follows Raoult's law and previous studies presented it as κ_Raoult (Petters et al., 2009b).

We thank the reviewer for this comment and have clarified that we are referring to the derivation of κ-Kohler as presented in Eq.1 and that other derivations do include terms for solution non-ideality.

Page. 12559, Line 18: ". . .not experimentally measured, especially as a function of particle aging." needs to be rephrased. Martin et al. (2013) experimentally measured hygroscopicity of non-spherical biomass burning aerosol as a function of particle aging, although they did not acquire χ.

We thank the reviewer for this comment. Martin et al. (2013) has been cited and the text has been changed to reflect their work.

For clarity, please add description of the relationship between effective density and material density, such as mp=π/6* rho_m * Dveˆ3=π/6 * rho_eff * Dmˆ3

The equation has been added as Eq. 7.

Page 12560, Eq. (2): Please show what formula was used for the Cunningham slip correction factor.

The slip correction factor has been included as Eq. 3.

Page 12562, Line 14: There are two “fractal”. Aren’t they “fractal-like” since the APM was used?

Both “fractal”’s have been changed to “fractal-like”

Page 12563, Line 26: “similar”, in terms of what?

The sentence has been revised to make clear the similarity is referring to particle number, size, and volume data compared to previous studies done in the same chamber.

Page 12566, Line 12: I don’t understand how primary particle diameter was calculated.

One method was to calculate the diameter from the projected area (A = pi/4 D^2), the other was to manually draw lines through the center of the primary particles and measure the length of the lines. The method has been clarified in the text.

Page 12567, Line 9 - 10: There are duplicate sentences. “Over 80% of. . .”.

The first duplicate sentence has been removed.

Page 12567, Line 19: “. . .overestimation” of primary particle size? Please specify.

Primary particle size has been added to the text.

Page 12568, Line 1: The impact of χ (=1.06 ~ 1.42) on particle volume should not be linear (1.06 ~ 1.42), but approximately cubed, although slip correction factor may also matter.

We thank the reviewer for this comment and the percent impact on particle volume has been corrected in the text while accounting for slip correction.

Page 12568, Line 8: Figure 4 → Figure 5

Figure 4 has been changed to Figure 5.

Page 12568, Line 11: please add reference for “not quite spherical” ammonium sulfate.E.g., (Kuwata and Kondo, 2009)

Biskos et al., 2006 has been added as a reference.

Page 12569, Line 14: diameter cubed is not equal to the volume. There is $\pi/6$.

The pi/6 term has been included in the text.

Page 12571, Line 4-5: How can shape factor contribute to a lower κ of the spherical reconstituted particles? Isn't that the opposite direction?

We thank the reviewer for this comment. The original intention was to write "…conditions that may influence particle composition". This has been changed in the text.

Page 12572, Line 8-10: "The data shown is data from the chamise experiments shown in Fig. 7". Are triangles in Fig. 9 actual measurements or interpolation/extrapolation of Ddˆ-3/2 curve fit? It appears to be the latter since there are four sc settings in Fig. 7 and eight in Fig. 9. Please clarify.

The data in fig 9 is an interpolation and this has been clarified in the text.

Page 12572, Line 13-16: The reference to mineral dust seems to be out of place since the mechanisms are likely to be very different (adsorption vs. absorption).

The reference to ATD is to fully acknowledge the experimental conditions of Kumar et al. (2011). Kumar et al. (2011) is referenced solely to facilitate discussion about the non-ideality of the experimental exponent (of κ). However, we have referenced the fact that differences in the droplet formation mechanisms are inherent between Kumar's system and ours.

Page 12573, Line 6: "to ensure a mobility diameter derived volume". I don't understand this. Do you mean to ensure accurate determination of volume-equivalent diameter?

We thank the reviewer for this comment and meant to say "accurately determine the volume of particles activating into droplets". This has been corrected in the text.

Page 12573, Line 15: "Biomass burning derived aerosol experience a decrease in hygroscopicity with aging" is a too general statement. You can only say this for those two fuels used in this study.

We thank the reviewer for this comment and were originally referring to Engelhart et al., 2012 as well as this and previous studies (Giordano et al., 2013). This has been clarified in the text.

Page 12573, Line 16: How can morphological changes (approaching sphere) explain decrease in hygroscopicity? It should increase the apparent hygroscopicity because non-sphericity leads to underprediction of κ.

We thank the reviewer for this comment. The sentence was meant to convey that lifetime in the atmosphere has an impact on the parameterization of particle hygroscopicity and has been amended in the text.

Fig. 4 Please add fuel-type and burn-regime (Flaming)

The text has been added to the figure caption.

Fig. 7 Does this data include both fresh and aged aerosol? Please specify. If aged aerosol is included, you cannot determine volume equivalent diameter since χ is only measured for fresh aerosol.

The caption has been edited to reflect that it is freshly emitted aerosol, which was previously only mentioned in the text.

Reference

Carrico, C. M., Petters, M. D., Kreidenweis, S. M., Sullivan, A. P., McMeeking, G. R., Levin, E. J. T., Engling, G., Malm, W. C., and Collett Jr, J. L.: Water uptake and chemical composition of fresh aerosols generated in open burning of biomass, Atmos. Chem. Phys., 10, 5165-5178, 2010.

Kuwata, M., and Kondo, Y.: Measurements of particle masses of inorganic salt parti- cles for calibration of cloud condensation nuclei counters, Atmospheric Chemistry and Physics, 9, 5921-5932, 2009.

Martin, M., Tritscher, T., Jurányi, Z., Heringa, M. F., Sierau, B., Weingartner, E., Chirico, R., Gysel, M., Prévôt, A. S. H., Baltensperger, U., and Lohmann, U.: Hygroscopic properties of fresh and aged wood burning particles, Journal of Aerosol Science, 56, 15-29, 2013.

Petters, M. D., Carrico, C. M., Kreidenweis, S. M., Prenni, A. J., DeMott, P. J., Collett, J. L., Jr., and MoosmÂÿller, H.: Cloud condensation nucleation activity of biomass burning aerosol, J. Geophys. Res., 114, D22205, 2009a.

Petters, M. D., Kreidenweis, S. M., Prenni, A. J., Sullivan, A., Carrico, C. M., Koehler, K. A., and Ziemann, P. J.: Role of molecular size in cloud droplet activation, Geophysical Research Letters, 36, L22801, 2009b.

Rose, D., Gunthe, S. S., Mikhailov, E., Frank, G. P., Dusek, U., Andreae, M. O., and Pöschl, U.: 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, Atmos. Chem. Phys., 8, 1153-1179, 2008.

Responses to Anonymous Referee #2

Major comments:

Symbols for parameters Symbols must be clearly defined in papers discussing particle morphology, since many of similar (but slightly different) concepts are employed, such as volume equivalent diameter, dry diameter, mobility diameter. In the case of effective density and shape factor, there are a few different definitions, as discussed in DeCarlo et al. (2004). Thus, the readers need to know which definitions the authors are using to understand the paper correctly. I suggest the authors to make a table summarizing those parameters used in this study.

We thank the reviewer for this comment. A table has been added to supplementary materials summarizing the symbols and their usage. The effective density has been defined in (new) Eq. 7 and the shape factor is that used by Kaspar (1982) as cited in the main text.

Meaning of Dd in kappa-Kohler theory and abscissa for Figures 6-9 Related to the above comment, it was not clear to me what the authors are trying to tell by figures 6-9. The authors explain Dd in equation (1) as follow: 'Dd is the dry particle diameter.' Then, conclusions of this paper include the following sentence 'These mobility diameters are relevant for CCN activation and therefore represent an underestimation of kappa since the volume of particle that is being activated is smaller than assumed.' Do the authors define Dd in equation (1) as volume equivalent dry diameter, and hence use of mobility diameter leads to underestimation of kappa? In that case, please clearly define Dd as dry volume equivalent diameter when this value appears in the paper for the first time. Meanings of figures 6-9 would not be easy to understand in that case. Why mobility diameter is plotted in those figures if Dd indicates volume equivalent dry diameter? (a similar statement would also be applied if Dd is defined as dry mobility diameter). This is an important question since it affects basic concepts of CCN study on non-spherical particles.

We thank the reviewer for this comment and we have added a crucial bit of information to the introduction of $\varkappa$-Köhler theory. The confusion occurs because in the derivation, Dd^3 should be representative of the volume of the particle (therefore the volume equivalent diameter). However, in practice it is commonplace to simply apply the electrical mobility diameter (due to the widespread usage of the SMPS-CCNC systems). We have tried to make this clearer in the text. We believe this also clears up the meaning of the "dry activation diameter" used in the axes of the appropriate figures.

Minor comments:

P12563 More detailed description about the chamber experiment is necessary. Especially,

description about change in size-distribution and mass concentration would be useful in interpreting Figure 5.

The following statements have been provided in the text: Raw data from electrical mobility sizing and aerosol mass data are provided in supplemental material, Fig. S1.

P12564L17 'CPC,TSI 3084' Would you check if it is the right model number?

The correct model, TSI 3760A, has been replaced in the text, we thank the reviewer for this correction.

P12566L3 'Once the mean volume of an aggregate at a certain mass was found with the above analysis, the diameter of the sphere with that volume was used as the volume-equivalent diameter for that particle.' Estimation of volume equivalent diameter by this method contains some assumptions and artifacts. For instance, material condensed in between primary particles would not be included in calculation of total particle volume. Would the authors be able to discuss potential errors of the method or uncertainties in volume equivalent diameter? One potential option is to estimate material density of biomass burning particles using APM and TEM data, and compare it with literature values of density for elemental carbon and organic compounds. The value should be reasonable if volume estimation is accurate.

This is an important comment and has been clarified in two separate ways. First, we only apply these equations to the fresh aerosol. Yes, once materials condense on the fresh primary particles then this analysis contains artifacts. Online measurements of fractal-like dimension are applied to the aged evolving CCN. We specified in the text that the section mentioned by the reviewer is applied to fresh aerosol only.

Second, in calculating the volume equivalent diameter of fresh aerosol, we make the assumption that there is no preferential partitioning of condensing material. If condensing material does not create a uniform film over the aggregate particle (and therefore the primary particles) then this analysis would contain large artifacts, even for fresh aerosols, as the reviewer points out. The question of preferential partitioning is an interesting one but is beyond the scope of this text. We have clarified this assumption in the text.

P12572L18 'The presence of black carbon (BC) in biomass burning may act as the sparingly soluble species for biomass burning generated aerosol.' Is black carbon insoluble or sparingly soluble? Please define insoluble and sparingly soluble materials clearly, and describe how the property of BC is related to those definitions.

We thank the reviewer for this comment and the text has been reworded to convey our intended meaning.

References 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 Science and Technology 38 (12), 1185-1205, 2004.