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Interactive comment on “Microscopic characterization of carbonaceous aerosol particle aging in the outflow from Mexico City” by R. C. Moffet et al.

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Received and published: 1 December 2009

Response to reviewer 1

We thank the reviewer for the helpful comments. We have responded to each specific comment below in italics. We have included the reviewer’s original comments in normal font.

General Comments: The authors have characterized single particles collected at three sites in Mexico City in order to better understand ageing processes, in particular with respect to organic carbon. The paper is generally well written and I suggest

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publication after the following specific comments are addressed. In particular, some sort of uncertainty analysis associated with the spectral deconvolution methods is needed as is some discussion of how the particles, as observed using the microscopy methods, may have been altered from their state in the atmosphere.

Specific Comments: p. 17002: For the STXM measurements it is stated that the optical density depends on, among other factors, the material thickness. It is my understanding that the STXM method cannot directly get at particle thickness and so some assumption must be made in order to properly determine optical density. What assumption was made here? Spherical particles with a diameter determined based on the spatial extent of the particles in the other two dimensions? How are non-spherical particles treated?

Lines 221-224 describe how optical density is obtained. In these experiments, OD is calculated from I_0 (measured in the absence of sample) and I , measured in the presence of the sample. Both I_0 and I are measured at each pixel. Using the relation given in the text, " $OD = \ln(I_0/I) = \mu \rho t$, where μ is the mass absorption coefficient, ρ is the mass density, and t was the material thickness." Hence, optical density can be obtained without knowing the sample thickness.

p. 17003, line 23 (and throughout in general): The EDX line scan data provide evidence that for particles at T0 many of the particles can be generally described as having sulfate cores surrounded by organic material. However, it is reasonable to think that the exact nature of the particles as they exist in the atmosphere is modified by the collection technique, transport to the analysis location and the removal of water from the particles. Can the authors comment on how in particular this last aspect (no water) might bias the results?

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The following was added to the text on p. 12, lines 259-263: Based on the ambient RH (never exceeded 71 %, Table 1) and density measurements made at T0 (Moffet et al., 2008b), particles collected at T0 were in the non-hydrated state. Therefore, for Figure 4, the crystalline morphology observed in the SEM is expected to be representative of particles in the ambient atmosphere.

p. 17003, line 24: The authors show that in addition to having sulfate cores with organic coatings, some particles have potassium cores with organic coatings. In Figure 4 it appears that the S and K cores are observed in the same particles, suggesting that the K and S are internally mixed. Presumably, K is from primary emissions and S is from secondary formation. Why then would these be so well internally mixed? Does this have anything to do with "missing" water during analysis (see the above comment)?

Particle cores containing both K and S elements may be attributed to particles composed of K_2SO_4 and $K_3Na(SO_4)_2$ inorganic salts. These are very common particles in emissions from biomass combustion (e.g. (Boman et al., 2004)). Posfai et al (Li et al., 2003; Posfai et al., 2003) observed similar particles from grassfires in Africa. They attributed these to internal mixing of K with SO_4 resulting from atmospheric aqueous phase processing. Similar processing could be possible at the T0 site. However, given that the relative humidity during sampling was below the crystallization relative humidity of K_2SO_4 and $(NH_4)_2SO_4$ and that biomass particles at T0 had densities of 2 g/cm^3 , it is more likely they were crystalline prior to sample collection. If particles had been collected in a more humid environment, dehydration upon collection could play a larger role in particle mixing state and morphology. In that case one would anticipate that the least soluble salts would precipitate first and that salts could separate within a particle.

p. 17003, line 24: From the STXM images below, it would appear that EC behaves

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quite differently than the inorganics in terms of how it mixes in the particles. Here, the inorganics are present as "cores". But EC appears to be scattered throughout the particles. Why would this be the case? Presumably, EC would not mix with OC any better than the inorganics?

The following was added to the text in Lines 277-284. Most often, EC was surrounded by organics. However, there are cases where fresh (uncoated) EC was observed. This will be more extensively quantified in a forthcoming publication. The mixing of EC and IN phases was similar for the T1 and T2 sites (Fig. 5B-5C), whereas at the T0 site the particle centers were dominated by large IN inclusions (Fig. 5A). For the T0 particles, the EC inclusions may have been displaced from the center of the particle upon crystallization of the IN phase.

Figure 5: It appears from the images shown in figure 5 that not only is the amount of OC increasing, but that the carbonaceous inorganic phase (IN) is decreasing in going from T0 to T1 to T2 (i.e. there are fewer/smaller "blue" areas in B and C compared to A). Can the authors comment on why this might be the case? Does it have anything to do with the 3D structure of the particles? In other words, where did the IN go?

This comment is addressed in lines 357-368 of the revised text, which states:

"The most probable reason for the increase in homogenous OC particles is the growth of nucleation mode particles. If organics and sulfate condensed simultaneously, they would be well-mixed and appear as homogenous particles, particularly if the aerosols have not undergone a deliquescence/efflorescence cycle. The inhomogeneous INOC type may be due to a source specific to T0 and not present at T1 and T2. In fact, the inorganic inclusions for T1 and T2 were typically smaller than at T0. Particles at T0

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bear resemblance to particles (likely primary) obtained from sampling grass fires (Li et al., 2003; Posfai et al., 2003). Such fires were observed at T0 during this time of day with a similar composition (organics and potassium) (Moffet et al., 2008a). The smaller inorganic inclusions at T1 and T2 could be the result of a different formation process (i.e. secondary condensation) from the primary formation of the large inorganic crystals at T0.”

p. 17004, Line 11 and Figure 6: Are the presented spectra averages over the three sites? Why not make a 9 panel figure breaking out the different sites as in Figure 5?

No, particle spectra in Figure 6 are average spectra obtained over multiple sampling sites for each of the defined phases, EC, OC, IN. Since figures 6 and 5 are organized differently it does not make sense to put them together into a 9 panel figure.

p. 17005, Line 27: The authors estimate the COOH as the difference between the C 1s \rightarrow pi* transition and the pre-edge intensity. Why not use the fits (as in Figure 11) to deduce the COOH fraction rather than the difference method used here?

The reviewers are correct that this could have been done differently. However, taking the difference of the peak height and the pre-edge intensity is a standard mapping technique used in STXM/NEXAFS (e.g. (Russell et al., 2002)).

Additionally, I am not convinced that the difference between the T0 and T1/T2 COOH vs. distance plots necessarily provides clear information on the physical mixing within the particles. Presumably, the results shown in this figure are averages from a number of particles. But in Figure 9 it is shown that the fraction of particles at T1 and T2 that contain OC and S is smaller than at T0 (similar information can be gleaned from

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Figure 8). So is this difference in the COOH distribution just a sampling issue (i.e. the number of particles looked at using STXM at T1/T2 were less likely to contain OC and S than at T0)? For particles at T1/T2 that did contain significant amounts of S was the core/shell morphology also observed? Or did these specific particles show generally different behavior than at T0? This would suggest something important about mixing. As it stands, I am concerned that this conclusion arises more from the statistics of the sampling.

To improve the interpretation of the figure 8, the T0, T1 and T2 data is presented in box-whisker plots demonstrating the spread in the data. From these plots it is seen that the distribution of COOH at T0 is significantly different than at T1 and T2. Additionally, the data at T0 exhibits considerably more variance. Whether or not the difference is solely due to sulfur cannot be determined because the radial scans were obtained at the carbon edge.

p. 17006, line 18: The authors suggest that oxidation of soot could have led to the formation of carbonyl moieties within the EC phase. However, given the timescale of the plume evolution (a few hours), would heterogeneous oxidation have been fast enough to explain the magnitude of the observed carbonyl fraction within the EC phase? Since the EC phase was identified by empirically (arbitrarily?) setting an sp₂ threshold of 35%, could the observation of a significant carbonyl component have more to do with the spectral deconvolution?

Yes, reaction of soot with O₃ is known to be so fast as to be almost instantaneous (complete reaction in 0.1s with [O₃]=50ppbv) (Chughtai et al., 1991). Therefore, the observed carboxyl groups would have orders of magnitude more time than needed to form on the surface of “fresh” soot.

The %sp₂ threshold was determined empirically. An sp₂ value of 35% was based

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on changing the %sp² threshold and determining the point at which the obtained spectrum resembled soot and where the organic coatings were not erroneously included as EC phase.

The carbonyl component (indicated in the raw data in Figs 5 and 6B by the COOH functional group) is clearly evident. The observation/identification of this peak is completely independent of the deconvolution analysis.

p. 17006, line 26: Since the STXM technique looks through the particle, to what extent might the sorting into groups be driven by differences in the vertical structure of the particles (e.g. OC-EC-OC or OC-IN-OC)? It would be extremely useful if the authors were to provide some sort of uncertainty estimate here.

STXM measures a column absorbance. As long as the chemical composition within the column remains the same, the distribution of components within the column (vertical structure) has no effect on the measurement.

If however, the reviewer means that the chemical composition varies within the column-yes, the reviewer is correct that differences in vertical structure will drive the classification to some degree. As the organic coating increases, the particles sp² content decreases (as well as relative inorganic content). The definition of the IN phase is meant to identify regions containing a dominant inorganic phase. The same line of reasoning holds for the sp² content. The limit of 35% sp² hybridization for the EC group represents the lowest sp² value where the particle is definitively EC. Particles with lower sp² values could contain some small fraction of EC. We have added this discussion to the text because it is important for the interpretation of the number fractions (lines 291-292 and 334-335).

Because the definitions of the different phases are identical for each site, the uncertainty resulting from label based definitions will be solely due to Poisson counting statistics. With > 200 particles per sample the uncertainty due to statistics is <7%. For the SEM analysis the uncertainty is further reduced. Uncertainties due to counting statistics are clearly shown in Figure 10.

p. 17008, line 24: The authors observed an increase in the total carbon mass per particle. How does this single particle result compare with the co-located bulk measurements (e.g. AMS)?

Unfortunately, there are no published AMS data for the day of March 22 from the T1 site and there was no AMS instrument deployed at T2.

Comparing the SMPS distributions from T0 and T1 we found that the total number concentration for the 0.1-1um size range were as follows:

T0: 12:30 = 3400/cm³, T1: 13:00 = 884/cm³, T1: 18:00 = 2600/cm³

We have OC mass concentrations from Doran et al.(Doran et al., 2007) at T1 , which for 13:00 and 18:00; they are 10.3 and 6.5 ugC/m³. The afternoon OC mass at T0 was 10.7 ugC/m³(Stone et al., 2008). Therefore, the organic carbon mass per particle at each site is:

T0: 12:30: 3.1 fgC/particle, T1: 13:00: 11.6 fgC/particle, T1: 18:00: 2.5 fgC/particle

While there is a 274% increase in OC per particle going from T0 to T1 at 13:00,

there is actually a 19% decrease in OC if we compare T0 and T1 at 18:00. The STXM estimates a 44% increase for T1 at 13:00 and a 33% increase at 18:00. While the magnitude of the increases obviously do not agree, both techniques predict a decrease in OC at T1 from 13:00 to 18:00.

There are large sources of systematic error in the above calculations. To do this calculation more accurately, requires organic carbon size distributions which are currently unavailable. Therefore, we have assumed that OC is evenly distributed throughout the number distribution from 0.1-1 μm . However, as we have speculated in the paper, we hypothesize that organic particles grow from smaller sizes (possibly smaller than 0.1 μm) to produce the dominant OC particle type at T1 and T2 as well as the increase in carbon mass as measured by the STXM.

Given the large degree of uncertainty present in these calculations, we hesitate to add this discussion to the formal text. However, we point out that these observations are consistent with those of Klienman et al. as discussed in the discussion and conclusions section.

p. 17008, line 26: Again, some sort of uncertainty estimate for the deduced fractions of COOH, O-CH₂, etc. would be extremely useful. Without knowing the uncertainty in the estimates, it is very difficult to know whether the observed changes in the particle COOH, etc. fractions are to be believed.

A detailed uncertainty analysis was performed and Table 2 and Figure 12 changed to show uncertainty calculated at the 95% confidence interval.

p. 17008, line 26: The authors state that the fraction of OCH₂ groups (identified as

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being from sugars) increases downwind from T0. If the biomass sources are in the city (or part of the aerosol background) why would this fraction (the O-CH₂ group) increase downwind since it is presumably derived from primary emissions. It would seem that the fraction should actually decrease as the amount of secondary material increased. I would naively think that the O-CH₂ group would track with the % sp² hybridization (since this is in some ways a marker for primary emissions).

In addition to sugars, it may also be possible that O-CH₂ bonds are present as a result of photochemical reactions producing compounds such as alcohols or organo nitrates or sulfates. We have added this to the discussion (414-415).

p. 17009, line 12: I don't agree. I think if these were both normalized to the value at T0, the decrease would appear similar in magnitude. Or at least reasonably similar. Again, uncertainty estimates would help here. I would also recommend pointing out more clearly that the variability in going from T0-T1-T2 for the EC and OC sp² bonds is quite similar. This would support your conclusion that the relative decrease in both is due to condensational growth. However, this still doesn't address the question of where the sp² bonds in the OC phase come from. Can the authors comment on the source of the OC sp² bonds (oligomers?)?

sp² bonds may come from molecules such as aromatics or any other molecule containing sp² hybridized carbon. There are countless organic compounds containing C=C bonds. Due to the lack of additional information, we hesitate to implicate oligomers here.

Both heterogeneous oxidation of OC and condensation of OC with lower sp² hybridization can contribute to the observed decrease in %sp². The data in figure 12A show that the amount of sp² hybridization in the organic phase is decreasing. As

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now stated in lines (428-431) ... the addition (condensation) of organic matter onto particles may play an additional role in the decreasing relative contribution of the sp^2 carbon within individual particles. Based on our results, these two processes cannot be decoupled.

Figure 2: minor note: the bars indicating the additional transport days appear more blue than they do gray.

Noted

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