Comment from Referee #2:

General:

This paper compares single-particle measurements of particle size, composition, and morphology of in-cloud and interstitial particles collected at a rural site in China. This paper mainly comments on the role of aqueous chemistry in forming organic shells and the observation of more branched soot particles in cloud. I have several comments about this work to be considered before publication.

We appreciate the constructive suggestions and comments from the referee. The referee's comments are in the black text followed by our response in the blue text as follows.

Major Comments:

1. A lot of the most important details and figures are in the SI rather than in the main text. Also, a lot of the main supporting data came from SPAMS analysis which was not described in the methods.

Thanks for your suggestions. We have moved some tables and figures from the SI to the main text, and we have added more information about the SPAMS in the methods. Please see below for specific responses.

2. The argument regarding core-shell and liquid-liquid phase separations was a bit confusing since previous work has shown that the core-shell morphology can break down as RH is increased.

We agree with your comment. What we want to express is that the oxidized organic matter formed in the cloud processes has a great influence on the mixing structure of organic particles after water evaporation within particles, which is conducive to the existence of organic particles in a core-shell structure after cloud events. Since we did not express clearly, we modified the relevant statements in the manuscript. Please refer

to lines 36-37 and 319-322:

Lines 36-37: The sentence, “Our results highlight the in-cloud formation of more oxidized organic shells on the activated particles.”, has been changed to “Our results highlight that the formation of more oxidized organic matter in the cloud contributes to the existence of organic shells after cloud processing.”.

Lines 319-322: The sentence, “The prevalence of OM shelled particles upon in-cloud processes also supports a recent laboratory observation depicting that rapid film formation and fast heterogeneous oxidation can provide an efficient way of converting water-insoluble organic films into more water-soluble components in aerosols or cloud droplets (Aumann and Tabazadeh, 2008).”, has been changed to “The prevalence of OM shelled particles after cloud processing also supports a current laboratory observation depicting that rapid film formation and fast heterogeneous oxidation can provide an efficient way of converting water-insoluble organic films into more water-soluble components in aerosols or cloud droplets (Aumann and Tabazadeh, 2008).”.

Specific Comments:

Introduction:

1. Lines 59-60: Nitric oxide is a gas, not particulate matter.

Thank you for pointing out this. In the article we quoted, the authors used “nitric oxide” to represent the NO^+ signal measured by ATOFMS, which refers to nitrate. In order to avoid ambiguity, we have changed “nitric oxide” to “nitrate”.

2. Line 63: not sure how “decomposed” is being used in this sentence.

We are sorry for the misunderstanding. The word (decomposed) has been removed, and the sentence has been changed to “These results indicate that both RES and INT present complex mixtures, and carbonaceous matter (i.e., organic materials (OM) and soot) is important material in the cloud mass.”. Please refer to lines 62-63.

3. Line 76: reword “this process might not be neglected”

The sentence, “this process might not be neglected.”, has been changed to “the influence of this process in atmospheric chemistry cannot be neglected.”. Please refer to lines 75-76.

4. Line 78: Also see [Moffet and Prather, 2009]

The literature has been cited in the main text. Please refer to lines 77-79:
“For another type of carbonaceous material, soot, there is extensive evidence that the absorption and cloud activation of soot-containing particles can be significantly affected by coatings (Adachi et al., 2010; Wu et al., 2018; Moffet and Prather, 2009).”

5. Lines 77-86: please also comment on the finding that organic coatings caused the collapse of soot particles from [Spencer and Prather, 2006].

The original sentence, “While some studies have found that soot compaction occurs after cloud processing (Bhandari et al., 2019; Ma et al., 2013; Mikhailov et al., 2006), Khalizov et al. (2013) suggested that soot with thin organic coating did not become more compact under high humidity.”, has been changed to “While some studies have found that soot restructuring occurs after water processing (Bhandari et al., 2019; Ma et al., 2013; Mikhailov et al., 2006), or being coated by OM (Spencer and Prather, 2006) and sulfate (Zhang et al., 2008), Khalizov et al. (2013) suggested that soot with thin organic coating did not become more compact under high humidity.” Please refer to lines 83-86.

Reference:

Spencer, M. T., and Prather, K. A.: Using ATOFMS to determine OC/EC mass fractions in particles, Aerosol Science and Technology, 40, 585-594,

10.1080/02786820600729138, 2006.

Zhang, R., Khalizov, A. F., Pagels, J., Zhang, D., Xue, H., and McMurry, P. H.: Variability in morphology, hygroscopicity, and optical properties of soot aerosols during atmospheric processing, Proceedings of the National Academy of Sciences of the United States of America, 105, 10291-10296, 10.1073/pnas.0804860105, 2008.

Methods:

1. Lines 100-101: What is meant by "almost unaffected by local anthropogenic sources"?

The sampling site is surrounded by a national park forest (273 km^2), and there are scarcely any emissions from anthropogenic activities.

2. Lines 117-120: I think that Table S1 and the air mass back trajectories should be shown in the main paper. It will help give context for what was different between the different cloud events to help interpret the results.

We agree with you. Table S1 and Figure S2 (the air mass back trajectories) have been moved to the main text, and are numbered as Table 1 and Figure 4.

3. Line 125: change "folds" to "fold".

It has been changed accordingly.

4. Line 128: change "vacuumed" to "vacuum" and define NH_4NO_3.

It has been changed accordingly. The sentence has been changed to "In the TEM vacuum chamber, some volatile substances (e.g., ammonium nitrate (NH_4NO_3) and volatile organic matter) would be lost.". Please refer to lines 129-130.

5. I couldn't follow the methodology given in section 2.4. Please add more details.

We have added detailed calculations in the section 2.4 (that is section 2.5 now). We have now included an introduction on two parameters including k_a and α, which depends on the degree of monomer overlap (δ) in the aggregate. Furthermore, we have also supplemented the calculation of δ herein. Please refer to lines 174-180:

"The value of k_a and α depends on the degree of monomer overlap (δ) in the aggregate (Oh and Sorensen, 1997), and δ can be determined by:

$$\delta = \frac{2a}{l}$$

where a is monomer radius, and l is the center distance of adjacent monomers. The value of parameters including a, l, A_a, A_p, L_{max}, and d_p can be obtained by analyzing TEM images. Then D_f can be calculated by the above four formulas."

Reference:

Oh, C., and Sorensen, C. M.: The effect of overlap between monomers on the determination of fractal cluster morphology, Journal of Colloid and Interface Science, 193, 17-25, 10.1006/jcis.1997.5046, 1997.

6. A lot of SPAMS data is brought in to corroborate the results. I suggest that details on the SPAMS needs to be added to the methods if the data is being used.

The detailed information of the SPAMS has been added in the methods (section 2.4). And the identification of particles measured by the SPAMS is provided in the SI.

Results:

1. Line 153: some fresh soot particles can have sulfate, see [Moffet and Prather, 2009].

We agree with your comment. Since there is hardly any anthropogenic source around our sampling site, the collected soot particles are assumed to experience long-distance

transport and complex aging processes. The aging state of the soot particles may also be reflected by the associated more intense sulfate peaks measured by the SPAMS, compared with those observed in urban areas, as discussed in our previous publication (Zhang et al., 2017). Considering that much secondary inorganic matter and organic matter might be generated during the cloud processes, this study distinguishes fresh and aged particles by the presence or absence of secondary inorganic matter (S-rich) and organic matter (OM).

Zhang, G., Lin, Q., Peng, L., Bi, X., Chen, D., Li, M., Li, L., Brechtel, F. J., Chen, J., Yan, W., Wang, X., Peng, P., Sheng, G., and Zhou, Z.: The single-particle mixing state and cloud scavenging of black carbon: a case study at a high-altitude mountain site in southern China, Atmospheric Chemistry and Physics, 17, 14975-14985, 10.5194/acp-17-14975-2017, 2017.

2. Lines 154-156: the methods for identifying each component should be moved from the SI to the methods section of the paper.

The identification of each component has been moved from SI to the methods section of main text (section 2.3), and original sentence of lines 154-156, “The details involving the identification of each component (S, OM, soot, mineral, metal, fly ash) are provided in the Supporting Information.”, has been canceled.

3. Lines 159-161: I would think it would be important to explicitly detail the mixture for your results. I found these classifications really confusing and hard to keep straight.

Thanks for your comment. Fresh mixture has been changed to “refractory” in the full text and SI, and the sentence has been changed to “Aged particle types containing two or more refractory components are named as “aged mixture”. It is worth noting that “refractory” refers to the refractory particles without S-rich and OM.”. Please refer to lines 188-190.

4. Lines 167-168: I recommend bringing Figure S1 into the main paper.

Thanks for your suggestion. Figure S1 has been moved to the main text, and is numbered as Figure 3.

5. Lines 168-169: Not sure what is meant by "influenced by air masses". More description of the different conditions and air mass conditions encountered for each cloud event will help the authors interpret their single particle findings.

To make it clear, "influenced by air masses" has been removed, and we moved the content about the influence of air masses on the distribution of particle types in the RES in the SI to the main text. Please refer to Lines 200-212:

"The different air masses are expected to affect the distribution of particle types. The distribution of several types of particles in the RES were observed to be divergent in different cloud events, corresponding to different air masses, as shown in Figure 3 and Figure 4. The number fraction of OM-containing particles was the highest (81%) in cloud event #2, which might be partly attributed to the higher concentration of O3 during cloud event #2 (Table S1). And the samples of cloud event #2 sampled at noon. Higher solar radiation at the sampling time might also promote heterogeneous photochemical oxidation reactions during the cloud process and increased the generation of OM within cloud droplets (Xu et al., 2017). Aged metal particles accounted a similar percentage (7-12%) for three cloud events. The proportion of aged mineral during cloud event #1 (14%) was nearly four times those in the other two cloud events. Aged fly ash particles had the highest proportion (10%) in cloud event #3 compared with the other two cloud events, which is most probably influenced by the different air masses (Figure 4). Aged mineral particles of cloud event #1 may be influenced by the long-distance transportation of dust from Southeast Asia (Salam et al., 2003). Clearly, aged fly ash particles of cloud event #3 are associated with the air

masses from the PRD region with a dense distribution of industrial facilities there (Cao et al., 2006)."

6. Lines 171-172: What is meant by "as confirmed by SPAMS data"?

That sentence has been removed in the revised manuscript.

7. Line 176: what is meant by "part of"? Can this be made more quantitative?

Since aged refractory and aged mixture particles include S/S-OM/OM-refractory and S/S-OM/OM-soot/mineral/metal/fly ash. OM-containing particles refer to S-OM/OM-refractory and S-OM/OM-soot/mineral/metal/fly ash, which is part of aged refractory and aged mixture particles. In the RES and INT during cloud event #2 and #3, OM-containing particles account for 63% and 32% of the aged refractory particles and 51% and 43% of the aged mixture particles.

8. Figure 3, should "coating" be "thin coating" instead to better distinguish the morphology?

Thanks for your suggestion. We have changed the mixing structure "coating" to "thinly coated" in the full text and SI.

9. I found the coating thickness definitions to be confusing especially because they overlap. I'm not quite sure how the coating thickness was used to robustly distinguish particles classified as "coating" vs "core-shell".

The electron beam of TEM penetrates the particle, and the internal structure of the particle can be observed (Li et al., 2016). Thus, although the organic matter wraps the internal material, the organic coating and shell can still be easily identified. The major difference between "coating (that is thinly coated now)" and "core-shell" is the relative

thickness of organic coating and shell in the particle is. Core-shell structure possessed thicker organics than thinly coated structure, and the thickness of OM-coating and OM-shell is 12-150 nm and 86-2110 nm in this study, respectively. Please refer to Lines 218-224.

Reference:

Li, W., Sun, J., Xu, L., Shi, Z., Riemer, N., Sun, Y., Fu, P., Zhang, J., Lin, Y., Wang, X., Shao, L., Chen, J., Zhang, X., Wang, Z., and Wang, W.: A conceptual framework for mixing structures in individual aerosol particles, Journal of Geophysical Research-Atmospheres, 121, 13784-13798, 10.1002/2016jd025252, 2016.

10. Lines 219-222 imply that the site is polluted, but the site was presented as a background site.

We are sorry for the misunderstanding. As we described, the results of this study are similar to those of unpolluted remote areas, but different from those in polluted areas. The original sentence has been changed from "Such a mixing structure is similar to those observed in the Arctic, background, or rural atmosphere (Hiranuma et al., 2013; Li et al., 2016; Yu et al., 2019), but is different from previous findings in polluted air where OM is typically mixed with sulfate (Li et al., 2016)." to "Such a mixing structure is similar to those observed in the Arctic, background, or rural atmosphere (Hiranuma et al., 2013; Li et al., 2016; Yu et al., 2019), but is different from other findings in polluted areas where OM is typically mixed with sulfate (Li et al., 2016)."

11. Line 223: reword "follow up strong interactions" to "heterogeneous and multiphase reactions"

It has been changed accordingly.

12. Lines 225-227 seem to imply that there is more data that was not presented. Please

rephrase.

Thanks for pointing out this. The sentence has been changed to “Recently, Gorkowski et al. (2020) came up with a particle morphology prediction framework developed for mixtures of organic aerosol based on the measurements from aerosol optical tweezers experiments and literature data, and they hypothesized the core-shell morphology dominated by secondary organic aerosols (SOA) in the shell phase.”. Please refer to lines 262-265.

13. I’m very confused as to how the O/C ratios were determined. Perhaps I missed something, but I thought that the detector used only detected elements heavier than C and it is not clear how the background from the carbon film is accounted for.

The O/C value is measured by EDS (energy-dispersive X-ray spectrometry), which can obtain the weight and atomic number proportion of elements heavier than carbon ($Z \geqslant 6$), and some limitations of O/C have also been expressed in the main text. Please refer to lines 266-271:

“It should be noted that the O/C ratio of organic coating and shell is underestimated herein due to the copper grid evenly covered by carbon film. And, while some loss of volatile organic compounds during the TEM/EDS analysis may affect the O/C of particles, the relatively higher O/C ratio for the RES is still affirmative. Droplets are expected to dissolve more abundance of volatile organic compounds (Chakraborty et al., 2016), evaporation of which would result in an underestimate of O/C to a higher degree rather than the INT.”

14. One of the main conclusions of this paper is regarding oxidized coatings formed via aqueous chemistry, yet the main table showing this is in the SI. I suggest bringing Table S2 into the main paper.

Thanks for your suggestion. Table S2 has been moved to the main text, and numbered as Table 2.

15. The O/C values should be stated in the main paper.

The O/C value of organic shell and coating has been in the main text. Please refer to lines 271-274:

"We found that the average value of the O/C ratio of RES is higher than INT, and the average value of the O/C ratio of RES with core-shell structure is 0.23, which is two times that with thinly coated structure (0.11) (Table 2), indicating that these RES with core-shell particles are more oxidized."

16. Lines 242-245: If ion peak ratios from SPAMS are discussed, then SPAMS must be included in the methods section and the interpretation of the ion peak ratios needs much more interpretation to connect to the data presented in this paper.

We agree with your comment. The operating principle of the SPAMS has been added in the method section (section 2.4), and the introduction of the relative peak area is also described, that is "The relative peak area of characteristic peaks of specific material in the mass spectra is generally applied to indicate its relative abundance in the particle.".

17. Line 251: also site [Moffet and Prather, 2009]

It has been added in the text. Please refer to line 289.

Lines 288-290: While some previous studies demonstrated that soot aggregates tend to be more compact (with larger D_f) after aging or cloud processing (Adachi and Buseck, 2013; Wu et al., 2018; Moffet and Prather, 2009), our results suggest that in-cloud processes may result in more branched soot, as shown in Figure 6.

Reference:

Moffet, R. C., and Prather, K. A.: In-situ measurements of the mixing state and optical properties of soot with implications for radiative forcing estimates, Proceedings of the National Academy of Sciences of the United States of America, 106, 11872-11877, 10.1073/pnas.0900040106, 2009.

18. Lines 254-256: I don't follow the logic regarding non-volatile material and branching. I suggest that the authors more clearly present this argument.

Thank you for pointing out this. We have described that in detail. The sentences have been changed to "The first and the most likely reason is that some of the soot aggregates are immediately encapsulated by non-volatile materials (such as organic matter) after emission by combustion sources. These coatings fill the spaces between the branches of soot aggregates, which inhibits the relatively large deformation and reconfiguration of the soot aggregates during transport and activation into cloud droplets (Zhang et al., 2018). Differently, soot aggregates may shrink easily and become more compact during long-distance transport, if the soot aggregates are emitted without non-volatile coatings (Adachi and Buseck, 2013)." Please refer to lines 292-298.

19. Lines 258-260: could this just be showing the role of particle size where unaged soot is larger and more CCN active than smaller, aged particles?

We are sorry for the misunderstanding. We described the D_f (fractal dimension) of soot particles in the RES and INT in the section 3.2, which is 1.82 ± 0.05 and 2.16 ± 0.05, respectively. And here, we described the ECD (equivalent circle diameter) of soot particles in the RES and INT, which is 266 nm and 247 nm. So, compared with soot in the RES, soot in the INT particles have larger D_f and smaller ECD. To be more clear, the sentence has been changed to "We show that soot aggregates have higher D_f and lower average ECD in the INT (247 nm) than in the RES (266 nm), which means that larger, less dense soot particles are easier to act as CCN.". Please refer to lines 298-300.

20. Lines 268-270: is there a figure showing the off-center positions of the soot?

Yes. The Figure S4 (a, b, c, g) show the off-center positions of the soot. “Figure S4” is added in the sentence. Please refer to lines 307-309:

“Our observations at the background site show that the majority of soot aggregates in both RES and INT (~80%) are located in off-center positions (Figure S4), having less compact shapes even after being coated.”

References:

Moffet, R. C., and K. A. Prather (2009), In-situ measurements of the mixing state and optical properties of soot with implications for radiative forcing estimates, Proceedings of the National Academy of Sciences of the United States of America, 106(29), 11872-11877.

Spencer, M. T., and K. A. Prather (2006), Using ATOFMS to determine OC/EC mass fractions in particles, Aerosol Science and Technology, 40(8), 585-594.