

Yang and co-workers describe laboratory measurements of internally mixed organic-inorganic aerosol systems. Mainly based on FTIR, their experiments demonstrate how replacement reactions in aqueous aerosols can alter the composition, with subsequent implications for the aerosol phase state, an important property that determines the impacts of aerosol particles on air quality and climate.

Overall, I find the experiments interesting and the topic falls within the scope of Atmospheric Chemistry and Physics. However, I would like the authors to address the points below, before their work can be considered for publication.

L16: Please rewrite and clarify the list of numbers: Do you mean 65.5% to 60.1%?

L17: Please add RH uncertainties to your quoted DRH values. Consider also adding the DRH values of pure inorganics in parenthesis at the end of this sentence, so that the increase in DRH becomes more quantitative.

L29: Please check your reference formatting. This reference is from the year 2011, not 2001.

L33: Please check your reference formatting. This reference should read "Kreidenweis".

L37: "... with carboxylic acids/salts and ammonium salts as one of the most abundant..." Please add appropriate references to this statement.

L44: "Organics can decrease...". Please add appropriate references to this statement, as well as to the following sentence.

L47: Please add more relevant references, e.g.: 10.1021/jp0556759

L50-51: Please either give a review article here as reference, or add further primary refs for each of the named processes, i.e. reactivity, heterogeneous uptake...

L52: This is the first time you mention "replacement reaction". I would encourage the authors to give a brief, general definition and maybe a relevant example, so that a reader can follow more easily.

L54: Check reference: "Ma et al. (Ma et al., 2019)"

L56: "... the impact of ... on hygroscopic growth": It would be good to more precisely specify the impact. Did oxalate formation lead to a decrease or increase in hygroscopic growth?

L57: Check reference: "Ma et al. (Ma et al., 2022)"

L60: Consider changing "liberate" to "release" or "formation"

L64: No need to write Chen et al. twice in the sentence. Rewrite as : "Chen et al. (2020) elucidated..., respectively." Also, is it really appropriate to say "elucidated", since in the next sentence you write how information on aerosol phase state was missing.

L64: I am unclear what "lack of information" or "uncertainty in aerosol phase state" you refer to, please specify? Do you mean a lack of knowing the crystallization RH?

L70-72: This sentence reads cumbersome, please reformulate. I think you are trying to say that phase states such as LLPS can promote the inhomogeneity of components? Your references seems appropriate for the first part ("The inhomogeneity of aerosol components can significantly impact the degree of reactivity"). I would move it there and then consider adding other references for the occurrence of LLPS, liquid-solid coexistence etc.

L76-79: “Therefore, ...” I am a bit stuck with this statement. On L69-70 you write that “replacement reactions and phase state are intercorrelated parameters”, which I think is a fair way to put it. Now, on this line here you argue about the impact of replacement reactions on aerosol phase state. However, at the same time these replacement reactions to in turn depend on the aerosol phase state. What is the correct line of reasoning, i.e. replacement reactions affecting phase state or phase state affecting replacement reactions...? Maybe it would be fairer to reformulate this here to something like: “Exploring the interplay of different organic and inorganic salts on reactivity, particularly the reactivity of replacement reactions, on the one hand side, and aerosol phase state on the other hand side, is important to understand atmospheric aerosols”. The title of the manuscript should be adjusted accordingly.

L77: Change “significance” to “important”

L87: See my comment above: It might be good to replace “correlation” here with “interplay”

L93: What is “three distilled water”?

L97: Please indicate compound purities when introducing the chemicals, along with supplier.

L97: How was this diameter measured? Please specify. Also, were FTIR experiments done for differently sized particles? How was particle homogeneity verified, i.e. absence of e.g. liquid-liquid phase separation, that could affect results.

Table 1: Please add spaces between numeric values and units, e.g. 100 g instead of 100g.

L104: bump → pump

Section 3 general: It would be helpful to add a Table to the SI where the different peaks and the corresponding chemical groups and inferred phase state were summarized, as it is in parts very hard to follow the discussion throughout this Section.

L126: add “is” shifted to

L140: I would encourage to specify here and elsewhere as “crystalline solid phase”, as the “viscous phase” can also be solid (== glassy) or semi-solid, which both denote amorphous solid phase states.

L142: Here and elsewhere, please give RH uncertainties.

L145-147: I am unclear about what you write here. If the sodium citrate aerosol is highly viscous, why is the water uptake than not gradual, but “abrupt”, as you write? To me the humidification curves on sodium citrate and sodium tartrate look like curves with a sharp deliquescence, which I would only expect for crystalline material. Please clarify why you nonetheless think that these phase states are “viscous”, which you seem to use to describe an amorphous solid state.

Section 3: This Section has many different subsections and the connection of these is not always obvious. It would be good to add a brief description of what topic is treated where to guide the reader a bit at the start of the Results and Discussions.

Section 3.1 general: It could make sense to move your Fig. S2 to the main text. That way, a reader could follow the described spectral changes with changes in RH better. Also, Fig. S2 misses a proper legend indicating what the black and red data points correspond to.

L153-155/Fig.1: In the blue-framed enlarged image: Where is the blue and the red lines? Please color your lines as in the left most panel or the violet-framed enlarged image. Otherwise

it is impossible to connect the RH values to the individual lines. Note, this also concerns Fig. 1c.

L159: Reference formatting: No need to have “Tan et al.” twice in this sentence, please change.

L185-195: Please add appropriate references the subpanels of Fig. S3, to make it clearer what you are describing here.

Section 3.3 general: The structure of this section should be improved. In the beginning, the authors introduce relevant replacement reactions. The middle part (L202-210) then discusses some literature findings. The last part (L210-235) then discuss hygroscopicity data from the present manuscript, but the link to the topic of replacement reactions remains unclear. This requires improvement in a revised version.

L198-200: Please indicate phase states of reactants too. Please also indicate whether these reactions take place for decreasing or increasing RH.

L206: “larger specific surface area” compared to what? Bulk solutions? Unclear.

L215: “...water loss or uptake”. Add <https://doi.org/10.1021/cr990034t> or other appropriate refs.

L221: “These processes...”: Can you quantify “sudden” here? Also, please elaborate how spectral changes in this case do not reflect the water content. What does this mean to the spectral changes in your Fig. 1 (and others) discussed above?

Fig. 2: Please add labels for the red and pink shaded area directly into the Fig. to make interpretation easier.

L224-241:

- Please add references to appropriate subpanels in Fig. 2 directly to the text, as you jump quickly between the individual panels.
- Please add information on the rate of RH changes during your experiments to the text. Was the rate slow enough to allow for equilibration of the particles and the surrounding RH?

L261: Check title, should this read: “The effect of molar ratio on the replacement...”

L265: Please provide reasoning for the chosen ratio in the context of typical organic-to-inorganic ratio found in atmospheric aerosols.

L267-270: I suggest to repeat in parenthesis the meaning of the named peaks at e.g. 3130 cm⁻¹ etc., to make it easier for the reader to follow here.

L278: “From Fig. 4a...” Looking at the red squares in Fig. 4a, the shift from 1176/cm to 1186/cm appears to be pretty broad from about 40% RH to 20% RH. How can you get such a precise ERH value as 41% for the 1:1 mixture? Also, for the 2:1 mixture the peak shift seems to appear over an even broader RH range, so how do you get to the quoted 23.7% RH? Please clarify in the text.

Fig. 4: What is the difference between grey symbols with a horizontal vs. vertical grey line across the symbol?

L294: Please delete “et al.”

L295: mixing → mixed, was → were

L303: Replace "escalated" with more appropriate wording.

Fig. 7: Why was there no crystallization observed in the left-hand side images at 12.1% RH? Please clarify in text.

L332-341: More information should be added how these experiments were done? What was the rate of RH changes? Was the first RH cycle started at high or low RH? How long were the particles exposed to these (high) RH conditions? The latter would help to get a better idea how fast these replacement reactions are.

L352: "substantial work" should be followed by appropriate refs.

L354: "retained in a viscous"

L359: Please check if you really mean "dehydration" here or "hydration"?

L360: "Grayson..." verb is missing. Please avoid repetition of references; otherwise check for correct punctuation, i.e. "Grayson et al. have demonstrated..."

L361: "As the RH decreased..." Please add ref to this statement and provide a brief explanation of "gel" for the reader here (you could move the explanation you give on L367 up).

L371: which → where

L372: How does this trapping work? Just by physical uptake of water due to capillary condensation or is this due to chemisorption? This should be added to the text.

L373: Break up sentence: "... bound around fibres. Hence, migration of SO₄²⁻ and Na⁺ ions was inhibited, so that these ions cannot come in contact and nucleate a crystalline phase."

Fig. 8: I like the idea of having a schematic, but I think this figure can be improved to clarify aspects described in the text. It is unclear what the different colors correspond to. A legend is missing to indicate the fibrous particles as "gel-like". Is there a better way to make the "OH groups and SO₄²⁻ ions bound around the fibers" (L372) more obvious? Outgassing of NH₃ is depicted but not mentioned in the text.

L387: "of atmospheric SOA." Please add more appropriate refs.

L401-404: Please see my previous comment: Replacement reactions can certainly impact the aerosol phase state as you document, but in turn these are also dependent on the phase state of the aerosol particle. This aspect should be better represented in your Conclusion section.

L397-398: "Additionally, we observed..." This is certainly a very interesting finding of this study. I would like to see some more discussion, which atmospheric processes could be influenced by such "crystallization upon hydration". Also, can the authors speculate how important this process is and if they would expect it for other atmospherically relevant aerosol systems?

L405-409: I am unclear what "targeted strategies to mitigate air pollution" the authors refer to. Please elaborate or remove this statement.

Fig. 9: This figure is not mentioned and discussed in the text, please do that or delete the figure.