Review of Manuscript acp-2021-53: Ice nucleation ability of Ammonium Sulfate aerosol particles internally mixed with Secondary Organics

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Bertozzi et al present a very interesting and worthwhile study on the cirrus temperature regime ice nucleation abilities of crystalline ammonium sulphate and secondary organic material derived from the dark reaction products of α-pinene ozonolysis. The experiments are carefully conducted with interesting and valuable conclusions that would be of significant interest to the ice nucleation community. I enjoyed reading this contribution and commend the authors on the experiments. I recommend publication after the following comments are addressed.

Major points:

The experiments conducted here in are done systematically with 5 different systems investigated (Experiments A – E). I think the discussion of cloud processing and its impacts have been kept too implicit. I think the authors could do a better job in addressing how cloud processing of organic coated AS can enhance the ice nucleation activity compared to unprocessed particles. The discussion is often presented from the other point of view, i.e. compared to pure crystalline AS, the cloud processed particles are less IN active, however, given the cloud cycling is a commonly occurring (REF) process (both through liquid and ice clouds) in the atmosphere, I recommend also making the comparison and bringing out the cloud processing aspect of the study more. Also, in the atmosphere more often than not, particles are internally mixed, as such their cloud processing studies would be most relevant for the troposphere.

Can the authors better justify their definitive claim that the particles experimented with had core-shell morphology in the paper, even in the case of the thick coatings in Experiment B. To me it seems like this is being taken for granted, but there is no definitive evidence being provided. Especially in Experiment B where the coatings are conducted at room temperature and low RH, glassy state for the SOM is favoured and thus how likely is it to form core shell morphology.

While reading the paper, I think there is some evidence to possibly infer the presence of core-shell morphology, but the way the paper is written now, it is assumed from the get-go, that indeed this is the case, without leaving room doubt. I think at best the authors claim they believe it is core-shell morphology, or it should be clearly stated how they can definitively support this claim. I make suggestions below, of how such a claim could be inferred based on their ice nucleation results.

Specific comments and suggestions:

Line 49: Change “accordance” to “agreement”

Line 59: Oxalic acid can also act as an INP in the deposition mode [*Kanji et al.*, 2008]

Line 67: could add *Möhler et al.* [2008] here as a reference for homogeneous freezing of pure SOM

Line 68: could add references *Möhler et al.* [2008] and *Kanji et al.* [2019] as examples of studies that used the same SOM as proxies for organic particles and coatings

Line 106: it maybe more accurate to say, “ice nucleation active” or “not ice nucleation active”. Ice inactive is a little too colloquial and can have broader meaning.

Line 108: Delete comma after “humidity”

Line 121: consider using “ice nucleation active” instead of “ice-active”

Line 122-126: here the authors describe Experiment D and refer to it as also forming liquid droplets, then why not just call this process liquid cloud processing. This would be more consistent with the terminology used in Experiment E. It is after all a process where liquid drops are formed first, followed by evaporation. So liquid cloud processing would be more suitable. Afterall the only difference between D and E is the absence of ice cloud formation. See comments on Figure 1.

Line 176-177: Should read “The coating procedure in the APC chamber was performed at ambient temperature and low relative humidity and in the AIDA chamber at low temperature and ice saturated conditions.”

Line 183: Can the RH in the injection line be better quantified. For injection into AIDA 10% RH_w at room temperature could be very high for the cold temperatures conducted below 233 K. Thus, this could imply that the particles deliquesced upon entering the AIDA chamber. Please clarify this point in the manuscript.

Line 197: Delete the word “again”

Line 222-223 where the coating thicknesses are given, can the RH_w be given as well, to have an impression of the phase state of the SOM. The temperature is given in Table 1. Ideally the RH_w could also be included in Table 1.

Line 237-238: should read “In the backward direction, the polarization-resolved scatter light intensity is detected so that …”

Line 256: should read “The nucleated ice quickly grows to large crystals and…”

Lines 281-285: What is the temperature of the evaporation section set at. Is it set at the sample temperature, cold wall or warm wall temperature? This should be mentioned followed by the justification that the authors correctly address that the evaporation section will not influence the measurements in this study since it is conducted at cirrus conditions and any further ice nucleation in the evaporation section would require RH_i to be larger than 100% which is not the case in the evaporation section. However, in the case liquid drops form in the growth section and if the evaporation section is at the cold wall temperature, then the drops could freeze before evaporating. This should not be of issue in the current study because of the low temperatures investigated, but should be clarified in terms of how the INKA chamber operates.

Line 311: the core-shell morphology at this point is stated with certainty. How can this be verified? Either provide more evidence that this is indeed the case, or the authors can suggest at this point that “we believe it to be core-shell morphology”. See further below for how this can be inferred based on the arguments the authors already provide.

Line 314-315: the thicknesses are calculated assuming uniform/even coating. This should be added to the end of the sentence. E.g. “…thickness ***of*** 44 nm assuming an even/uniform coating”.

Line 332: replace “notified” with “noted”

Line 335-339: one may want to simply state that longer equilibration times are possible in the AIDA chamber compared to the CFDC, which is sort of stated, but not explicitly.

Lines 358-365: What is shown in Figure 6a, that cannot be deduced from Figure 6b. The time perhaps, but this doesn’t come up in any discussions or an anchor point for an argument. It looks like figure 6a is redundant and figure 6b nicely shows the point the authors are trying to make and with more clarity. I suggest removing Fig. 6a or make clearer what additionally it contributes to the discussion.

Line 368-369: The measurements definitely demonstrate the possibilities of combining CFDC with ageing experiments, but I don’t think the statement about combining AIDA with CFDC is needed as mentioned in this sentence. AIDA is a complex chamber with highly sophisticated instruments coupled to it and capabilities. For the experiments being proposed here a chamber that can be cooled to low enough temperatures can be used here coupled with a CFDC. i.e. this is in reference to the step wise coating experiments in Experiment C. A chamber as complex and sophisticated as AIDA would not be necessary.

Line 370 – 377: Could the authors also comment on the onset S_i in Fig 6c for experiment C1-C3 at the same organic coating % i.e. why is the onset S_i lower for the warmer T experiments than the colder T experiments at the same organic coating %? From ice nucleation perspective the ice germ should be smaller at colder T, so the onset for colder T should be at lower S_i or the same. Is it a diffusional growth limitation to when the OPC detects ice crystals or is it a limitation of diffusing water vapour into the organic coating? Some comment addressing the difference in onset S_i for the same organic coating percent as a function of temperature should be made here.

Line 421: should read “….with INKA at -54 °C immediately…”
Line 422: delete “at -54 °C”

Line 424: having the diffusion dryer upstream of the INKA instrument, could have modified the phase state of the organic from liquid to glassy, as such would it not be correct to state that INKA is already sampling glassy or phase separated aerosol since the LLPS occurs at RH_w < 90%.

Line 423-434: This argument presented here is quite interesting and can be exploited to support the authors' claim that core-shell morphology or complete coating was achieved in the thick coating experiments (B). The reason being that Experiment B completely suppressed the het. ice nucleation signal compared to that of pure AS in experiment A. Then coatings as thick as those in Experiment B but in Experiment D (liquid cloud processing) resulted in intermediate IN activity. As the authors point out that this must have resulted in changes in morphology allowing the initially thickly coated particles to become ice nucleation active after the liquid processing. This observation together with Experiment B and A would then more concretely support the core-shell morphology of the thick coatings. I think before this point, it is hard to lay claim to it so definitively without more concrete evidence.

Line 451: I think the authors should specify that they mean > 5% by coating mass when they say "even thin coatings" because below 5% there was ice nucleation activity below the homogeneous freezing threshold suggesting that coatings with mass % < 5% will not completely suppress the het. IN activity.

Line 456: why would the crystalline AS core not dissolve. It was not clear to me how immersion freezing by the crystalline core is being explained here. Shouldn't the AS core dissolve in water if it is immersed?

Line 461-462: Why would AS efflorescence be inhibited at low temperatures, can this be explained more clearly to make the connection to the point above this sentence.

Line 479: The authors should be careful in describing the freeze-drying process. After activation into drops and freezing, just completes the freezing part of the freeze drying, and then upon sublimation comes the drying part, as such saying that all aerosol particles underwent freeze-drying in line 479 is still too early. It is only after line 481 where the authors state "…thereby quickly sublimated" is when the freeze-drying process has been accomplished.

Line 499. Here one more discussion point could be added is the how cloud processing enhances ice nucleation of organic coated particles. This is not brought out explicitly enough. See major comment 1.

Line 505 and elsewhere where troposphere is mentioned. A mention that the SOM here may not be representative of tropospheric SOM is warranted because almost always photochemistry would play a role in the nature of SOM in the atmosphere, and here no UV source is mentioned in the production of SOM. This should be acknowledged somewhere in the manuscript. I suggest once in the methods where the SOM production is described and then again in the conclusion section.

Line 510-513: this part ignores the fact that coating mass % below 5% still yield het. ice nucleation active particles. This should be acknowledged here.

Line 527: should read “(i.e., ice nucleation ability between pure AS and AS with a compact…)”

Figures and Tables

Figure 1: Why is experiment D not called liquid cloud processing, to be consistent with Experiment E which can be called cold cloud or ice cloud processing. The only difference between the two is freezing followed by sublimation vs. droplet activation followed by evaporation. Alternatively, D could be called liquid cloud processing and E could be called cloud processing since E involves both liquid and ice. I would consider making the labelling more consistent. Even in the figure caption the authors state in the last line that E involves droplet activation thus it demonstrates the similarity between D and E (thus I would suggest both be part of a cloud processing label).

In the figure caption “upper tropospheric conditions” is mentioned, but I think to be more specific the authors should say upper tropospheric temperature, since photolysis is not part of this work, or UV is not been simulated in this study which would be part of UT conditions.

Table 1: O_3 concentration can be changed to ppm and scientific notation removed and all numbers harmonised in terms of how many significant digits are given. Significant digits can also be harmonised for all experiments of α-pinene concentrations.

Figure 3. Would be helpful for reading if more than 3 ticks are added to the x-axis of panels a and b. i.e. every 0.1 μm and also add the scale on the x-axis of panel a.

Figure 5: panel a, either label all experiments as Exp A/B1/B2 or then AS, AS/SOM thick coating etc. but currently it is switched from AS then EXP B1/B2. Choose one style to be consistent.

Panel b. the contrast between the literature results in red and the orange data from the current study isn’t that great. Also, the distinction between the green from the current study and literature is not that clear either. To make this clearer, I would suggest keeping the data from this study in black since AIDA and INKA are already shape differentiated. This will make it very clear to a viewer of where and how the data from this study compare to the literature.

Figure 6: As mentioned in the text above, the purpose of panel a is not clear to me. It could be removed. Also, in the text of the manuscript one could describe that experiment C nicely shows that gradually increasing the coating thickness progressively suppresses the IN activity. So far it is discussed as though this happens as a step function at 5%, but the experiments nicely show that this is a gradual process of S_i increasing with organic mass fraction.

Figure 7. One could consider another panel, where the activation curves for Exp A1, and 3 mass fractions of C2 and B1 are plotted, to show the progressive nature and that experiments with coatings larger than 5% yield the same result as that of ~30%.

Figure 8. what are the different blue coloured dots in panel b? This is not described in the caption. Also, the green curve crossing the yellow curve in panel D is not discussed or addressed anywhere in the text. This crossing suggests that at a certain saturation the thickly coated particles are more active than the cloud processed particles (even if it is in the homogeneous freezing regime).

References

Kanji, Z. A., O. Florea, and J. P. D. Abbatt (2008), Ice formation via deposition nucleation on mineral dust and organics: dependence of onset relative humidity on total particulate surface area, *Env. Res. Lett.*, *3*(2), doi:10.1088/1748-9326/3/2/025004.

Kanji, Z. A., R. C. Sullivan, M. Niemand, P. J. DeMott, A. J. Prenni, C. Chou, H. Saathoff, and O. Möhler (2019), Heterogeneous ice nucleation properties of natural desert dust particles coated with a surrogate of secondary organic aerosol, *Atmos. Chem. Phys.*, *19*(7), 5091-5110, doi:10.5194/acp-19-5091-2019.

Möhler, O., S. Benz, H. Saathoff, M. Schnaiter, R. Wagner, J. Schneider, S. Walter, V. Ebert, and S. Wagner (2008), The effect of organic coating on the heterogeneous ice nucleation efficiency of mineral dust aerosols, *Env. Res. Lett*, *3*(2), 025007, doi:10.1088/1748-9326/3/2/025007.