Author Response

RC1 Review of "Ice Nucleating Properties of Glassy Organic and Organosulfate Aerosol" by Christopher Rapp et al., 2024

Anonymous Referee #1, 22 Jan 2025

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RC1: Rapp et al. performed a series of ice nucleation measurements in the cirrus temperature regime for a class of proxy components for organosulfates, which contribute to the atmospheric load of (secondary) organic aerosol particles and may play a role in heterogeneous ice formation. The measurements were carried out using the SPIN continuous flow diffusion chamber (CFDC) and involved pre-conditioning the generated aerosol particles in a custom-built pre-cooling unit to promote their transition to a glassy phase state. Control experiments with ammonium sulfate and ammonium bisulfate particles were used to train a model that uses backscatter measurements to classify the particles as aerosol, water uptake, cloud droplets, and ice. The suitability of the setup to detect a heterogeneous freezing mode was demonstrated by further control experiments with citric acid. Furthermore, a kinetic multi-layer model was used to estimate the timescales for partial and full deliquescence of the particles at SPIN T and RH conditions. I favor the publication of the results in ACP because the manuscript presents new ice nucleation data for proxy components of a potentially relevant type of organic aerosol particles, and because a number of experimental parameters that are crucial for performing such ice nucleation measurements with a CFDC are critically discussed and also useful for the community. However, there are several places in the manuscript where I could not follow or understand the authors' line of thought, and these will need to be addressed in a careful revision.

The authors thank RC1 for their time reviewing our manuscript, providing feedback, and supporting publication. We have performed a careful revision to address all major and minor comments.

Point-by-point responses can be found below in red along with further discussion/commentary when relevant. Substantial changes made to the manuscript in response to review comments are quoted in red and italic.

We also would like to explicitly mention to RC1 that minor changes were performed such as punctuation, grammar, and formatting that were also identified in our careful revision. This includes formatting some references to meet ACP guidelines (titles missing subscripts, missing DOIs, journal titles not abbreviated, etc.). Modifications to citations or references is strictly limited to formatting (no insertions or deletions), except in cases where it is discussed in the scope of a comment response.

General comments:

1) In the introduction and throughout the manuscript there are a number of notations used to refer to organic aerosol, e.g. OA, SOA, pure OA, which in my opinion are not always used accurately. For example, in line 54 the authors refer to studies with "certain pure OA" - what do you mean by "pure" here - the studies cited mostly refer to secondary organic aerosol particles. Also, the recommendation by Kasparoglu et al. (2022) mentioned in line 58 refers specifically to "complex secondary organic matter (SOM)" and "dust coated with SOM", but not to "pure and mixed OA" in general as stated in lines 58/59. OA in general could also include crystallizable organic compounds already identified as active in heterogeneous ice formation, such as oxalic acid. The world of OA is therefore a complex zoo of compounds involving crystalline and amorphous solid states - certainly difficult to summarize and do justice to in a short paper introduction, but I think the authors could be a bit more careful in their notation in some places.

The authors appreciate this feedback and have examined all instances where OA, SOA, or another combination were used. We agree with the reviewer that SOA and OA lack a full description of the material. In our reference to (Kasparoglu et al., 2022), we want to remain consistent with the overall literature and will replace pure and mixed OA with "SOA and SOA-coated dust".

We have since opted to use the following nomenclature to maintain consistency:

- SOA for any aerosol originating from oxidized gas-phase precursors
- Proxy SOA (e.g., citric acid/MBTCA or other compounds used to simulate atmospheric SOA)
- Proxy SOA constituents (simple organosulfates (OSs), such methyl, ethyl and dodecyl sulfates analyzed in this study).

Changes to match this nomenclature were made throughout the manuscript and supplement accordingly.

2) Line 61ff, reference to Froyd et al. (2010): If I recall correctly, one hypothesis in that paper was that the sulfate component in the particles could be completely neutralized by ammonia, leading to a situation/particle morphology that was later investigated by Schill et al. (2014) and Schill and Tolbert (2013) - see lines 77/78 in the introduction, where crystalline ammonium sulfate could be embedded in an aqueous organic solution and be the actual ice nucleating entity in these particles. It may be useful to point out this potential connection between these studies.

We have included commentary on the neutralization of sulfate found in subvisible cirrus ice residuals (Froyd et al., 2010). This includes the proposed particle morphology where crystalline ammonium sulfate initiates ice formation. This also includes some discussion of investigations in the context of ice initiated by submerged sulfate cores in aqueous organic layers or by the glassy surface alone. (Schill et al., 2014; Schill and Tolbert, 2013). An additional reference for single particle measurements of organic containing IRs during the CRYSTAL-FACE study (Cziczo et al., 2004) was added to strengthen this argument.

3) Line 69ff, deposition nucleation vs. pore-condensational freezing (PCF), also lines 451-453 in Sect. 5.2: Do the authors really assume that atmospheric freeze-drying took place in their PCU unit, a very complex sequence of events involving droplet activation, freezing, and subsequent sublimation of ice? I cannot really see this happening, especially in the very dry conditions of thermal generation of citric acid aerosol. The sentence in line 451, as it is currently worded, suggests that atmospheric freeze-drying is a mechanism for inducing a glassy phase state, whereas I would rather describe it as a process for changing the morphology of glassy particles from a compact to a porous form. In my opinion, atmospheric freeze-drying is not a prerequisite for the glassy aerosol to become active in heterogeneous ice formation. Why can the solidified, glassy surface itself not provide sites for the "classical" deposition ice nucleation pathway to occur? For example, this was certainly the most likely explanation for the heterogeneous ice nucleation mode of citric acid aerosol observed in the Murray et al. (2010) experiments, which did not involve atmospheric freeze-drying. Of course, atmospheric freeze-drying could be an opportunity to increase the heterogeneous ice nucleation capability by enabling a new ice nucleation mode due to the structural change of the particles, namely PCF. So please check and revise the description of these processes in the manuscript.

We thank the reviewer for this comment and in combination with recommendations from RC2 we have removed references of atmospheric freeze drying as a process occurring in the PCU in L451-453 as well as L437. Physical process that the PCU is applying to particles is now simply referred to a phase transition from liquid to glassy aerosol. Mentions of freeze-drying as a mechanism to enhance ice nucleating properties of SOA is now limited to the introduction.

4) Fig. 2 and related discussion: You discuss the results for ABS in terms of homogeneous freezing (line 295), which seems reasonable given that ABS droplets are difficult to crystallize and any crystals formed would have a low deliquescence RH. However, in Fig. 2b, the ice nucleation onset at -40 and -45°C appears to be well below Sice = 1.4; in Table S2, there is even one experiment that gives an onset Sice of only 1.31 for -45°C. Are these differences compared to the homogeneous freezing lines depicted in Fig. 2b, which are much higher, still within the experimental uncertainty (in older SPIN-related studies like Wolf et al. (2000) or Li et al. (2024) (https://doi.org/10.1021/acs.est.4c06285) smaller uncertainties for RHice are given), or how do you interpret the results?

Experiments conducted with ABS revealed difficulty in obtaining an ice saturation onset coinciding with expected homogeneous ice nucleation onset. Further measurements using the same solution of ABS several months later showed the onset moved toward lower ice supersaturations (data point referenced in Table S2) and more closely resembled

AS. We have renamed these experiments from ABS to “ABS, aged” to distinguish between these experiments. We attribute this shift as neutralization of the ABS (Abbatt et al., 2006; Cziczo and Abbatt, 2001) in combination with measurement uncertainty within the SPIN. As ABS is converted to AS, any crystalline AS will skew onsets to the left. Regardless, we showed no activation of ABS for -35°C, a feature that should be exclusive to AS.

In accordance with the above, we have added the following statement in 2.7.2 to briefly note this and refer readers to the results:

“Unlike AS, ABS did not show ice formation below temperatures necessary for homogeneous freezing (i.e., -35 °C, see Sect. 3.1.1).”

where we have included the following:

“Ice activation onsets for ABS occurred at S_{ice} lower than the expected homogeneous freezing thresholds (see Fig. 2) due to a combination of measurement uncertainty in S_{ice} and neutralization of ABS to AS (Abbatt et al., 2006). This neutralization effect is particularly noticeable for post-calibration ABS measurements (see Table S2) where “aged” (sampled several months later) ABS resembled the ice onset conditions for crystalline AS.”

I also had some problems understanding the data in Fig. 2 at first - the colored lines (curve-fitting data) are perhaps a bit misleading, as they suggest at first glance that for the AS experiments, for example, we have a transition from aerosol to droplets to ice. But if I understand correctly, only ice forms directly on the aerosol by deposition nucleation. How are the colored lines actually calculated? How do I interpret the fact that, for example, at ice saturation ratios of about 1.25 - 1.30, these lines indicate a depolarization ratio of about 0.2 - 0.3? Is this an average for the whole aerosol population, i.e. aerosols with low and ice crystals with high depolarization ratios, or are there also smaller ice crystals at the beginning of the nucleation process that have a lower depolarization ratio? I appreciate the inclusion of some basic SPIN measurement data, but a slightly more detailed description would be warranted.

We thank RC1 for this feedback and have opted to remove the smoothing lines. They were added initially to show the average onset of either droplets or ice activation within the SPIN but as suggested are a bit misleading as currently implemented. We have additionally restricted the shaded region for droplets to better reflect Table S1 and improved shading/labeling within the figure.

5) Line 382/383, Fig. 4: I felt a bit “left alone” with Fig. 4. It contains a long figure caption, but I would expect a bit more detail also in the manuscript text about what the authors want to show with the depicted data. There are two orange lines for full liquefaction – are these representative for the uncertainty of the relevant citric acid parameters (like glass transition temperature, water diffusivity) in the model calculations? And why only citric acid but not dodecyl-OS shows timescales favorable for being able to observe heterogeneous ice nucleation within SPIN?

We have replaced the text proceeding Fig. 4 with the following:

“Among the compounds evaluated, only citric acid exhibits liquefaction timescales favorable for ice nucleation within the SPIN, as evident from a comparison of simulated liquefaction timescales and measured ice onsets of citric acid in Fig 4. The lowest temperature and humidity at which ice nucleation was observed for anhydrous citric acid (-45 °C, S_{ice} = 1.23) coincides with the point at which the model suggests partial liquefaction to occur (dashed line in Fig. 4). The highest temperature and humidity at which ice nucleation was observed for anhydrous citric acid (-40 °C, S_{ice} = 1.26) is at or near the point for which the model suggests full liquefaction to occur, depending on the assumed characteristic nucleation time of 1 s (Fig. 4a) or 0.1 s (Fig. 4b). We interpret such ice activation onsets between partial and full liquefaction conditions as immersion freezing. Dodecyl sulfate did not show significant water uptake at the temperatures and humidities for which ice nucleation could be expected, while methyl and ethyl sulfates equilibrated rapidly with the humidity in the SPIN, irrespective of temperature.”

In addition to the changes above, we named the ice nucleation boundaries (previously only listed as 1, 2, 3) with their expected freezing mechanisms in bold font to emphasize the relevance of these results. This is proceeded by an insertion of the necessary reference (Berkemeier et al., 2014).

Regarding the second question of this comment: while dodecyl sulfate does have timescales favorable to heterogeneous ice nucleation within SPIN, there was no measured ice nucleation for model comparison. In the model simulations, dodecyl-OS did not show an onset for water uptake due to its high glass transition temperature (and hence low water diffusivity coefficients in our parameterization). Thus, we would expect that dodecyl-OS can only nucleate ice in the deposition mode in our experiments. However, in the experiments presented in this study, we do not find evidence for this deposition freezing. Notably, this is also the case for citric acid at low temperatures for which the model does not predict significant water uptake and the experiments do not show ice nucleation.

The changes above also necessitated minor modifications to the Fig. 4 caption to reflect the above:

"Magenta colored line indicates the modeled partial liquefaction timescale where particle volume has increased by more than 5 % due to water uptake" now reads "*Magenta colored line indicates the modeled partial liquefaction timescale (10 s characteristic residence time of the SPIN) where particle volume has increased by more than 5 % due to water uptake."*

6) Line 437: Here is again the idea of the atmospheric freeze-drying process, but in which step of your setup did you want to simulate this?

See response to major comment 3.

7) Line 447/448: I don't quite understand the logic here; if droplets are smaller than a certain size threshold for ice, then they could be distinguished from ice by size alone. It is again mentioned in line 530/531: Characterizing water uptake and droplet formation is of course very useful, but how does this interfere with the selective counting of larger ice crystals?

The authors thank the reviewer for this comment and indeed the logic here is confusing as currently presented. We have replaced the sentence *"Particles activated as droplets at sizes smaller than the 2.5 μm size threshold, requiring scattering profiles to distinguish droplets from ice as size alone would have been insufficient"* with the following *"Particles that activated as droplets in the SPIN exited the evaporation section with diameters ≥ 2.5 μm, a size threshold frequently used to distinguish ice from droplets. We emphasize that using a traditional size cutoff was not a reliable method classify ice in these SPIN measurements."*

The original intention was to discuss that droplets were frequently detected larger than the 2.5 μm diameter but smaller was mistakenly used instead of larger. We also correspondingly corrected the sentence in L530/531:

"We classified water uptake and/or droplet formation for particles as small as 1.5 μm in diameter, noticeably smaller than size thresholds attributed to ice in previous studies." This now reads: *"Particles classified as droplets frequently exceeded the 2.5 μm size threshold, demonstrating a nominal size cutoff as being unreliable in quantifying the ice nucleating properties of SOA."*

Minor comments/technical corrections:

1) Line 18: Better: "… and ice saturation ratios"

Changed ice supersaturations to ice saturation ratios as suggested

2) Eq. (1), left side, add subscript "org" to indicate the organic mass fraction

Added subscript

3) Line 169: "radius of 0.225" – Table 1 suggests that this is the particle diameter

Changed radius to diameter as originally intended

4) Line 201: Please indicate whether the size is radius or diameter.

Added diameter to clarify

5) Line 208: section 2.5

Modified to the correct section number 2.5 "…sampled due to size selecting irregularities (see section 2.5)."

6) Line 238: Maybe: "… using a microcontroller board (Arduino Mega) …"

Changed as suggested.

7) Line 252: Wegener

Corrected spelling from Wegner to Wegener

8) Eq. (4): Please also indicate the scattering angle for the detectors. Shouldn't P1 and P2 be the same quantity, just measured by two different detectors (but at the same scattering angle, see Garimella et al., 2016)? Why did you use the sum of P1 and P2 in this equation?

We have included the scattering angle and half angle for the detector optics: *"Backscattering optics for both S and P components have a detection angle of 135° and a half angle of 20°."*

Initially, we used the sum of the two parameters because the resulting ratio was between 0 and 1 with virtually no outliers or scaling needed. The previous $\log_{10}(S_1/P_1)$ method did not explain the variance of scattering data as much as a ratio including P_2.

With this feedback we have redefined this ratio using the average of the S and P components. This results in the expected perpendicular polarization intensity divided by the parallel polarization intensity. We then normalized this value to 0 and 1. We were able to retain all empirical classification parameters (Table S1) as introduced in 2.7.2 for this new ratio by using a slight scaling factor to account for outliers.

9) Line 336: Sect. 2.7.2

Corrected section reference from 2.8.2 to 2.7.2

10) Fig. 3: Please label the central panel as "Droplet Breakthrough"

Renamed the central panel to "Droplet Breakthrough"

11) Line 358: "of various liquid saturation ratios."

Modified captions in Figure 3 and 4 so that "…lines of various liquid saturation" now reads "…lines of various liquid saturation ratios".

12) Sect. 3.2: Please include also here a reference to Table S2 for the collected results of the organosulfate proxies.

Added "(see Table S2 for compilation of OS proxy results)" to the third sentence of 3.2 so readers are referred to the table for a compete collection of results

13) Please check the sentence in line 404, I do not really understand it.

Removed this sentence as it was an incomplete reference to increases of uncertainty in RH with decreasing temperature which is addressed in the following sentence about calibration using ultra high purity nitrogen.

We additionally replaced *"Method Section"* for uncertainty in T_g calculations with *"procedure described in Section 2.2"* two sentences proceeding the deletion of the sentence above.

14) Line 444: "crystalline" ABS: Are you sure that the particles have crystallized temporarily?

Removed the incorrect reference of crystalline ABS as that was only possible for the AS experiments.

15) Line 533ff: Here is again a mixture of OA and SOA nomenclature, see my first general comment.

Changes have been made accordingly in combination with first general comment.

References

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