SUMMARY

This manuscript has examined the heterogeneous ice nucleation properties of biogenic secondary organic aerosol (SOA), made from the ozonolysis of α-pinene. These experiments were conducted in the Cosmics Leaving Outdoor Droplets (CLOUD) chamber at CERN during the CLOUD9 campaign. Specifically, a commercial, parallel-plate continuous flow diffusion chamber, the SPectrometer for Ice Nuclei (SPIN) from Droplet Measurement Technologies, was utilized to determine depositional freezing of α-pinene SOA at approximately -38 °C. To determine the phase state of the particles, a newly developed technique that determines the transition of the shape of a particle from oblate to spherical was utilized and presented in a companion paper (Järvinen et al., 2015).

The SPIN was first validated by determining the homogeneous freezing conditions of ammonium sulfate particles at approximately -38 °C. For the heterogeneous ice nucleation chamber experiments, the authors found that highly viscous semi-solid α-pinene SOA was an "efficient" depositional ice nucleus, based on maximum frozen fractions (6-20%). Ice nucleation measurements were accompanied with a scanning mobility particle sizing (SMPS) and an Ultra High Sensitivity Aerosol Spectrometer (UHSAS) to determine aerosol size up to 1 μm, as well as the aforementioned depolarization measurement to determine particle sphericity. From the data, the authors interpreted that this α-pinene SOA had nucleated ice below water saturation/the homogeneous freezing threshold and, therefore, was nucleating ice depositionally. The authors then used the generic SOA glass transition conditions found in Koop et al., (2011) in conjunction with the GLObal Model of Aerosol Processes (GLOMAP) to conclude that highly viscous biogenic SOA may exist at altitudes relevant to cold-cloud formation.

This well-written manuscript that directly addresses an understudied topic (highly vicious organic aerosol) in a field with many outstanding questions (cold-cloud ice nucleation). I do, however, have several major comments regarding the instrument calibration and data interpretation; these concerns are outlined by section in the general comments section. Specific comments, which are of less concern, have also been outlined in their own section.

GENERAL COMMENTS

Ice Nucleation Measurements:

As the first publication for this instrument from this group, this manuscript would benefit from more detailed descriptions of instrumental calibrations; most notably missing are an explicit description of the optical particle counter (OPC) calibration as well as a description of the instrument backgrounds. While the former omission, the OPC calibration, was partially described in the experimental section, more details are needed e.g., how many sizes of glass beads and what assumptions/analysis was conducted to get the full size distributions in the upper right panels of Figures 1 and 3. As for the latter, it seems qualitatively clear that signal is above the background in the upper right panels of Figures 1 and 3, but establishing background counts will be crucial to correctly quantifying frozen fractions and outline the frozen fraction limit of detection.

Instrument Performance Validation by Homogeneous Freezing of Highly Diluted Ammonium Sulphate Droplets:

Taking a closer look at Figure 1, it looks like the transition from regime A to regime B occurs at 97% RH, which corresponds to an ice saturation ratio (S_{ice}) of 1.38. This is lower than the value reported for homogeneous freezing, likely because the authors have chosen a 10% activated fraction as their onset conditions for homogeneous freezing of ammonium sulfate. Given the onset conditions of the α-pinene SOA were at 1%, would not a 1% activated fraction for homogeneous freezing be a better comparison? This choice may have large implications for the results of the paper and should be addressed by the authors. For example, if 1% activated fraction for homogeneous freezing does indeed occur at an S_{ice} of 1.38, then those homogeneous freezing points would overlap with the points that the authors consider to be heterogeneous freezing for their viscous α-pinene SOA. To add clarity to this discussion, the authors may also choose to show a frozen fraction vs. S_{ice} plot as a supplemental figure; in doing so, the authors will increase the manuscript's transparency by allowing the reader to compare the maximum activated fractions from heterogeneous nucleation to those activated fractions seen in homogeneous freezing.

Size Distributions:

The authors mention that they first show "size distributions in order to distinguish depositional nucleation from homogeneous freezing;" however, no explicit description of how the size distributions facilitate this was explained. To the reviewer, the size distribution B in both Figure 1 and 3 do look qualitatively different, but I am not sure how that correlates to depositional vs. homogeneous freezing. In the reviewer's opinion, an explicit explanation of this differentiation and all underlying assumptions would greatly increase the clarity provide further transparency to the results section.

The authors also mentioned in this section testing for "droplet breakthrough," or that RH where a fraction of the formed liquid droplets survive the evaporation region; from size distribution C in Figure 1 it looks like droplet breakthrough may happen at relatively low supersaturations. Do the authors have any quantitative numbers for droplet breakthrough RH at the temperatures explored? Additionally, it appears from the upper right panel of Figure 3 that, when droplet breakthrough occurs (regime C), the authors also seen a large suppression of homogeneous freezing despite being at -36.8 °C and above water saturation. The reviewer suggests the authors address this behavior to increase the utility of the paper.

Ice nucleation onset conditions for viscous SOA:

The error bars here are represented by the statistical standard deviation (1.96σ) between measured points. While the reviewer appreciates the authors providing this metric as it indicates that the ice nucleation onsets are reproducible between experiments and/or the aerosol is physio-chemically similar between experiments, the reviewer would argue that this does not necessarily conclude that these points are statistically different from homogeneous nucleation. The authors are comparing experimentally derived ice nucleation points to water saturation derived from a parameterization. This analysis ignores the instrumental uncertainties associated with the SPIN. The authors mention throughout the text the temperature uncertainty (± 0.4 K); however an

associated RH/S_{ice} error has not been explicitly addressed for the heterogeneous nucleation points. Interestingly, the authors did provide a maximum S_{ice} error for the α-pinene SOA homogeneous freezing point and it was +0.13/-0.11. Similar-sized instrumental uncertainties for the heterogeneous freezing regime would clearly put at least 1% of the aerosol into homogeneous freezing conditions. The authors should explain, in detail, how their instrumental uncertainties factor into how they differentiate homogeneous and heterogeneous freezing.

SPECIFIC COMMENTS

Page 35721, line 18: Delete "(IN)," this abbreviation is unnecessary here

Page 35722, line 2: Delete "e.g.," this is unnecessary here

Page 35722, line 5: Change "and contributes" to "and can contribute"

Page 35722, line 7: Given the references, did the authors mean "cold-cloud" instead of "mixed-phase cloud?"

Page 35724, line 26: Please give a brief description of why aspherical here means viscous as this does not make sense out of context of (Järvinen et al., 2015)

Page 35725, line 3: If 80% RH is the transition RH_w for this α-pinene SOA, the authors may consider to re-define their freezing mode as immersion-mode freezing as per (Berkemeier et al., 2014)

Page 35726, line 29: If the absolute concentration is always under 1000 cm^{-3}, what is the frozen fraction limit of detection?

Page 35729, line 9: While interesting, I am not sure why the authors report the freezing depression for 200 nm particles as 500 nm particles were used in this study

Page 35730, line 6: Change "Analogously" to "Analogous"

REFERENCES

Berkemeier, T., Shiraiwa, M., Pöschl, U. and Koop, T.: Competition between water uptake and ice nucleation by glassy organic aerosol particles, Atmos. Chem. Phys., 14(22), 12513–12531, doi:10.5194/acp-14-12513-2014, 2014.

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Koop, T., Bookhold, J., Shiraiwa, M. and Pöschl, U.: Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere, Phys. Chem. Chem. Phys., 13(43), 19238, doi:10.1039/c1cp22617g, 2011.