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Interactive comment on “State transformations and ice nucleation in glassy or (semi-)solid amorphous organic aerosol” by K. J. Baustian et al.

Anonymous Referee #1

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This manuscript describes an experimental study investigating the water uptake and ice nucleation ability of aqueous organic and inorganic/organic particles in various amorphous phases such as semi-solid and glassy states. Sucrose, citric acid, and glucose species were employed as surrogates for atmospheric secondary organic aerosol (SOA) and ammonium sulfate as inorganic material. Raman spectroscopy was applied to determine respective glass transition points and optical microscopy for detection of ice nucleation. Glass transition points as a function of relative humidity (RH) and temperature (T) were determined and ice nucleation onsets as a function of ice supersaturation, S_{ice} . It is found that amorphous organic particles nucleate ice for S_{ice} between 1.1–1.4 for 235–200 K. Addition of ammonium sulfate to the organic particles

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causes the particles to remain liquid over a greater temperature range and resulted in ice nucleation onsets of $S_{ice} = 1.25\text{--}1.48$. The glass transition curves are implemented in the Community Aerosol Radiation Model for Atmospheres (CARMA) to estimate the fraction of glassy aerosol in the middle upper troposphere and tropical tropopause region.

Overall this manuscript reads well and the topic fits nicely within ACP. The experiments are based on previously established methods and setups. In this regard I have no reservation to recommend the manuscript for publication. However, I have some comments regarding the data analysis, interpretation and model application which need to be addressed before the manuscript can be recommended for publication.

Throughout the manuscript more care should be taken in regard to the definition of the particle phase states. For example an amorphous particle can be liquid, semi-solid, or glassy. So “glassy or amorphous (semi-)solid organic particles” is an incorrect expression. What are aqueous organic glass particles? Within the glassy matrix some water molecules will be incorporated, however, it is doubtful to define this particle as aqueous in the common sense. It may be better to write glassy organic or glassy organic/water particle. There are many of these types of ambiguous/incorrect definitions which should be corrected (e.g. “as highly viscous (semi-) solids in amorphous or glassy states”).

A major point of discussion which is lacking in this manuscript is in regard to particle size, viscosity, and time scales to achieve water diffusion throughout the particle (Shiraiwa et al., 2011). These parameters are crucial when comparing experimental results with other studies and for application in models. Furthermore, it should be emphasized that the glass transition curve does not represent a phase transition curve but will depend on the rate of change in RH and T. Experiments applying different conditions may obtain different glass transition points. The atmospheric time scales with respect to changes in RH and T might be different again. For example the size of the citric acid particles employed by Murray et al. is 150 nm whereas the particles here are

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up to 10 μm in diameter. Looking at Koop et al. the mixing time scale τ (which leads to liquefaction/deliquescence of the particle) at around 220 K differs by an hour to a year for smaller and larger particles. So, one would not necessarily assume to obtain the same results for water uptake and/or ice nucleation onsets. The Murray et al. study uses much faster cooling rates at cirrus conditions compared to this study. Maybe the different experimental conditions may result by chance in similar results. Clearly more discussion is needed regarding these points. Having said this, I am not sure how meaningful the modeling results are since dynamics, i.e. convection and diffusion time scales, governed by particle size are not considered. Here, only if T is below or above T_g , determined from particles 1–2 orders of magnitude larger than in the atmosphere, the glassy or liquid state, respectively, is inferred. Smaller atmospheric particles will need less time to transform from a glassy to liquid state. As is, the model may be biased towards solid particles? In general this application needs more explanation and maybe elaboration of the model.

I think Saukko et al. deserves more reference in the introduction since they investigated how addition of sulfates to organic aerosol affects T_g . Also, the study by Wang et al. which shows derived T_g from complex “real” SOA particles (no single component surrogates) and ice nucleation onsets deserves more reference since the other studies mostly investigate simpler particle system. It seems that the Wang et al. T_g is on the upper end of the estimated range by Koop et al.

Derivation of glass transition curves. As outlined by Koop et al. there have been physical/semi-empirical descriptions of T_g . Those are employed in many different fields rather successfully and form the base for the Koop et al. T_g estimation. It seems also to work for the SOA particles studied by Wang et al. So, why are the T_g curves here just described by a polynomial fit fixed at RH = 100 and 0%? The extrapolation of these fits beyond the data may not be correct. Would the Gordon-Taylor description of T_g predict similarly lower T_g when adding ammonium sulfate?

Specific comments:

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p. 27337, l. 7–10: You could mention a new study by Shiraiwa et al. (2012) who looked at chemical aging of glassy levoglucosan by NO_3 .

p. 27337, l. 20: Deposition ice nucleation occurs from the supersaturated vapor phase.

p. 27337, l. 22: Immersion freezing occurs from a supercooled aqueous droplet.

p. 27337, l. 23: Contact freezing occurs from a collision of an ice nucleus with a supercooled aqueous droplet.

p. 27338, l. 20: Here but also for the remainder of the manuscript (see below) what is meant by “fraction of time”? I assume it is meant the fraction of all particles which are solid? I don’t see a “time dependence” in this analysis. I feel this is an unfortunate expression and should be exchanged in text and figures and more clearly defined.

p. 27339, l. 24: How do you know that “Water uptake by a glassy or amorphous (semi-)solid substance generally requires higher RH at colder temperatures”? Mikhailov et al., 2009 did not study deliquescence as a function of temperature as far as I recall.

p. 27339, l. 27: How do you know that “If supersaturation (with respect to ice) is reached before the RH necessary for water uptake, depositional ice nucleation will be observed.” If the particle is not a good ice nucleus than ice nucleation may not occur. This statement is too general.

p. 27342, l. 2: Define “ VP_{ice} ”.

p. 27343, section 3.1: I suggest to show an additional figure of the spectral subtraction since the actual figures do not readily indicate substantial changes due to a phase transition. Also, how is the subtraction performed? Is the raw data subtracted or do you perform a background correction and actually fit the peaks and then subtract the fitted peaks?

p. 27345, l. 2–3: Semi-solid is not glassy. Thus liquid and semi-solid should be left of the T_g curve and glassy to the right.

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p. 27345, l. 5–8: However, water uptake/ice nucleation is determined at temperatures much lower than “ambient temperature”. I assume this means about room temperature? At lower temperatures the diffusion coefficient for water in a glassy matrix significantly decreases (Koop et al. 2011).

p. 27345, l. 27: What does it mean that the Zobrist et al. data is “shifted slightly”? This and the following discussion may refer to different particle sizes or RH rates as mentioned above.

p. 27346, section 3.4: I feel that the study by Saukko et al. could be included in this discussion. Here only a 1:1 organic to inorganic mixture was studied. However Saukko et al. determined particle phase states for different ratios. Can it be expected that for less ammonium sulfate the particles exhibit a higher T_g ?

p. 27348, l. 24–26: Wang et al. determined the phase state at room temperature and RH smaller than 50% to be semi-solid. However, at deposition ice nucleation temperatures the particles are solid. “proposed to be glassy” should be changed to “solid/glassy naphthalene SOA”.

p. 27348, last paragraph: How can ice nucleation and water uptake be observed simultaneously? This is only possible if immersion freezing occurred. If at a certain RH one particle took up water and another one not, this would imply that the composition of both particles is different. An explanation should be given for this.

p. 27351, chapter 4: See general comments above on model application. Why was a trajectory of 90 days chosen? The mean residence time of aerosol particles is much shorter. It would be much more meaningful knowing if the particles transform within 1–2 weeks.

p. 27354, l. 6: Only one ice nucleation pathway was discussed in this manuscript, i.e. deposition ice nucleation. The amorphous phase will also dictate water uptake.

Figures 3–5: For which particle size has the Koop et al. parameterization been em-

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ployed?

Technical correction:

p. 27343, l. 15: Omit “dramatic”.

p. 27343, l. 19: Omit “exact”.

p. 27343, l. 21: I suggest “up” instead of “on”.

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