

Reply to Referee 2:

We would like to thank the reviewer for her/his comments, which helped to greatly improve the manuscript!

Please find our replies to the comments (which are typeset in bold) below:

**The manuscript by Frey and co-workers investigates the ice nucleation ability of secondary organic aerosol (SOA) particles under so-called mixed-phase cloud conditions. SOA particles have been found to nucleate ice under so-called cold cloud conditions found at high atmospheric altitudes, an ability which is often ascribed to their glassy solid phase state, but their ability for cloud formation at much higher temperatures /lower altitudes has not yet been proven. This work is well-written and addresses this very relevant problem by connecting an aerosol formation vessel (Manchester Aerosol Chamber, MAC) and a vessel for probing the ice nucleation ability of particles (Manchester Ice Cloud Chamber, MICC) in an innovative experimental setup. The authors tested an array of different SOA particles by using three different precursors: one from biogenic and two from anthropogenic origin, making the work relevant for the ambient atmosphere and hence publication in ACP. The main result of this work is that none of the investigated organic aerosols facilitated ice nucleation in the observed temperature and RH region. Such negative results are important to direct future works on the relevance of these particles for cloud formation. However, in my understanding, there was no possibility that ice nucleation should be observed due to the way the experiments were operated. This greatly diminishes the value of this publication and might disincentivize further research on the topic if it won't be stressed clearly by the authors why ice nucleation did not occur. I would like to outline my thoughts in the following and already encourage the author's to disagree with me in their rebuttal in case I misunderstood the experimental setup. At this point, however, I cannot recommend the manuscript for publication.**

The reviewer stresses a very important point and we are confident that we will be able to convince the reviewer to support the publication of our manuscript.

Generally, we tried to follow an experimental path that is as closely aligned with processes in nature as possible: The generation of SOA was performed at conditions which are close to realistic conditions in the lower boundary layer, where precursor gases for SOA formation are emitted (i.e. room temperature and relative humidities wrt water of 45-50%). Previous studies often did not follow such a realistic path, generating SOA at below 10% humidity, some even down to almost 0% humidity (e.g. Prenni et al., 2009, Baustian et al., 2013, Wagner et al., 2017). From ground the aerosol is lifted to regions, where mixed-phase clouds potentially form, implicating cooling of the aerosol and changes in humidity. The transfer of the aerosol in our experiments from the aerosol to the cloud chamber and the subsequent cooling of the transferred air including the aerosol could be seen to mimic those conditions. Then, first a water cloud is formed (therefore, water saturation is needed) from which ice nucleation could take place to form a mixed-phase cloud. This is achieved by quasi-adiabatically cooling of the chamber by performing a chamber expansion.

The modelling study by Shiraiwa et al., 2017 suggests that SOA already is in a semi-solid state over the mid-latitudes and semi-arid regions as Europe, India, Australia, Mexico, and western US. Going up to higher altitudes, the particle phase state becomes more frequently solid or semi-solid. According to Shiraiwa et al. almost all SOA will be solid at 500hPa, corresponding to about 5.5km or roughly -20°C (according to standard atmosphere). And -20°C is the starting temperature of our experiments. They mention convective uplifting of the air in their model, however, whether the RH follows a similar trajectory as in our measurements, we cannot say. Also Mikhailov et al. (2009), based on

measurements of hydration and dehydration with a hygroscopicity tandem differential mobility analyzer (H-TDMA), conclude that the (semi-) solid phases should not only be important at high altitudes but also influence cloud processes at the relative humidities and temperatures of the lower troposphere and the boundary layer. Therefore, our measurements seem relevant as some of the tested systems are known/shown to be semi-solid after formation in the aerosol chamber (see bounce measurements, and also Saukko et al., 2012, and Pajunoja et al., 2015) and we conduct our experiments under these conditions where, according to the above mentioned studies, SOA should exist in (semi-) solid phase state and behave in a way that influences cloud processes, as cloud formation and ice nucleation.

Our measurements start at (close to) water saturation, which facilitates a quick start of cloud formation. Furthermore, ice saturation is needed in order to nucleate ice, thus, being at ice supersaturation is prerequisite as well. According to Koop's (schematic not representational) phase diagram (Koop et al., 2011), all particles (including the amorphous solid) are deliquesced at 90% RH<sub>w</sub>. So the RH at which we operated in no way diminishes the general applicability of the results.

### **General critique**

**In the following I will assume that a glassy phase state is necessary for SOA particles to nucleate ice. If this is the case, a look at the phase diagram of glassy organic material should have sufficed to predict the lacking ice nucleation ability of the SOA particles observed in these experiments (e.g. Koop et al., 2011). The authors state that the MICC was at water saturation before expansion and during the filling of the vessel. At water saturation, a hygroscopic substance cannot be in a viscous or glassy phase state, no matter the glass transition temperature of the pure substance.**

According to Koop's schematical phase diagram (as mentioned above) all particles are deliquesced at about 70% RH (amorphous solid should be deliquesced at about 60%). Given that the schematic is correct and glassy aerosol needed for ice to nucleate from SOA, Ignatius et al., 2016 should not have observed ice nucleation at roughly -39°C and Sice of 1.3 (coldest example of their figure 5, showing alpha-pinene experiments), as RH<sub>w</sub> would be about 89% in that case. Either, the particles in Ignatius et al.'s study were not glassy, or the schematic phase diagram might have a different look for varied SOA species.

If we assume water saturation in mixed-phase clouds (and according to e.g. Ansmann et al., (2009) the ice phase in mixed-phase clouds is observed after the liquid phase had been established) your argument above would mean that there will never be ice nucleation from SOA in any mixed-phase cloud. This should be tested as hypothesis in a future study. On the other hand, Shiraiwa et al. (2017) and Mikhailov et al. (2009) suggest that these particles should have an impact on cloud processes in the lower troposphere. Thus, we think that our experiments in the way they were conducted are relevant.

**In previous chamber experiments showing the ice nucleation ability of organic aerosols (e.g. Murray et al. (2010), Wilson et al. (2012)), expansion was always initialized at around ice saturation, thus far below water saturation level. The only reason particles could be in a viscous state in the experiment at hand would be if they would cool faster than they could take up water upon entering MICC and hence maintain a non-equilibrium state. These dynamics however seem very difficult to predict since the exact temperature and humidity profiles between MAC and MICC are probably difficult to obtain. Hence, the authors investigated in this study not only if organic aerosols could induce ice nucleation at higher**

**temperatures than expected, but also when initialized at higher humidities than in previous studies. Ice nucleation by organic aerosols under mixed-phase cloud conditions should only be possible if the glassy state is somehow maintained despite the high temperatures and humidities.**

Please see reply above. Correct, most studies generate their SOA particles in very dry conditions, except Wang et al. (2012), who also generated their SOA in more humid conditions at  $35\pm 5\%$ .

**In general, the authors miss to mention that not only temperature is important to determine aerosol phase state, but also humidity. A study by Berkemeier et al. (2014) investigating the kinetics of water uptake of viscous organic particles shows that there is a sensitive interplay between temperature, initial humidity and humidification rate that enables organic aerosols to be in the glassy state at humidities relevant for ice nucleation.**

The reviewer has a good point here; we now mention the importance of relative humidity for the aerosol phase state in according places (mainly introduction and discussion).

**If it was not the goal to use the glassy phase state of organic aerosols to trigger ice nucleation this has to be stated more clearly in this manuscript. In this case however, the discussion devoted to bounciness of particles would be superfluous (or even misleading) and a different incentive to discuss organic aerosols as ice nuclei would have to be presented. It is hard to imagine ice nucleation on liquid aerosol particles.**

First of all, we aimed at characterising the ice nucleation (or lack thereof) in terms of SOA phase state. Here, we show that deposition nucleation is not happening to the SOA particles under the conditions of our experiments. Also immersion freezing does not happen to the SOA generated in our experiments, which means that there are no efficient solid/insoluble IN inclusions in the liquid droplets we see. As stated in Berkemeier et al. (2014), solid inclusions in liquid SOA particles can well be realistic in the atmosphere (we added to the discussion accordingly):

“Berkemeier et al. (2014) further state that humidification in typical atmospheric updrafts (or cloud chamber experiments) may be fast enough to cause a difference in phase state from that of equilibrium, as the time for diffusion of the water into the particle is longer than the time for humidification. This can result in a particle that has a liquid outer shell but still contains solid inclusions/a solid core even at RH above the quasi-equilibrium glass transition. Thus, SOA particles could potentially act as immersion freezing nuclei in conditions where they are supposed to be liquid, if in equilibrium.”

### **Specific remarks**

- **In the introduction, it seems worth mentioning that many more studies have investigated ice formation from organic aerosols. Examples here are works from the Knopf group (e.g. Wang et al., 2012; Charnawskas et al., 2017), the Tolbert group (Baustian et al., 2013) or at the AIDA chamber (e.g. Wilson et al., 2012). Overall the number of references in this paper is very lacking and too much focused on the author's own work.**

We gave the introduction a major overhaul and also revised the discussion to include more references and compare to the referenced works.

- **As mentioned above, the introduction too much focused on temperatures, too little on relative humidities. The biggest problem with ice nucleation and glassy SOA are the high relative humidities necessary to nucleate ice on the particles, which in turn leads to non-viscous phase states. A discussion on this competition**

**process can be found in Berkemeier et al. (2014). "p. 4, l.11 – Out of curiosity, why would the oxidation be conducted with ozone and not also under irradiation with UV light to generate OH radicals? Most products of SOA formation should not be susceptible to reaction with ozone."**

We have moved the section about 'Particle bounce measurements' from the supplement into the main manuscript. These measurements show that TMB and alpha-pinene do exist in a semi-solid phase state even at high relative humidities. Heptadecane indeed is in a liquid phase even at very low relative humidities. We enhanced the discussion to account for the effect of relative humidity on phase state.

Regarding your question about the cleaning procedure: We regularly also perform SOA background experiments, which include UV radiation. Based on experience with the chamber, we found that regular weekly background experiments are sufficient to keep the chamber walls clean enough, such that the daily cleaning (overnight) between two experiments can be performed without irradiation. This combination of cleaning and background cycles furthermore allows enough time to run the actual SOA experiments and not stretch the time frame for experiments too far. We have expanded the cleaning section in this regard.

**• The usage of the words “bouncy” and “non-bouncy” in this study are misleading. What the author’s should say are the conditions under which these particles bounce (RH and T). Do they bounce at -20°C and water saturation? Hence, in the context of p.8, l.23, this is not a meaningful statement.**

Considering the comments by the other reviewer, we changed wording here since bouncy/non-bouncy is not really a physical parameter. We now use the phase state definitions instead (in our experiments 'semi-solid' and 'liquid'). Furthermore, we moved the section about 'Particle bounce measurements' from the supplement into the main manuscript. From those measurements it becomes clear that heptadecane is in a liquid phase and alpha-pinene and TMB are semi-solid even at high RH, see reply above.

**• The effects of cloud processing in the TMB vs heptadecane SOA experiment are an interesting finding. Is the picture of TMB SOA showing lower activated fractions in the second chamber evacuation run consistent among repetitions of the experiment?**

There was, unfortunately, only one TMB experiment day. Thus, we only have those evacuations shown.

#### ***Minor and technical comments***

**• p. 4, l.2 – boiling point of water**

Done.

**• p. 4, l.11 – Out of curiosity, why would the oxidation be conducted with ozone and not also under irradiation with UV light to generate OH radicals? Most products of SOA formation should not be susceptible to reaction with ozone.**

See our reply to this point above (section starting with “As mentioned above, the introduction ...”

**• p.5, l.11 – A closing parenthesis “)” is missing here.**

Parenthesis added.

**• p.5, l.17 – It is not entirely clear what is meant with “to achieve this”. I assume it refers to the cleaning of the chamber, not the particle formation described in the previous sentence.**

It actually refers to the particle formation. We rephrased the sentences:

“To prepare the system for injection of relevant gases for particle formation in MAC the volatile organic compound (VOC) injection glass bulb is heated and flushed with nitrogen. The precursor gases for the SOA and NO<sub>x</sub> are then injected during the last filling of the MAC air bag.”

• **p. 7, l.6 – I believe the word “one” is superfluous here.**

The sentence should use the singular of “particles” as there really only was one particle imaged by the CPI.

“Only one spherical particle was imaged by the CPI.”

• **p.9, l.12 – Not the precursors are bouncy, the SOA from these precursors are, at a specific RH and T.**

Rephrased: “The aerosol particles formed from these precursors are both in a semi-solid phase state, i.e. more viscous than the heptadecane particles at the same temperature and relative humidity.”

• **p. 9, l.13 – The statement confuses kinetics and thermodynamics, please clarify that not a higher supersaturation is needed to activate viscous particles, it just takes longer time.**

We rephrased: “Thus, it takes a longer time for these viscous precursors to take on water vapour and grow due to diffusion limitations.”

References:

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