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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The efficiency of secondary organic aerosol particles to act as ice nucleating particles at mixed-phase cloud conditions" *by* Wiebke Frey et al.

Anonymous Referee #2

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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

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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.

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. 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

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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. 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. 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.

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.
- 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).
- The usage of the words "bouncy" and "non-bouncy" in this study are mislead-

ing. 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.

- 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?

Minor and technical comments

- p. 4, l.2 – boiling point of water
- 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.
- p.5, l.11 – A closing parenthesis ")" is missing here.
- 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.
- p. 7, l.6 – I believe the word "one" is superfluous here.
- p.9, l.12 – Not the precursors are bouncy, the SOA from these precursors are, at a specific RH and T.
- 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.

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