Response to review #1

We thank the anonymous referee #1 for his/her encouraging comments and suggestions for improvements. Below, the referee comments are in green, our response in black and the changed/added sections to the manuscript in *italics*.

1) SPIN is a new instrument and I think this might be the first published ice nucleation data making use of this instrument. Hence, the paper needs to 'validate' the instrument as thoroughly as possible. The homogeneous freezing results for ammonium sulphate are valuable in this respect. However, this paper is about heterogeneous nucleation and I would like to see some heterogeneous results for a material which has been studied in the past and a comparison made.

In addition to homogeneous freezing of ammonium sulphate droplets, heterogeneous ice nucleation of mineral dust was investigated with SPIN, and the results were compared to literature. In particular, deposition and immersion freezing of NX-illite was investigated, with both the version of SPIN used in the present study and the final version of SPIN, and the observed ice nucleation onset conditions were found to be in good agreement with those measured by Welti et al. (2009). These results, as well as instrumental calibrations, are described in detail in a current SPIN technical paper by Garimella et al. (2016). At the time of submission of the present study, the technical paper was not yet available online and we could not cite it.

We have included the following paragraph on page P35725, line 19:
"The final version and the performance of SPIN are described in more detail by Garimella et al. (2016). The main difference between the version of SPIN used in the present study and the final version is related to better temperature control of the final version. "

2) P35722 ln 7-8. The Kramer et al. and Cziczo et al. references are for cirrus clouds, not mixed phase clouds. There are plenty of papers out there which discuss mixed phase clouds including two relatively recent review articles:(Hoose and Möhler, 2012; Murray et al., 2012).

The referee is correct – the Krämer et al. (2009) and Cziczo et al. (2013) references are for cirrus clouds. We have modified lines 6-8 on page P35722: *"Heterogeneous ice nucleation is considered to be an important pathway for ice formation in the troposphere, especially in mixed-phase clouds (Hoose and Möhler, 2012; Murray et al., 2012), but also in cirrus clouds (Krämer et al., 2009; Cziczo et al., 2013)."*

3) P35722 ln 20. The reference to Zobrist et al. in the context of 'suggestions that these SOA particles could play a role in ice nucleation' is incorrect. Zobrist et al. (2008) suggested the opposite – they suggested that glassy aerosol would not nucleate ice. This was one of the reasons why it was so surprising that Murray et al. (2010) showed that aqueous glassy aerosol could nucleate ice under upper tropospheric conditions. Also, Virtanen et al. (2010) did not discuss SOA nucleating ice in any detail – it is just mentioned in the abstract.

We thank the referee for pointing out the misplacement of the citation. We have moved the references to Zobrist et al. (2008) and Virtanen et al. (2010) after the first part of the sentence and inserted a reference to Murray et al. (2010) at the end of the sentence. The sentence now reads: "*Secondary organic aerosol (SOA) can exist in a semi-solid, amorphous state in the atmosphere (Zobrist et al., 2008; Virtanen et al., 2010), and it has been suggested that amorphous SOA particles could play a role in ice nucleation (Murray al., 2010).*"

4) P35723, ln 10-13. The authors refer to modelling studies. It is important to also note the modelling studies performed by Murray et al. (2010) and also Price et al. (2015). These studies are highly relevant here.

We have added references to Murray et al. (2010) and Price et al. (2015), as well as Lienhard et al. (2015) to the text and also discuss these studies throughout the paper.

5) P35723, ln 25-30. The authors suggest that the SOA in Mohler et al. (2008) liquefied and froze homogeneously. The SOA only nucleated well above water saturation. This implied that it was so hydrophobic that it did not take up water until an extreme supersaturation.

In Möhler et al. (2008) the pure α-pinene SOA nucleated ice at very high ice supersaturation (S_{ice}=1.7), but still at subsaturated conditions with respect to water. Therefore, we do not agree with the referee comment here. We have clarified the sentence on page P35723, line 26: *"Thus, it is likely that these particles never featured a high viscosity, liquefied easily and the resulting droplets froze homogeneously."*

6) P35731, I am confused by the discussion of the dependence on size here. It seems to be stated in the text that there is no significant size dependence of ice nucleation, but when I look at fig 4 I see that there is a clear dependence on size. Bigger particles nucleate ice at a lower S.

There is no clear dependence on size. When looking at Fig. 4, it can be seen that 330 nm particles indeed nucleate ice at highest saturation ratios, but 550 nm particles nucleate ice at lower saturation ratios than 800 nm particles. Therefore it is inconclusive whether there is a size dependence or not. We have also created a supplementary Table S1 listing the ice nucleation onset conditions for 1, 5 and 10 % frozen fractions for each experiment, from which it is easy to see that no clear size dependence can be observed.

7) The authors need to discuss and use the results from Price et al. (2015) throughout their paper. In Price et al. the diffusion coefficient of water in the water soluble fraction of SOA from alpha pinine was quantified over a range of temperatures and RHs. Using these measurements the uptake of water into a solution droplet was modelled for a variety of conditions. They conclude that 'SOM can take hours to equilibrate with water vapour under very cold conditions' and 'for 100 nm particles predicts that under mid- to upper-tropospheric conditions radial inhomogeneities in water content produce a low viscosity surface region and more solid interior, with implications for heterogeneous chemistry and ice nucleation' This is highly relevant and complementary for this paper. For example, when making a judgment concerning the timescale of transformation from a glassy solid to a liquid the pertinent

quantity is diffusion. The diffusion coefficient can be used to estimate this timescale. This should be done, for example, on P 35733 (ln 18-30) where the authors note that they observe ice nucleation at an RH well above the RH at which they observe these aerosol to transform to liquid aerosol.

The referee is correct in pointing out that the findings of this paper support the conclusions of Price et al. (2015). However, quantifying the diffusion coefficient of water in the alpha-pinene SOA is beyond the scope of this paper. We have added a new section 3.4 *“Freezing mechanisms”* on page P35732 where the results and implications of Price et al. (2015) are discussed. For more details, please see our response to comment #10 below.

8) P35736, ln 5-10. When commenting that biogenic SOA may be mixed with sulphates and that this may be important for ice nucleation, it would be sensible to bring in the work of Wilson et al. (2012) who showed that glassy aerosol containing a mixture of carboxylic acids and ammonium sulphate also nucleated ice.

We have added the following sentence on page 35736, line 9: *“It has already been shown that glassy aerosol containing a mixture of carboxylic acids and ammonium sulphate nucleates ice (Wilson et al., 2012).”*

9) P35736. A discussion is needed about how their fraction ‘frozen’ is far higher than previous investigations at the AIDA chamber (Wilson et al., 2012; Murray et al., 2010). Could this be related to the particle size? The studies at the AIDA chamber were with smaller particles than those used here.

Our study indicates that seed particle size does not seem to be an important parameter in the size range we have investigated. The substances studied by Wilson et al. (2012) and Murray et al. (2010) are not the same as what we studied, and their experimental approaches and procedures were different, so we would not necessarily expect similar frozen fractions.

We have added a paragraph on this topic to the literature comparison in section 3.5:

“When comparing the frozen fractions of this study to earlier studies with SOA proxies, such as the substances studied by Wilson et al. (2012) and Murray et al. (2010), it is worth noting that much higher frozen fractions are achieved in this study. Most likely the difference lies in the experimental methods used: in Wilson et al. (2012) and Murray et al. (2010), the freezing was studied in an expansion chamber, not a continuous flow diffusion chamber such as SPIN. Thus, we would also not necessarily expect similar frozen fractions. ”

10) The authors use the term deposition mode. This should be caveated. Is this true deposition? i.e. deposition of ice directly onto glassy aerosol particles? Or could nucleation occur in the layer of lower viscosity solution which the modelling of Price et al. (2015) (and others) show will form when RH around glassy aerosol is increased? This layer of lower viscosity water has also been experimentally observed in the work from Jonathan Reid’s group.

We agree that the ice nucleation could occur in the liquid or lower viscosity layer on the particles rather than as direct deposition of ice onto glassy particles. We have limited the use of ‘deposition mode’ and replaced it with ‘heterogeneous ice nucleation’ in the text.

Another possible freezing mechanism could be immersion freezing of large, suspended, ice nucleating organic macromolecules formed through oligomerisation during the ageing process in the CLOUD chamber. Organic macromolecules have been suggested to be the ice nucleation active entity causing the observed immersion freezing of e.g. birch pollen washing water (Pummer et al., 2012). That could explain why we do not observe any clear particle size effect on the ice nucleation behaviour.

We have added a new section 3.4 to the text discussing possible freezing mechanisms (below). Due to partly overlapping content between sections 3.4 and 3.5, we have also shortened section 3.5 considerably.

“The results presented in the section above clearly indicate heterogeneous freezing of SOA particles below saturation with respect to water vapour. Various freezing mechanisms could potentially be in play. It can be speculated that we observe (i) deposition nucleation occurring directly onto highly viscous SOA particles; (ii) immersion freezing of partly deliquesced SOA particles, where the core of the particle is still (highly) viscous; (iii) hygroscopic growth of the particles leading to freezing of droplets due to suspensions of large organic molecules. The relevance of the first two potential freezing processes are related to the relative timescales of the viscosity transition vs the freezing of the SOA particles for increasing humidities as discussed e.g. by Berkemeier et al. (2014), Lienhard et al. (2015) and Price et al. (2015). Lienhard et al. (2015) conclude that heterogeneous freezing of biogenic SOA particles would be highly unlikely at temperatures higher than 220 K in the atmosphere since according to their modelling, the timescales of equilibration would be very short. On the other hand, the modelling results presented by Price et al. (2015) indicate that α-pinene SOA particles are likely to exhibit viscous core-liquefied shell morphologies on timescales long enough to facilitate ice nucleation via the suggested mechanism (ii) in our study.

In this context, it is worth mentioning that the maximum ice nucleation time in SPIN is of the order of 10 s. However, nucleation taking place on much shorter timescales can be observed if the nucleation rates are high enough to yield detectable numbers of ice crystals. In other words, the observed number of ice crystals corresponds to the time integral over the nucleation rate distribution. This implies that from our measurements, no further conclusions concerning nucleation times and rates can be drawn.

The (iii) potential freezing mechanism has been reported for ice nucleating macromolecules (INM) originating from pollen (Pummer et al., 2012). It is not likely that the molecules formed in the current study grow to masses comparable to the several kDa reported for the pollen macromolecules (Pummer et al., 2012), but it does not necessarily rule out that large enough molecules or agglomerates to facilitate freezing may have been produced during the conducted experiments, even though it did not seem to be the case in previous comparable studies (Möhler et al., 2008; Ladino et al., 2014). Based on the current study, it is not possible to conclude which heterogeneous freezing mechanism(s) may be dominating.”

We have also removed the words *"in the deposition mode"* from the Conclusions (P35736, line 17) and added a sentence to line 24: *"We were not able to distinguish between three possible freezing mechanisms: i) deposition nucleation onto highly viscous SOA particles; ii) immersion freezing of partly deliquesced SOA particles; or iii) hygroscopic growth and subsequent freezing of the SOA particles due to presence of organic ice nucleating macromolecules."*

11) The data for SOA proxies from (Wilson et al., 2012; Murray et al., 2010) must be shown in Figure 6. I suggest the authors focus on the onset RHs where the aerosol was thought to start in a glassy state.

These data are now included in Fig. 6, with the following extension to the caption:

"The red squares show the deposition ice nucleation onsets for glassy citric acid (Murray et al., 2010) and the freezing results of 4 glassy SOA proxies from (Wilson et al., 2012) are shown by blue squares (raffinose M5AS), green squares (levoglucosan), magenta squares (raffinose), and black squares (HMMA)."

12) I note that the co-authors of the Leinhard et al. ACP 2015 paper have posted a comment, so I won't write much about this. But, I reinforce that comment and state that the Leinhard paper should be discussed in the present manuscript.

Please see our response to the open comment by Ulrich Krieger. The work by Lienhard et al. (2015) is also discussed in the new section 3.4 (for details, please see our response to comment #10 above).

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