Our response to referee 1's comments are in red.

General comments

This study investigates whether glassy aerosols nucleate ice heterogeneously under cirrus conditions. Cirrus clouds are ubiquitous in the upper troposphere and their climatic effect depends on ice crystal number density. Heterogeneous ice nucleation on glassy aerosol might lead to low particle densities and sustained supersaturation in cirrus clouds. This work extends the results presented for citric acid aerosols in a former study to four additional model systems that can be considered as representing organic atmospheric aerosol. It supports the results found for citric acid that a small fraction of glassy aerosols lead to heterogeneous ice nucleation. This is a thorough study that is in some parts a bit lengthy and might be shortened. Some points need clarification before publication in ACP. Specifically, the atmospheric implications (section 3.5) need revision (see comments below).

General questions:

How many expansions were performed with the same aerosol? Are there any indications that IN were used up during the first expansion?

Repeated experiments with the same aerosol particles were avoided in general to eliminate the possibility of causing aerosol pre-activation (which is discussed in our companion paper {Wagner, 2012}). This is discussed in the methodology section (line 16 p.8989).

In our previous work on glassy citric acid aerosol (Murray, Nature Geoscience 2010), repeated experiments were performed with the same aerosol particles without any observed significant decrease in the fraction of aerosol that nucleated ice heterogeneously.

The fraction of particles that froze was generally low. Do the authors consider the ability to nucleate ice as a general property of glassy aerosols or just as the ability of only few with special surface properties?

Our results show that a small fraction of particles in an aerosol dispersion (independent of aerosol composition) serve as ice nuclei. Hence, we state that heterogeneous ice nucleation is a general property of glassy aerosols. We have addressed some possible explanations for why only a small proportion of particles in an aerosol activate to ice (line 10, p. 9000 of the original manuscript). Within this discussion we have adjusted the text in order to emphasise the fact that if active sites are responsible for ice nucleation they are only present on a small fraction of the aerosol. The pertinent line has been adjusted to: "This study and the previous study using citric acid aerosol {Murray, 2010 #276} show clearly that a small fraction of glassy aerosol particles of varied compositions are able to act as ice nuclei in the deposition mode. The surfaces of this subset of glassy aerosol may therefore possess some ‘active sites’ that are able to stabilise nascent germs of the ice phase.”

We have also adjusted the pertinent line in the abstract to read: “A small fraction of aerosol particles of all compositions were found to nucleate ice heterogeneously in the deposition mode at temperatures relevant to the TTL (< 200 K).”

Can the authors exclude the crystallization of a small fraction of the particles? Would this be an alternative explanation of the results? (See also specific comments to pages 8993 – 8995).

We argue that the data presented to support the lack of crystallisation in these experiments in Section 2.1 (line 3, p. 8990) provide very strong evidence against crystallisation. We refer in particular to the dedicated experiment that was performed during the campaign at AIDA, in which raffinose solution droplets were cooled into a region in which they were highly supersaturated with respect to crystalline raffinose then warmed back up to temperatures at which only homogeneous ice nucleation was expected and an expansion performed. The lack of any heterogeneous nucleation during the expansion strongly supports the view that the heterogeneous ice nucleation observed by raffinose and other glassy aerosols was not the result of crystallised solutes. We have now also added reference to our companion paper {wagner 2012}, in which experiments using HMMA and raffinose/M5AS with similar results to that described for raffinose above. See below for more detail on specific comments.

How is the condition for onset of nucleation defined? (See also specific comments to Figure 6).

The onset of ice nucleation in experiments is inferred from a change of at least 1% in the depolarisation ratio. To clarify this we have adjusted the text on p. 8988 to read:

“Ice particles are aspherical and cause a clear increase in δ. A change of at least 1% is used to infer the onset of ice nucleation”

And also the Fig 6 and Fig 7 captions:

Fig 6 “The time/RH_i onsets of ice nucleation are marked with dashed black lines. In each case the onset was observed as an increase of at least 1% in the backscattering linear depolarisation ratio, δ, which is the most sensitive indicator for the presence of ice particles. This allows the detection of ice particles before they have grown large enough to be counted by the WELAS instruments.”

Fig 7 “associated with each trajectory is an ice nucleation onset determined using the depolarisation measurement (defined by a change in the depolarisation ratio of at least 1% – for example see **Error! Reference source not found.**), with orange triangles representing homogeneous ice nucleation onsets and blue stars representing heterogeneous ice nucleation onsets.”

It should also be noted that the more quantitative measurements of ice particle concentration, fraction of aerosol frozen (f_{ice}) and ice active surface site density (n_s) shown in Figs 8, 10 and 11 do not rely on depolarisation data and instead are inferred from the WELAS optical particle counter data.

Presentation of results:

The authors should consider presenting the results of all experiments in figures analogous to figures 5 or 9 in a supplement.

This is an enormous amount of data that we do not think would add much to the paper. We have included data from 15 separate expansion experiments in a summarised form in fig 7 and 8. Inclusion of 15 pages of raw data in a supplemental section would be over the top.

The fonts used in figures 4-7 and 9 are too small. It is impossible to read axis titles and labels from a print out and even on the screen strong zooming is needed.

We agree that the some of the figures are hard to read and will check that text in all the figures is of a sufficient size in the final version. We have increased font size in the problem figures.

The labeling of the panels in the text and in the figures is not consistent. Capital letters are used in the figures and small letters in the text.

The figures have been adjusted to include only lower case labels.

Table 2 that is mentioned in the main text and the caption to figure 11 is missing!

Table 2 was present in the last typsetting document from Copernicus that we saw. Unfortunately it seems to have disappeared from the Discussions paper. The table will be restored in the final version.

Specific comments

Introduction:

Page 8981, line 9: the number in the bracket has to be explained better.

This now reads: ”Cirrus which forms in situ in the TTL, rather than as the product of convective outflow, is horizontally extensive (up to 10^5 km^2), but very thin (200 – 300 m deep)”

Methodology:

Page 8993, line 19 to page 8994, line 23: The discussion of potential crystallization of the aerosol is lengthy. At the same time, the cited studies cannot rule out crystallization of a small fraction of aerosol particles: crystallization of < 1 % of the particles would be enough to account for the fraction of aerosol that froze in the AIDA chamber. Such a low fraction of crystallized particles would not have been detected by most studies that are cited by the authors to argue that crystallization of the aerosol can be excluded. The authors might consider citing just Zobrist et al. (2008), who showed that the investigated aerosols formed glasses in DSC experiments. They should also mention that crystallization of a small fraction of the particles cannot be excluded. The implications of this for the interpretation of the results should be discussed.

As the reviewer makes clear, it is very important for us to thoroughly address the issue of potential crystallisation. We do not think that a reference to only Zobrist et al. (2008) would suffice and also think that the weight of experimental evidence strongly suggests that crystallisation of the solute does not happen. In response to the reviewer we have placed a greater emphasis on Zobrist’s work as follows:

“At low temperatures, the solution droplets in the AIDA chamber are highly supersaturated with respect to their solutes’ crystalline phases. For example, the solubility of raffinose at 273 K is 30 g L^{-1}{Hungerford, 1934 #279}(and will decrease at lower temperatures), whereas the predicted aerosol composition when at ice saturation at 238 K(based on water activity data from {Zobrist, 2008 #75})is 782.5 g L^{-1}. Under similarly supersaturated conditions, oxalic acid or ammonium sulphate solution aerosol would be expected to slowly crystallise {Wagner, 2010 #281;Wagner, 2011 #285;Abbatt, 2006 #266}. This is important because crystalline solid salts are known to catalyse ice nucleation {Wise, 2009 #267;Wise, 2010 #308;Abbatt, 2006 #266;Baustian, 2010 #280;Shilling, 2006 #310;Eastwood, 2009 #311}, as are crystalline hydrates {Wise, 2012 #406}. However, nucleation and crystal growth in highly viscous or glassy aqueous aerosol particles is much slower. For example, none of the species investigated in this study were observed to crystallise during the experiments carried out on droplet in oil emulsions by Zobrist et al. (2008).”

In addition to the experiment that looked for heterogeneous nucleation by crystallised raffinose aerosol (none was observed, See Fig. 4), we have also added reference to experiments described in our companion paper {wagner 2012}. These experiments used HMMA and raffinose/M5AS aerosol and show that aerosols which had nucleated ice heterogeneously when in the glassy temperature regime only nucleated ice homogeneously after warming to higher temperatures. This indicates strongly that like the raffinose aerosol, HMMA and raffinose/M5AS aerosol liquefied on warming. This would not be expected for crystalline particles We have modified this section which now reads as follows:

"In order to further test if the solution aerosol were crystallising we performed a dedicated experiment with raffinose aerosol in which raffinose solution was injected at ~241 K and the resultant aerosol was cooled to 217.5 K over a period of ~6 hours before warming the chamber to 229 K, at which point an expansion experiment was performed (**Error! Reference source not found.**A). If raffinose had crystallised during injection of the aerosol or during the subsequent temperature cycling, it would most likely have nucleated ice heterogeneously like other crystalline materials such as ammonium sulphate {Wise, 2009 #267;Abbatt, 2006 #266} and oxalic acid {Wagner, 2010 #281;Wagner, 2011 #285}. During the expansion, no significant heterogeneous ice nucleation was observed, with < 1 cm^{-3} ice particles nucleating prior to a rapid increase in N_{ice} when the chamber RH_i was within 2% of the predicted homogeneous freezing threshold (based on AIDA freezing data for liquid H_2SO_4 solution aerosol {Möhler, 2003 #202}) (Fig 4B). This offers very strong evidence that the raffinose aerosol did not crystallise at low temperature and that any heterogeneous nucleation observed in other experiments was not due to crystalline raffinose.

Further experimental evidence of the lack of crystallisation of the glassy aerosols used in this study come from our companion paper Wagner et al. (2012). In that study, run 1C (Fig 5) took place at ~232 K using HMMA aerosol that had previously heterogeneously nucleated ice when in the glassy state at a lower temperature (in run 1B). In run 1C, only significant homogeneous ice nucleation was observed. This shows that the glassy aerosol had liquefied on warming. Had the aerosol been crystalline it would still have been expected to nucleate ice heterogeneously. Similarly, our companion paper also shows the results of an expansion performed on raffinose/M5AS aerosol particles at ~216 K (run 4A, Fig 12), that had previously nucleated ice when glassy. Again, after warming into the liquid regime, the only significant ice formation occurred homogeneously. This again strongly indicates that that the heterogeneous nucleation at lower temperatures was by glassy particles which were able to liquefy on warming rather than crystallites. In both cases, to ensure that those particles that nucleated ice in the first run were not lost by sedimentation, ice crystals were sublimed quickly by refilling the chamber immediately after pumping had stopped.

These experiments and the literature discussed above strongly suggest that solute crystallisation from the aqueous solution aerosols did not occur and instead the aerosol were in either a liquid, semi-solid glassy state depending on chamber temperature and humidity. Hence, heterogeneous ice nucleation was due to the presence of glassy aerosol rather than crystalline particles."

Page 8995, lines 19-21: Is this method able to detect crystallization of a small fraction of the particles?

The ability of the depolarisation technique to detect small numbers of crystallised particles is discussed in lines 3 - 19 of p. 8995, with specific reference to the work of Liu and Mishchenko (2001). We have added to the end of this section a discussion of the detection limit for depolarisation by crystallites and the required fraction of crystallised particles required to reach this limit. The text reads as follows:

"The detection limit for a change in depolarisation at AIDA is about 1%. No such change in δ was observed during experiments with the aerosols used here or in the previous work with citric acid aerosol {Murray, 2010 #276}, strongly suggesting the absence of crystallisation. If we assume that the crystallized particles have the same size and refractive index and a reasonable depolarisation ratio of about 0.2 for these particles, then 5% of the aerosol particles in the chamber would need to crystallise in order to produce a detectable change in depolarisation. A similar fraction of crystallites would also be required for detection with FTIR extinction measurements. One might therefore argue that the heterogeneous ice crystal modes observed in our study were due to nucleation on a small subset of particles which had crystallized instead of forming a glassy solid. However, the following experimental data provides strong evidence that this was not the case."

Results and discussion:

Page 8998, line 14: the value 0.04 seems to be too high and does not correspond with the maximum value reached in Figure 6 (which is ca. 0.007).

The value of 0.04 was quoted in error and has been changed to 0.005 to reflect the value reached in Figure 6 panel b2.

Page 8999, line 11: the expression "amorphous deliquescence" is not familiar to me. The authors should give a reference for it or replace it by liquefaction.

We have used the terminology outlined by Mikhailov et al. (2009) who define the term amorphous deliquescence as follows:

"Overall, the transformation of (semi-)solid amorphous particles (glassy, rubbery, gel-like, or ultra-viscous) into liquid aqueous solution droplets by uptake of water vapor (combined humidification and liquefaction) can be regarded as a deliquescence transition ("amorphous deliquescence")."

Since neither referee knew this term we have modified the sentence to read: “Aerosol particles in expansions that start close to but still below T_g’ may take up water, which serves as a plasticiser, and liquefy on crossing RH_g. This solid-to-liquid transition is also known as amorphous deliquescence {Mikhailov, 2009 #259}) and may occur before ice can nucleate heterogeneously.”

Page 9002, line 23 – page 9004 line 7: in this paragraph, the authors speculate whether the particles might have persisted in the glassy state for the duration of the experiments, allowing them to be available for heterogeneous ice nucleation although they have passed the RHg line. This paragraph is lengthy and might be shortened. On the other hand, the authors miss to mention Zobrist et al. (2011) who have shown that for a given solute concentration, the diffusion of water molecules in sucrose particles strongly decreases with decreasing temperature. The parameterization for water diffusion in aqueous sucrose particles (equations 5 and 11-13) should be used to estimate timescales of liquefaction for the experiments performed.

We have added a reference to Zobrist et al. (2011) in this section. However, we do not think that it is appropriate to apply a parameterisation for sucrose solutions in this case due to the difference in glass transition temperatures. We have instead estimated the viscosity of the aerosol during the expansion experiments shown in Figure 9 using an approach previously described by Murray et al. (ERL, 2008) in a study of glass formation and crystallisation in citric acid solutions. For both the experiments shown in Fig 9 we have displayed the time to diffuse 85 nm as a colour map overlaid on the RH_i time series in panels a1 and b1. The paragraph in section 3.3 has been modified to:

“There are several potential explanations for the nucleation of ice above RH_g but below the homogeneous nucleation threshold. Firstly, at the temperatures at which this behaviour was observed, and also at those found in the upper troposphere, the absolute amount of water vapour for a given relative humidity is much smaller than at room temperature. For this reason, the aerosol may take longer to liquefy than the 10s – 100s of seconds found in experiments performed using glassy sucrose droplets at room temperature {Tong, 2011 #303}. This would also be supported by the observations of Zobrist et al. {, 2011 #291}, who found that sucrose viscosities increased strongly with decreasing temperature. In the presented iso-humid experiments the aerosol could therefore have persisted in the glassy state for the duration of the experiments, allowing them to be available for heterogeneous ice nucleation. To further investigate this possibility, we have estimated the viscosity of the aerosol during the expansion experiments shown in Figure 9 using an approach used my Murray {Murray, ERL, 2008; murray, ACP, 2008} to understand glass formation and crystallisation in citric acid droplets. The super-Arrhenius dependency of viscosity with temperature (η_T) above the glass transition temperature (T_g) at an RH_i can be approximated by the Williams-Landel-Ferry (WLF) equation:

$$\log \eta_T = \log \eta_{T_g} \left(\frac{17.44[T - T_g]}{51.6 + [T - T_g]} \right) \tag{2}$$

Where viscosity is in cP and T is the chamber gas temperature. The numerical values are typical for glass forming systems {Debenedetti, book}. The molecular diffusion coefficient for the water molecules in the aerosol was then estimated based on the viscosity (converted to Pa s) using the Stokes-Einstein equation:

$$D_{H_2O} = \frac{kT}{6\pi\eta_T r_{H_2O}}$$

(3)

Where k is the Boltzmann constant and r_{H2O} is the hydrodynamic radius of water (0.94 Å; {Murray, erl, 2008}). Finally, we estimated the time, t, for a water molecule to diffuse a root mean distance (x_i) of 85 nm (the average radius of the aerosols used in this study, see Fig 2) using the estimated diffusion coefficients:

$$t = \frac{x_i^2}{6D_{H_2O}}$$

(4)

For both the experiments shown in Fig 9 we have displayed the time to diffuse 85 nm as a colour map overlaid on the RH_i time series in panels a1 and b1. From this it can be seen that at even the highest humidities reached in the two experiments, the time to diffuse 85 nm is estimated at days, much longer than the duration of the experiments, suggesting that the aerosols would not have had time to liquefy.”

Page 9006, line 23 – page 9007, line 2: The suggestion that the fit to ns for the citric acid data is representative for any glassy aerosol is not justified if one considers the large variation of crystallization onsets from 120 – 140 % RH found for the model compounds of this study.

We agree that it is not representative of all the aerosols tested and did not intend to give this impression. Rather, we suggest that since heterogeneous nucleation in cirrus is dominated by the best ice nuclei we should focus our description of ice nucleation by the subset of atmospheric aerosol which fall into this category. We have adjusted the following paragraph to emphasise this:

”The range of observed onset humidities makes the parameterisation of glassy aerosol for modelling purposes non-trivial. The atmospheric aerosol particles in a particular location are likely to have a range of compositions and any that are glassy are likely therefore to have a range of ice nucleating abilities. Ice nucleation will be dominated by the ice nuclei in the aerosol that can catalyse ice formation at the lowest humidities. Since citric acid is amongst the materials which nucleate ice at the lowest humidity it seems sensible to use the parameterisation for ice nucleation on aqueous citric acid in cirrus models. In addition, the fit to citric acid is valid over the widest range of RHs which also lends itself to use in models.”

Page 9007, line 13 – page 9008, line 19: In section 3.5, the authors suggest that glassy aerosol provide an explanation for the sulphate-organic ice residues observed by DeMott et al. (2003) in heterogeneously nucleated ice crystals. However, closer inspection of the data shows that this conclusion is not valid. The ns value of 10^{10} m-2 at 125 % RHi taken for the sulphate-organic aerosol is too high on the basis of the data obtained from this study: more than half of the runs that led to heterogeneous ice nucleation had onset RHi above 125 %. For citric acid, the value that can be read off figure 11 at RHi = 125 % is 3 x 10^9 m-2, which is also lower than the value adopted for the estimate. The experiments by DeMott et al. (2003) were performed between 218 – 238 K. However, at T > 220 K, all runs performed in this study showed only homogeneous nucleation. All this taken together, heterogeneous nucleation on glassy organic-sulphate aerosol is not a valid explanation for the organic-sulphate residues in the heterogeneously nucleated ice crystals observed by DeMott et al. This section needs to be revised.

In the revised section 3.5 we have made a number of changes:

1) Selected n_s values representative of those in the figures (i.e. adjusted down).
2) Removed reference to DeMott's ice residues which were for higher temperatures.

The main point is that heterogeneous nucleation on amorphous solid aerosol may compete with mineral dusts outside of the TTL.

The new section reads:

"The results presented here show that glassy aerosol can nucleate ice under conditions relevant for ice cloud formation in parts of the atmosphere which are warmer than the very cold TTL. In the following lines we explore the possibility that ice nucleation on glassy aerosol might compete with ice nucleation on mineral dusts at warmer cirrus temperatures. Starting with a total of 300 cm^{-3} aerosol particles and, based on the measurements of DeMott et al. (2003) that 1% of these were mineral dust particles and 86% were organic sulphate particles. We assume that mineral dust particles have a diameter of 500 nm and the organic-sulphate particles have a diameter of 150 nm. We also assume that only 50% of the organic-sulphate aerosol particles are glassy and that 50% of the mineral dust particles have been deactivated by coatings. Using an n_s value for mineral dust of 3 x 10^{10} m^{-2} and a value of 3 x 10^9 m^{-2} for sulphate-organic aerosol at 125% RH_i (see Fig 11), we estimate that mineral dust and organic-sulphate particles would nucleate comparable numbers of ice particles (0.033 vs.0.027 cm^{-3}). The total number of ice particles nucleated would be ~0.060 cm^{-3}, which is consistent with the observed mean ice particle number density in mid-latitude cirrus (Krämer et al., 2009). This estimation suggests amorphous solid organic aerosol could play a role in mid-latitude cirrus formation."

Accordingly we have also removed the last paragraph from the conclusions.

Conclusions:

Page 9010, line 15 – Page 9011, line 5: These conclusions have to be revised. See comments to sections 3.4.2 and 3.5.

See earlier comment on the citric acid parameterisation and the cirrus ice crystal calculation above.

Figure 4: The “C” is missing in panel C. The frozen fraction should be added to panel C as it is done in e.g. Figure 5. Last sentence of the figure caption: do the authors want to imply that the aerosol froze when it was still amorphous, rather than having liquefied before crystallizing? Homogeneous nucleation of an amorphous aerosol is not expected.

‘C’ added to plot.

We agree that this sentence was confusing; the text has been adjusted to read:

> “Homogeneous ice nucleation was observed at the predicted humidity, indicating that the aerosol had liquefied on exposure to increasing humidity, which would not have occurred had it crystallised.”

Figure 6: I would have put the onset of nucleation in run B (panels B1 and B2) rather at ca. 130 s than at ca. 110 s. This would also agree better with the peak RHi. Is there any objective criterion for the onset of ice nucleation (e.g. in terms of frozen fraction or absolute number of ice crystals per volume) that was applied to all experiments?

The onset of nucleation is inferred from an increase in the depolarisation ratio. This allows the detection of ice particles before they have grown large enough to be counted by the WELAS instruments. The apparent gap between the onset in Figure 6 B1/B2 and the increase in the number of ice particles is the result of this delay. This has been clarified in the caption.

Figure 8: Not all data shown in Figure 7 are shown in Figure 8. Namely, Raffinose/ M5AS at 190 K and levoglucosan are missing. Is there any reason for this? Could they be added?

At lower temperatures there is less water vapour available so ice crystals do not grow as large on the experimental timescales at AIDA. This prevents the application of a size threshold to the WELAS data to infer N_{ice} by excluding background aerosol. For this reason we do not show f_{ice} or n_s for experiments below 198 K. We state in the text:

“At lower temperatures ice particles do not grow as large because of the lower absolute humidity. Consequently for experiments which took place below ~200 K it was not possible to apply a size threshold to distinguish ice crystals from the larger of the background aerosol particles.”

To make this clearer we have also added now added to the Figure 8 caption – “At temperatures below 198 K, the ice crystals were too small to allow N_{ice} to be inferred accurately from the WELAS data using a size threshold, preventing the calculation of f_{ice} for those experiments.”

Figure 8 also includes data with freezing temperatures below 200 K. This number should therefore be adjusted or deleted.

Number adjusted to 198 K

The symbols for raffinose (stars and squares) seem to be mixed up when one compares with the data shown in figure 7. The solid line is green, not cyan.

The symbols in Figure 7 – blue stars and orange triangles correspond to heterogeneous and homogeneous ice nucleation onsets respectively, see caption for details. They are not related to the symbols used in figures 8, 10 and 11.

Our graphing software describes this colour as cyan, it is distinguished from the clearly blue symbols and lines.

Figure 10: The legend should be included in the figure.

Legend added to Figure 10

Technical comments:

Page 8998, line 2: “of” after “sublimation” is missing. Done.

Page 8998, line 25: one “that” has to be deleted. Done.

Page 9001, line 25: the “a” after “despite” needs to be deleted. Done.

Page 9003, line 3: is there a “few” missing between “only” and “grew”? No.