

Interactive comment on “Glassy aerosols with a range of compositions nucleate ice heterogeneously at cirrus temperatures” by T. W. Wilson et al.

Anonymous Referee #1

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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

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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?

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?

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).

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

Presentation of results:

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

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.

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.

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

Specific comments

Introduction:

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

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.

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

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).

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.

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 diffu-

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sion in aqueous sucrose particles (equations 5 and 11-13) should be used to estimate timescales of liquefaction for the experiments performed.

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.

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 1010 m^{-2} at 125 % RH_i 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 RH_i above 125 %. For citric acid, the value that can be read off figure 11 at RH_i = 125 % is $3 \times 10^9 \text{ m}^{-2}$, 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 $T > 220 \text{ K}$, 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.

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.

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

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not expected.

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 RH_i. 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?

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

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

Technical comments:

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

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

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

Page 9003, line 3: is there a “few” missing between “only” and “grew”?

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 8979, 2012.