

We thank Referee #2 for his comments to improve the quality of the paper. Below we will give a point-by-point answer the individual comments.

#### COMMENT:

Major concerns and questions:

-Previous literature is cited many times, for e.g. line 11 page 8922 ...this is discussed in detail in a separate ..., this slows down the reading and the reader has to refer the cited article to understand the present article. Also, the companion paper, Wilson et al. (2012), is cited many times. I would suggest either add briefly the Wilson et al. (2012) statements that are referred to or reduce the scope of the paper to stand on its own with few Wilson et al. citations. For any other suggestions to improve to readability of the paper I will leave the option open to the authors.

#### ANSWER:

It is mostly the Wilson et al. (2012) companion paper that is referred to, also on page 8922, line 11. So it is indeed a good idea to summarise the statements from this paper which are important for the scope of our own manuscript. The most important information, which is referred to several times, is the upper threshold temperature as well as the critical ice saturation ratio where heterogeneous ice nucleation in the deposition mode on the various glassy aerosol particles could be observed. Our experiments on the pre-activation behaviour then explicitly cover the temperature range between this threshold temperature and  $T_g'$ . We will include these data in a tabular form in Appendix A. The data correspond to the blue stars from Fig. 7 in Wilson et al. (2012) which represent the heterogeneous ice nucleation onsets. The table will also include the  $T_g'$  values for all compounds as well as a brief description of the chemical functionality and atmospheric relevance of the investigated compounds (see next comment).

On page 8925, line 26, we have added a reference to this new appendix in the revised manuscript text:

“As a supplementary information for the reader, we summarise in Table A1 of Appendix A the upper threshold temperatures and associated supersaturation levels where heterogeneous ice nucleation in the deposition mode on the various glassy aerosol particles has been observed. Our manuscript explicitly addresses the ice nucleation behaviour of the various compounds in the glassy regime above these threshold temperatures for heterogeneous ice nucleation. Table A1 additionally includes the  $T_g'$  values as well as brief description of the chemical functionality and atmospheric significance of the investigated compounds, as discussed in detail in the introduction of Wilson et al. (2012).”

The new Appendix A will be as follows:

#### **Supplementary information from the companion paper by Wilson et al. (2012)**

“The experiments described in this manuscript probe the ice nucleation ability of various glassy aerosol particles in the temperature range between  $T_g'$  and the upper threshold temperature,  $T_{\max}^{het}$ , where heterogeneous ice nucleation in the deposition mode is observed at a given critical ice saturation ratio,  $S_{ice}^{het}$ . The latter mechanism is analysed in the companion paper by Wilson et al. (2012). As a look-up table for the reader, we have compiled the  $T_g'$ ,  $T_{\max}^{het}$ , and  $S_{ice}^{het}$  values for all investigated compounds (Table A1). The  $T_{\max}^{het}$  and  $S_{ice}^{het}$  values correspond to the blue stars on the

trajectories of the expansion runs shown in Fig. 7 of Wilson et al. (2012), representing the heterogeneous ice nucleation onsets. The final column of Table A1 briefly describes the chemical functionality and atmospheric significance of the employed compounds.”

**Table A1.** Supplementary information on the heterogeneous ice nucleation ability, chemical functionality, and atmospheric significance of the investigated compounds from the companion paper by Wilson et al. (2012). See text for details.

Solute	$T'_g$ / K	$T_{\max}^{het}$ / K	$S_{ice}^{het}$	Functionality and atmospheric significance
HMMA	236.5	218	1.20	Aromatic compound, surrogate for water soluble organic compounds in atmospheric aerosol
Levogluconan	211.7	191	1.55	Monosaccharide anhydride, major component of biomass burning aerosol
Raffinose	240.6	215	1.33	Trisaccharide, component of biomass burning aerosol
Raffinose/M5AS	209.6	200	1.21	Multi-component oxidised organic/sulphate mixture, representing internally mixed atmospheric aerosol in the tropical tropopause layer

Further manuscript changes in this context:

- Page 8925, line 11: The quoted threshold temperature of 217 K corresponds to the starting temperature of the expansion run. Heterogeneous ice formation upon expansion cooling was actually observed at 215 K as shown in Table A1. 217 K will therefore be replaced by 215 K.
- Page 8927, line 11: Sentence will be shortened to: “Actually, we have observed heterogeneous ice nucleation on a subset of the aerosol particles starting at only  $\sim 65\%$  RH<sub>w</sub> (point X2) along the trajectory (Wilson et al., 2012).”
- Page 8935, line 11: We will include a reference to Table A1 and delete the unnecessary extension “...as analysed in detail by Wilson et al. (2012)”. As shown in Table A1, Wilson et al. have quoted a critical ice saturation ratio of 1.20 for the onset of heterogeneous ice nucleation in this expansion run with HMMA whereas we have quoted a slightly lower value of 1.16 in our manuscript. This is because the nucleation onset in this particular experiment is not as sharply defined as in a homogeneous freezing event where large numbers of ice crystals are instantly formed at the threshold relative humidity (see e.g. run 1C in Fig. 5). In run 1B, the ice particle number concentration gradually increases. We have set the nucleation threshold to the time where the very first ice crystals have appeared in the OPC scatter plot, corresponding to only very few ( $< 1 \text{ cm}^{-3}$ ), very ice-active HMMA particles. Wilson et al. (2012) have chosen a more conservative estimate for the threshold, setting it to the time where the ice particle formation could also be evidenced by an increase in the depolarisation ratio. For the sake of a uniform representation, we will adopt the threshold quoted by Wilson et al. (2012), both in Fig. 4 by shifting the vertical dashed line in the right panel and in the revised manuscript text on page 8935, line 11:  
“The vertical dashed line indicates the onset of ice nucleation during the expansion at an ice saturation ratio of  $S_{ice} = 1.20$ . Ice nucleation initiates clearly before reaching the homogeneous freezing threshold and is due to heterogeneous nucleation on the glassy seed aerosol particles (Table A1).”

- Page 8940, line 14 will be changed to:  
“Heterogeneous ice nucleation on glassy aqueous raffinose particles in the deposition mode only occurs below a threshold temperature of about 215 K and requires a higher ice saturation threshold than observed in run 2C (Table A1).”
- Page 8941, line 4 will be changed to:  
“The starting temperature of run 2D, however, is already below the threshold of 215 K where heterogeneous ice nucleation on glassy aqueous raffinose particles can also be detected (Table A1).”
- Page 8941, line 27: The reference to Wilson et al. (2012) is now obsolete and will be deleted.
- Page 8945, line 21: The Wilson et al. (2012) citation will be replaced by a reference to Table A1.
- Page 8946, lines 4 – 9: These two sentences are in fact an issue for our companion paper, strongly suggesting that crystallised particles or impurities do not cause the observed heterogeneous nucleation modes. They are not necessary within the scope of our manuscript and will be removed.

#### COMMENT:

-What was the motivation to study four different glassy aerosol particles described in this paper from atmospheric implications point of view (end of page 8924 and beginning of 8925). It is mentioned that these are selected on the basis of phase state diagrams. I wonder if these solutes have been observed in the atmosphere. If so, please cite the work. Please comment.

#### ANSWER:

This issue has been addressed in detail in the introductory section of our companion paper. The substances were not only chosen because they are well characterised systems, but also because they have a diverse chemical functionality and can be considered as representative of organic atmospheric aerosol. A part of the substances have indeed been identified as components of biomass burning aerosol (citations are given in Wilson et al.), and the Raffinose/M5AS system is a complex, multi-component oxidized organic/inorganic (sulphate) mixture that is representative of internally mixed atmospheric aerosol found in the tropical tropopause layer (TTL).

Instead of completely duplicating this information from the companion paper in our own manuscript text, we have decided to incorporate a brief description of the chemical functionality and atmospheric significance of the investigated compounds from the discussion in Wilson et al. (2012) into our new Table A1 (see above). On page 8924, line 28, we have inserted the statement:  
“The compounds feature a diverse chemical functionality and, as addressed below, can be considered as representative of organic atmospheric aerosol.”

#### COMMENT:

-The paper is focused on the pre-activation behavior of the aerosol particle. This ice nucleating property is briefly described in the section 1, where it is mentioned that enhanced ice nucleating ability is termed as pre-activation behavior. Please elaborate the definition of the pre-activation clearly defining why do you call enhanced ice nucleating ability as pre-activation, the enhancement can be also possible via modification of the aerosol surface property. Although these concepts are

clearly described in the discussion section of the paper, there is not enough material in the introduction section.

ANSWER:

Yes, pre-activation is only one (however the most likely) explanation for our observation. We think that a modification of the surface area of the glassy particles during ice-cloud processing also pertains to the phenomenon of “pre-activation”. For example, Zuberi et al. (2001) speculate about a modified surface with “active” sites that closely match the ice lattice, which is formed when ammonium sulphate crystallises in the presence of ice. But as outlined in Sect. 4.5, crystallisation of the freeze-concentrated organic solutions upon homogeneous ice nucleation, although less probable, cannot be completely excluded. We just wanted to introduce a brief acronym for our observation of “the enhanced ice nucleation ability of the ice-cloud processed glassy aerosol particles in the second expansion run”, in order to enhance the readability of the manuscript. We will clarify this by adding a statement on page 8925, line 22:

“The term “pre-activation” is a well-known phenomenon in heterogeneous ice nucleation, representing a “memory” effect where insoluble ice nuclei show an enhanced ice nucleation ability after they have already been involved in ice crystal formation (Pruppacher and Klett, 1997). As discussed later in this article, a similar mechanism is the most likely explanation for our observations and we therefore chose to use the term pre-activation throughout the manuscript text.”

Additionally, for the sake of completeness, we have extended the description of the various mechanisms for pre-activation in Sect. 4.5 on page 8951, line 21ff with the following statement that refers to an alternative pathway without the need for a preceding ice nucleation event:

“Note that such ice embryos in capillaries of solid particles might also be formed in a subsaturated environment without a preceding ice nucleation event by a two-step process involving freezing of condensed supercooled water (Higuchi and Fukuta, 1966; Kovács et al., 2012).”

Higuchi, K., and Fukuta, N., Ice in Capillaries of Solid Particles and Its Effect on Their Nucleating Ability, *J. Atmos. Sci.*, 23, 187-190, 1966.

Kovács, T., Meldrum, F. C., and Christenson, H. K., Crystal Nucleation without Supersaturation, *J. Phys. Chem. Lett.*, 3, 1602-1606, 2012.

COMMENT:

-Paragraph beginning from the line 26, page 8929 till line 22, page 8930 describes the TDL system. Except first sentence, the remainder of the paragraph can be removed as there are discussions about the instrument calibrations and saturation ratio calculations (these are repeated here) that are not necessary to understand this article. Similarly, I would also recommend removing any unnecessary material from the article to improve the readability.

ANSWER:

Yes, as also suggested by Referee #1, we have greatly condensed the information from Sect. 3.1, not only with respect to the TDL description but also concerning unnecessary details of the chamber operation. From the TDL paragraph, we have indeed only kept the first sentence plus a statement on the accuracy of the system:

“The water vapour pressure, both under cloud-free and in-cloud conditions, is measured in situ with high-resolution tuneable diode laser (TDL) absorption spectroscopy at near-infrared wavelengths between 1368 and 1372 nm with an uncertainty of  $\pm 5\%$ . The absolute accuracy of  $p_w(T)$  is mainly determined by the uncertainty of the line strength of the rovibrational water vapour transition that is scanned during the measurements (Wagner et al., 2008).”

COMMENT:

- I would suggest break down the sub-section 4.5. It has plenty of material to get the readers lost. Also at the end of this section, atmospheric implications are discussed. You may want to create a new section on this topic. Also in this section please discuss how such measurements can be used in the cloud models or can be parameterized.

ANSWER:

It is a good suggestion to further split the rather long section 4.5. It is quite intuitive to create the following four sub-sections:

#### **4.5.1 Overview of the experimental results**

(until page 8949, line 9)

#### **4.5.2 Evidence against ice catalysed solute crystallisation**

(until page 8951, line 20)

#### **4.5.3 An alternative explanation: Pre-activation of the glassy aerosol particles**

(until page 8953, line 20)

#### **4.5.4 Atmospheric implications**

(remaining part).

Concerning the cloud models, we have extended the final sentence as follows:

“The importance of this potential mechanism needs to be assessed by quantitative cloud models in which pre-activated aerosol are tracked until they enter a new cloud and nucleated ice or become deactivated.”

COMMENT:

Minor comments:

-Page 8929, line 7: define PI

ANSWER:

This part has been deleted in the revised manuscript version (unnecessary details of the chamber operation), following the suggestion of Referee #1.

COMMENT:

-Page 8931, line 18-19: please elaborate the sentence ... as the only 99% degree....It is not clear.

ANSWER:

The laser has a finite polarisation ratio of about 100:1, leading to a small residual value for  $I_{\text{back,per}}$  and thus the depolarisation ratio  $\delta$  even in the presence of only spherical particles. We have changed the manuscript text as follows:

“The small background level results from Rayleigh scattering by air molecules and minor misalignments in the optical set-up. Furthermore, the laser has a finite polarisation ratio of about 100:1, leading to a small residual value for  $I_{\text{back,per}}$  and thus the depolarisation ratio  $\delta$ .”

In the paragraph describing the depolarisation measurements, we have cited a new article that has been published in the meantime: “Schnaiter, M., Büttner, S., Möhler, O., Skrotzki, J., Vragel, M., and Wagner, R., Influence of particle size and shape on the backscattering linear depolarisation ratio of small ice crystals – cloud chamber measurements in the context of contrail and cirrus microphysics, Atmos. Chem. Phys. (Discuss.), 12, 15453-15502, 2012.”

#### COMMENT:

-Page 8951, line 26-28: Does the ice survival also depend upon the time? If the dust is exposed to ice sub-saturated conditions for long time periods (days) and then exposed to ice saturated conditions to activate the particle-would you still define this behavior pre-activation? I imagine if you expose the particle for long duration of time, the ice will sublime and may also modify the surface properties, and thus pre-activation behavior may or may not be observed. Therefore I think time parameter becomes important. Any comments? Also, why you think ice survives in the cavities or crevices of the particle surface?

#### ANSWER:

Yes, we have briefly addressed this issue in the context of the higher threshold  $S_{\text{ice}}$  value in run 2C compared to run 3C (page 8954, line 3 ff). We have speculated that this might be related to the longer time period between the homogeneous freezing run and the succeeding pre-activation run in run 2C. But, as outlined by Referee #1, it could also be simply due to the different starting temperatures in the two runs. We also imagine that exposure time will be an important factor for the pre-activation behaviour. Because there was not enough time in our campaign to study this effect in a systematic manner, we had to conclude with the statement that further measurements are needed to resolve this issue. Furthermore, it is not only the time but also the degree of sub-saturation that might modify the pre-activation behaviour. We have extended the paragraph on page 8954, line 3ff. to further highlight the importance of the time parameter:

“The nucleation threshold in the pre-activation run 2C, however, was slightly higher than in typical pre-activation runs conducted only 30 min after the homogeneous freezing run (e.g. run 3C). On the one hand, this might be simply due to the different starting temperatures between run 2C (224 K) and run 3C (230 K). On the other, potential ice embryos in pores might sublime when the particles are exposed to  $S_{\text{ice}} < 1$  for long time periods or the surface properties of the porous glassy aerosol particles might change, thereby explaining the different nucleation thresholds between run 2C and run 3C. Further experiments are needed to confirm whether this was just a singular observation or a general trend which might even get more dominant for longer time periods of one or several days before the second freezing cycle and/or exposure to ambient relative humidities lower than 70% with respect to ice.”

The retention of ice embryos in cavities or capillaries where ice survives even at relative humidities below ice saturation (as proposed in earlier work like e.g. Mossop, 1956) is only one potential explanation for the observed pre-activation behaviour. Equally probable explanations are the imprinting of the ice surface on the substrate or the higher surface area of the ice-cloud processed glassy aerosol particles. One could imagine an experiment where the pre-activated glassy aerosol particles are temporarily raised to a temperature  $>0^{\circ}\text{C}$  and then cooled again to the starting temperature of the pre-activation run. If pre-activation were due to physically trapped ice, the particles would lose their enhanced ice nucleation ability by this treatment. If it were due to a modification of the surface area, the pre-activation behaviour might be conserved.

COMMENT:

-Page 8952, line 2-3: who proposed? Please cite the article.

ANSWER:

This refers to the two citations given three lines below (Vali 2008; Zuberi et al., 2001): Vali (2008) stated that “imprinting the ice configuration on the substrate” could be one possible reason for pre-activation. And as already mentioned above, Zuberi et al. (2001) speculate about a modified surface with “active” sites that closely match the ice lattice, which is formed when ammonium sulphate crystallises in the presence of ice. We will move these two citations to line 3.