Supplementary information for ‘Heterogeneous nucleation of ice particles on glassy aerosols under cirrus conditions’

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1. Supplementary discussions

1.1 Discussion of Figure 2

This figure shows the experimentally determined onset of ice formation and fraction of citric acid aerosol particles which nucleated ice ($f_{\text{ice}}$) in a number of expansion experiments. See Möhler et al.\textsuperscript{1} for details of the AIDA instrumentation used to make these measurements. The black dashed idealised trajectories are based on fits to the RH$_{\text{i}}$ and temperature data shown in Figure 1 and Supplementary Figure 2. Values of $f_{\text{ice}}$ are shown up to the point where the rate of increase in RH$_{\text{i}}$ decreases, i.e. when the growth of ice crystals begins to limit RH$_{\text{i}}$ at about $3\times10^{-3}$. Uncertainties in RH$_{\text{i}}$ are indicated. Experiments 1-5 were with the same citric acid aerosol in the chamber, which was initially introduced at 234 K before the whole chamber was cooled. Experiments 6 and 7 were performed in an identical way to 1-5, but where the citric acid aerosol was introduced directly to the chamber at 194 and 202 K, respectively. Only ice onset conditions are shown for experiments 6 and 7 for clarity. $f_{\text{ice}}$ for runs 6 and 7 were very similar to runs 2 and 3, indicating the temperature history of the glassy aerosol did not influence its ice nucleating properties. The solid green line is a fit to AIDA literature data for homogeneous ice nucleation onset conditions for a liquid sulphuric acid aerosol\textsuperscript{2}. Note that the order of the experiments (1-5) was such that we went from the liquid regime to the glassy regime, back to the liquid regime and finally...
back to the glassy regime. Since all five of these experiments were performed with the same citric acid aerosol we can be confident that heterogeneous nucleation observed in the glassy regime could not have been caused by impurities or crystalline citric acid and must be an intrinsic property of the glassy aerosol particles.

1.2 Discussion of the relationship between current AIDA study and previous emulsion studies.

The vertical red line in Supplementary Figure 1 illustrates a typical trajectory through the state diagram employed by Murray\(^3\) and Zobrist et al.\(^4\). In these literature experiments droplets were suspended in oil (an emulsion) and then cooled down, hence their concentration was fixed. These experiments were ideal for mapping the state diagram shown in Supplementary Figure 1 and also those presented in Zobrist et al.\(^4\). However, these trajectories do not simulate the conditions experienced by atmospheric aerosol. In the atmosphere, as an air parcel cools the relative humidity increases and liquid aqueous aerosol will take up water to become more dilute. Before our experiments in the AIDA chamber, it was unknown how glassy aqueous aerosol would behave under the atmospherically relevant conditions; that is, of increasing humidity and simultaneously decreasing temperature.

The authors of the previous experimental studies\(^3,4\) conclude that atmospheric aerosol may be glassy. They also showed that homogeneous nucleation and crystal growth was suppressed in this glassy material, but they were only able to speculate what the impact would be on cloud formation. Murray\(^3\) suggested that glassy aerosol would not take up water readily and hence droplets would not freeze homogeneously. Zobrist \textit{et al.}\(^4\) suggested that glassy aerosol would undergo a deliquescence-like transition to become liquid as soon as the humidity crossed some threshold. The experimental evidence presented in this paper shows that glassy aerosol particles do not undergo a
prompt deliquescence-like transition (we do not observe a burst of ice particles at the homogeneous limit, as would be expected if liquid aerosol were present). Zobrist et al.\textsuperscript{4} also state that glassy aerosol would be unlikely to nucleate ice heterogeneously. The experiments in the AIDA chamber clearly show this to be incorrect and glassy aerosol particles do serve as effective ice nuclei.

1.3 Discussion of the relationship between relative humidity, water activity and solution concentration

The water content of liquid aqueous aerosol particles in the Earth’s atmosphere is mainly determined by the relative humidity (RH\textsubscript{w}, relative humidity with respect to liquid water) of the air in which they are suspended. RH\textsubscript{w} is the partial pressure of water vapour (\(P_{\text{H}_2\text{O}}\)) divided by the saturation vapour pressure of pure liquid water (\(P_{\text{liquid}}\)). The water activity (\(a_w\)) of a solution is also defined as \(P_{\text{H}_2\text{O}}/P_{\text{liquid}}\); hence, when a droplet is in equilibrium with the surrounding atmosphere its \(a_w\) is equal to RH\textsubscript{w} (expressed in a fractional form). Since, \(a_w\) is directly related to the concentration of a solution (\(a_w = \gamma x_w\), where \(\gamma\) is the activity coefficient and \(x_w\) is the concentration of water in a solution) the RH\textsubscript{w} of an atmosphere controls the concentration of liquid solution droplets. In the AIDA chamber prior to expansion, RH\textsubscript{w} is controlled by the ice coated walls of the chamber, hence the composition of liquid aerosol droplets is defined by the ice-liquid equilibrium line in Supplementary Figure 1. Obviously, the same rules do not apply for glassy droplets. Diffusion within glassy solids is negligible and they therefore do not remain in equilibrium with their surroundings, hence their composition is fixed at the value when they first became a glass. For citric acid aerosol particles cooled along the ice-liquid equilibrium line in the AIDA chamber, this occurs at approximately 77 wt\% at 212 K. The rate at which glassy droplets take up water in a humid environment to become liquid, should be investigated in the future.
1.4 Discussion of citric acid as a proxy for atmospheric oxygenated organic compounds

Aqueous citric acid was chosen as a model system because: *i* it has similar functionality to oxygenated organic compounds known to exist in atmospheric aerosols;  

*ii* its glass forming properties are similar to a range of other atmospherically relevant aqueous organic solutions and aqueous organic-sulphate mixtures; and  

*iii* its state diagram was recently mapped out.

1.5 The determination of the glass transition temperature of 212 K

The $T_g$ of a solution depends on both the concentration of the solution and its temperature. In our case the chamber was close to 100% RH$_i$ before expansion and the composition was defined by the ice-liquid equilibrium line in the state diagram (see Supplementary Figure 1 and also the Supplementary Discussion 1.3). $T_g$ under these conditions was determined by the point at which the glass transition and the ice-liquid equilibrium line cross. According to the state diagram for citric acid (Supplementary Figure 1) a chamber temperature (prior to an expansion, when RH$_i$ in the chamber was close to 100%) of above 212 K would result in a liquid solution aerosol, whereas a lower temperature would result in a glassy aerosol.
2. Supplementary Figures

Supplementary Figure 1. State diagram for aqueous citric acid solution, adapted from Murray\textsuperscript{3}. The numbering of the black arrows corresponds to the numbering of the experiments shown in Figure 2. Runs 1 and 4 start with aerosol in the liquid regime, whereas runs 2, 3, and 5 start in the glassy regime. When droplets start as liquid aerosol they take up water during the expansion, as temperature falls and RH increases, until they become sufficiently dilute that they freeze homogeneously. The trajectories starting in the glassy regime are dashed since the glassy aerosol do not stay in equilibrium with their surroundings and will not readily take up water. These are the trajectories that would have been expected if these droplets were liquid.
Supplementary Figure 2. Ice number densities in three separate expansion experiments. The panels are the same as for Figure 2 in the main paper, but for runs 1, 2 and 5 (corresponding to numbering of experiments in Figure 2). Note that the uncertainty in RH_i in run 2 is greater than the uncertainty in the other runs. This was partly due to the much lower temperature, where water vapour concentrations were lower. Within uncertainty the number of ice crystals nucleating is the same in run 2 and 3. We have chosen to parameterise run 3 for use in the model and assume this parameterisation is valid at lower temperatures.
Supplementary Figure 3. Input parameters for the 1-dimensional Advanced Particle Simulation Code used for the model runs shown in Figure 3, 4 and Supplementary Figure 4. These are idealised profiles of temperature, pressure, RHq, and water mixing ratio. The values are within the range of aircraft measurements in the TTL, but the RHq profile is shaped in order to force cloud formation in a height range of 550 m.

Supplementary Figure 4. Model result for ice particle radius \( R \) and ice water content (IWC) for the same model case that is shown in Figure 4 of the main paper. Heterogeneous nucleation on glassy particles (HET) is included for a
range of cooling rates. For these model runs we used $f_{\text{ice}}$ based on experimental run 3, the initial profiles in Supplementary Figure 3 and a total aerosol concentration of 100 cm$^{-3}$, 50% of which were glassy. The parameters are averaged between 17.25 and 17.35 km. For the largest cooling rates, model runs are truncated when particles began to sediment out of this height range.

Supplementary Figure 5. Time profiles of $N_{\text{ice}}$, $R$, IWC and RH, for model sensitivity runs varying the temperature profile and also the number of glassy aerosol particles. These HET model runs were the same as in Figures 3 (main paper, i.e. 0.76 cm s$^{-1}$ cooling rate, total number of aerosol = 100 cm$^{-3}$) except that the temperature profile (Supplementary Figure 3) was shifted down by 5 K (T-5) and up by 10 K (T+10) compared to the standard (T0); thus the initial temperature in the cloud forming region of the model was varied between 185
and 200 K. The mixing ratio of water vapour was varied in order to maintain the RH, shown in Supplementary Figure 3. The extra water vapour at +10 K allowed stronger growth of ice crystals and sedimentation was clearly important in the $N_{\text{ice}}$ plot. The dashed lines ($N_{\text{glass}} = 10$) are for a run with the standard temperature profile (T0), but where the fraction of aerosol which were glassy was reduced to 10%, i.e. there were only 10 cm$^{-3}$ glassy aerosol as opposed to 50 cm$^{-3}$. It is clear from these sensitivity tests that our conclusion, heterogeneous nucleation on glassy aerosol leads to a small number of ice crystals and high in-cloud humidity, is valid over a wide range of TTL conditions.

3. Referenced


