

Reply to Referee #1 (Russell Perkins):

We appreciate your constructive feedback. After each comment, our response is given in italics, with revised text in red and unchanged text for context in blue.

1) Lines 170-180, sample preparation: More details should be included on the process for making the glassy sample: temperatures used, quench process, milling size, any characterization of final material.

*We have replaced the first paragraph at line 172 as follows :*

The crystalline K-feldspar comes from the Bureau of Analysed Samples (BCS-CRM No. 376/1), as used by Atkinson et al. 2013. ~~No further processing of this sample was done.~~ The sample was crushed in a ball mill with agate balls before being sieved using a fine mesh (aperture size 20  $\mu\text{m}$ ).

The glassy K-feldspar sample was made from the crystalline sample melted in a platinum crucible. It was held at 1250°C overnight to remove moisture, before being heated to 1600°C for two hours. After this, the sample was removed from the furnace and allowed to quench in air. A few sections of the glass formed were examined under a polarizing microscope and no birefringent regions were observed. The glassy sample was then crushed and sieved using the same method described for the crystalline sample.

2) Lines 170-180: Feldspar materials can weather in aqueous solution, especially when acidic. This may be particularly important for ice nucleation, which depends on the structure of the mineral surface. A brief discussion of this is perhaps warranted, given that samples were stored suspended for up to a week. The glassy samples may also weather differently from the crystalline one. See refs:

Lee, M. R. & Parsons, I. Microtextural controls of weathering of perthitic alkali feldspars. *Geochimica et Cosmochimica Acta* 59, 4465–4488 (1995). [https://doi.org/10.1016/0016-7037\(95\)00255-X](https://doi.org/10.1016/0016-7037(95)00255-X)

Lee, M. R., Hodson, M. E. & Parsons, I. The role of intragranular microtextures and microstructures in chemical and mechanical weathering: direct comparisons of experimentally and naturally weathered alkali feldspars. *Geochimica et Cosmochimica Acta* 62, 2771–2788 (1998). [https://doi.org/10.1016/S0016-7037\(98\)00200-2](https://doi.org/10.1016/S0016-7037(98)00200-2)

*After acid cleaning the glassware used to store the samples was very thoroughly rinsed in Milli-Q 18.2 M $\Omega$  water. The K-feldspar was not exposed to any extremes of pH. Recent literature suggests that the influence of aging in near-neutral aqueous solutions for the short periods our samples were stored is likely to be minor.*

*The following paragraph has been added to the end of the sample preparation section:*

Feldspar materials are susceptible to surface changes in aqueous solutions (Lee and Parsons, 1995) and when exposed to extreme pH (Kumar et al., 2018), which could lead to a change in their ice nucleating ability. Peckhaus et al. (2016) measured a 2°C decrease in freezing temperatures of K-feldspar stored in aqueous solution for five months. However, Kumar et al. (2018) recorded no change in the ice nucleating ability of crystalline K-feldspar after one week in water suspension and Harrison et al. (2016) noted no significant changes in freezing temperatures of crystalline K-feldspar due to time spent in water suspension. We assume that any aging of K-feldspar in aqueous solution is sufficiently slow to not

have an effect on our results. Due to the identical chemical composition of the glassy sample we assume that any aging effects are similarly slow.

3) Paragraph around line 180: It doesn't appear that stochastic/binomial errors in  $n(T)$  were considered for the error estimates, which is the conventional way of doing this analysis and is almost always the dominant source of error. This should be remedied. A "score confidence interval" is the best approach at low numbers of freezing events. Justification for this, as well as equations for the calculation (eq. 2), can be found in:

Agresti, A. & Coull, B. A. Approximate Is Better than 'Exact' for Interval Estimation of Binomial Proportions. *The American Statistician* 52, 119–126 (1998). <https://doi.org/10.2307/2685469>

*The analysis of the data has been changed significantly. In order to include the score confidence interval the data has been binned into 0.5°C bins. An example histogram with errors is shown in the updated supplementary information. The stochastic/binomial errors were then propagated with the surface area errors. We find that the stochastic error dominates at higher temperature, while the surface area error dominates at lower temperatures. Also, since this analysis was done we have started using an improved method to fit the liquid proportion curves which is also detailed in the supplementary information.*

*Figure 5 has been updated to reflect these changes.*

*The results and discussion section has been modified to reflect these changes (line 200):*

~~The dashed lines are generalised logistic functions (see supplementary information). These have no basis in theory, but provide good, monotonically decreasing, lines of best fit which can be differentiated analytically.~~ The solid lines are taken from a fit assuming the liquid proportion curves follow a non-homogeneous Poisson process, referring to the fact that the rate constant is changing as a function of temperature. A full derivation of the fit can be found in the supplementary information.

*A brief error section has been added to the supplementary information as follows:*

Stochastic errors were estimated using the Wilson score confidence interval on each temperature bin with more than one nucleation event. An example is shown in Figure S1. The errors in the liquid proportion were calculated based on how the minimum and maximum number of freezing events would affect the liquid proportion at that temperature bin, assuming the mean number of events were seen in all higher temperature bins. These errors were then combined with the errors in INP area in the calculation of  $n_s$  and  $J$  using standard propagation techniques.

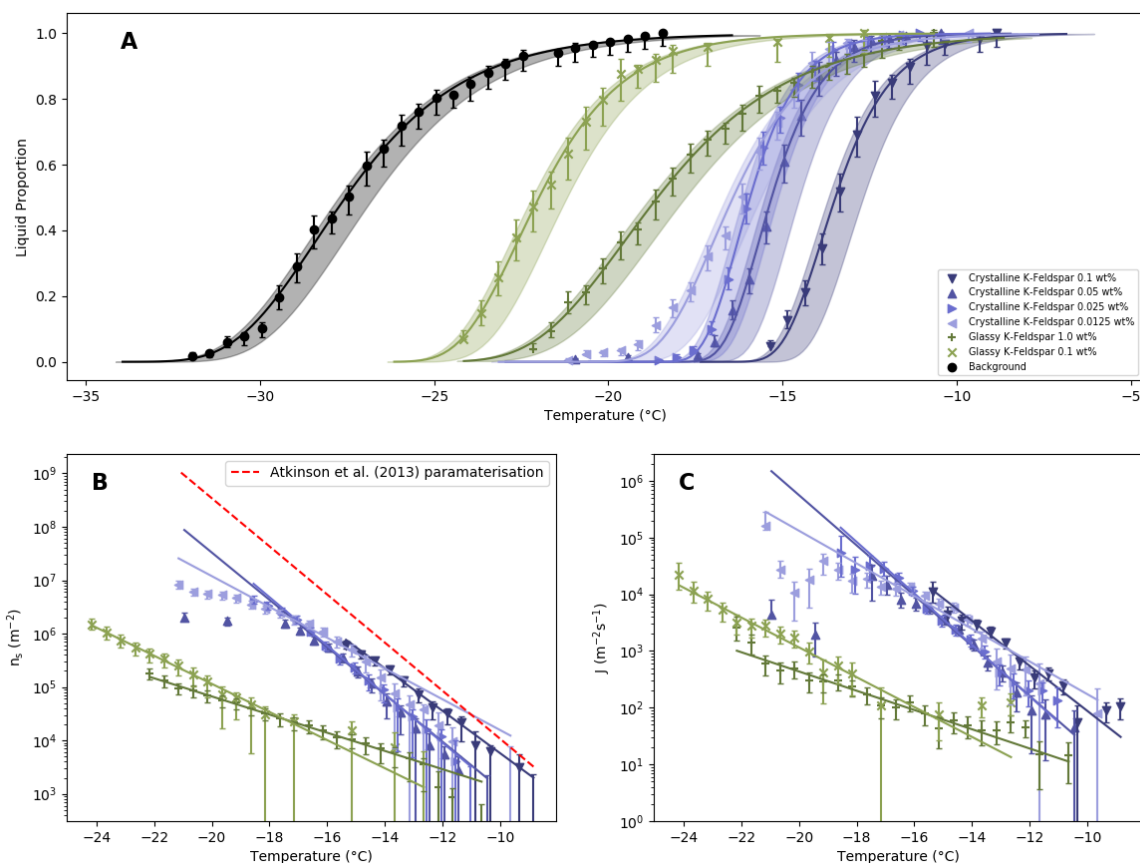


Figure 5. **A.** Liquid proportion frozen fraction curves for 1  $\mu$ l droplets of water containing different fractions of glassy and crystalline K-Feldspar. The background freezing rate of the instrument is also shown as the pure water frozen fraction. Temperature errors are shown by the shading. Details on the lines of best fit can be found in the supplementary information. **B.** Ice nucleation active site density, normalised by the surface area present in each droplet. The red dashed line is the parameterisation from Atkinson et al. (2013) which is partly based on microlitre sized droplets with similar concentrations to those used here. **C.** Nucleation Freezing rates normalised by the surface area present in each droplet. The nucleation rate calculated from classical nucleation theory. Only the error bars of the first datapoint of each sample are shown for clarity.

4) Due to the low mass fractions used in the solutions under study, effects noted in the following paper may become significant Although I believe good overlap in  $n_s$  values (as shown in this manuscript) is an indication that corrections are not necessary:

Beydoun, H., Polen, M. & Sullivan, R. C. Effect of particle surface area on ice active site densities retrieved from droplet freezing spectra. Atmospheric Chemistry and Physics 16, 13359–13378 (2016). <https://doi.org/10.5194/acp-16-13359-2016>

As our sample volumes are relatively large, the expected percentage error from sampling ( $1/\sqrt{n}$  for  $n$  particles per droplet) is low. Even assuming that after sieving every particle was 20  $\mu$ m in diameter, we would still expect over 100 particles per droplet at the lowest concentration used, and the reality will be

*many more. Furthermore, each suspension was ultrasonicated for 15 minutes immediately prior to pipetting to break up aggregates.*

*To confirm that the effect you bring up was considered we have added the following (line 199):*

There are also errors associated with the masses of K-feldspar and water when making suspensions, the volume of each droplet pipetted, and amount of material which settled out of suspension during pipetting (Tarn et al. 2018). These are particularly important for small droplet volumes and low concentrations (Beydoun et al. 2016, Knopf et al. 2020), however due to the relatively large droplet volumes used here they are insignificant compared to surface area per mass error.

Knopf, D. A. et al., (2020), NPJ Clim. Atmos. Sci. , 2, <https://doi.org/10.1038/s41612-020-0106-4>