

Reply to Referee #2 (Anonymous):

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.

Minor comments: The most important change to my mind would be some discussion of the likely limitations of the approach. This would be helpful for anyone looking to adapt pyroelectric sensors to other droplet freezing instruments or sample types. Specifically, some estimate of minimum droplet size and minimum supercooling (or combinations thereof) that could be detected would be of interest. For instance, could this instrument reliably pick out freezing of microlitre droplets at around  $-2^{\circ}\text{C}$  as can be induced by Snomax? (Wex et al., 2015) In this scenario the temperature change on freezing would be less than in the datasets presented and the freezing events would occur at much smaller time intervals.

*The smallest droplet size detected during testing was  $0.2\ \mu\text{l}$ . However, for this droplet size we came up against the non-uniform sensitivity of the PVDF we used in our experiments. The point that there is a pay-off between droplet size and minimum supercooling is a good one, which we have also added to the revised text at line 170:*

The spatial variation in pyroelectric coefficient also means that droplets smaller than  $1\ \mu\text{l}$  could be detected in places. However, in order to guarantee detection across the whole surface the minimum size was set at  $1\ \mu\text{l}$ . The minimum droplet size detectable is also dependent on the minimum supercooling: assuming the droplet temperature returns to  $0^{\circ}\text{C}$  before freezing completely, the lower the supercooling, the lower will be the absolute temperature change on freezing and hence the lower the voltage pulse detected by the pyroelectric foil.

*Regarding smaller time intervals the voltage was sampled at  $1\text{kHz}$ , and this was sufficient to detect all droplet freezing events. However, the sampling rate could be increased by several orders of magnitude by using a higher bandwidth analogue to digital converter, so this is unlikely to prove a limiting factor. Even with the converter used, the sampling rate could be increased to  $50\text{ kHz}$ .*

*We have added the following at line 142,*

The output from the charge amplifier was monitored using an analogue to digital converter (NI USB-6002), sampled at  $1\text{ kHz}$ , which is fast enough to detect all droplets freezing, without creating unnecessarily large data files. For INPs that freeze over a very narrow temperature range, the sampling rate for this analogue to digital converter could be increased to  $50\text{ kHz}$  to reduce the chance of near simultaneous freezes not being detected as separate events.

My view is that the rates presented are better described as freezing rates rather than nucleation rates (Vali et al., 2015). Also, the nucleation rate is not derived from classical nucleation theory as stated in the caption to Fig. 5. Classical nucleation theory could be used to describe the nucleation rate but is not needed for calculating rates from experimental data.

We agree. The mention of classical nucleation theory in the caption of Figure 5 has been removed and we changed the text at line 222 and in the figure caption to refer to freezing rate.

The value of  $j_{\text{het}}$  found for glassy and crystalline K-feldspar here represents the freezing rate (Vali 2014) divided by the surface area measured by BET the average particle.

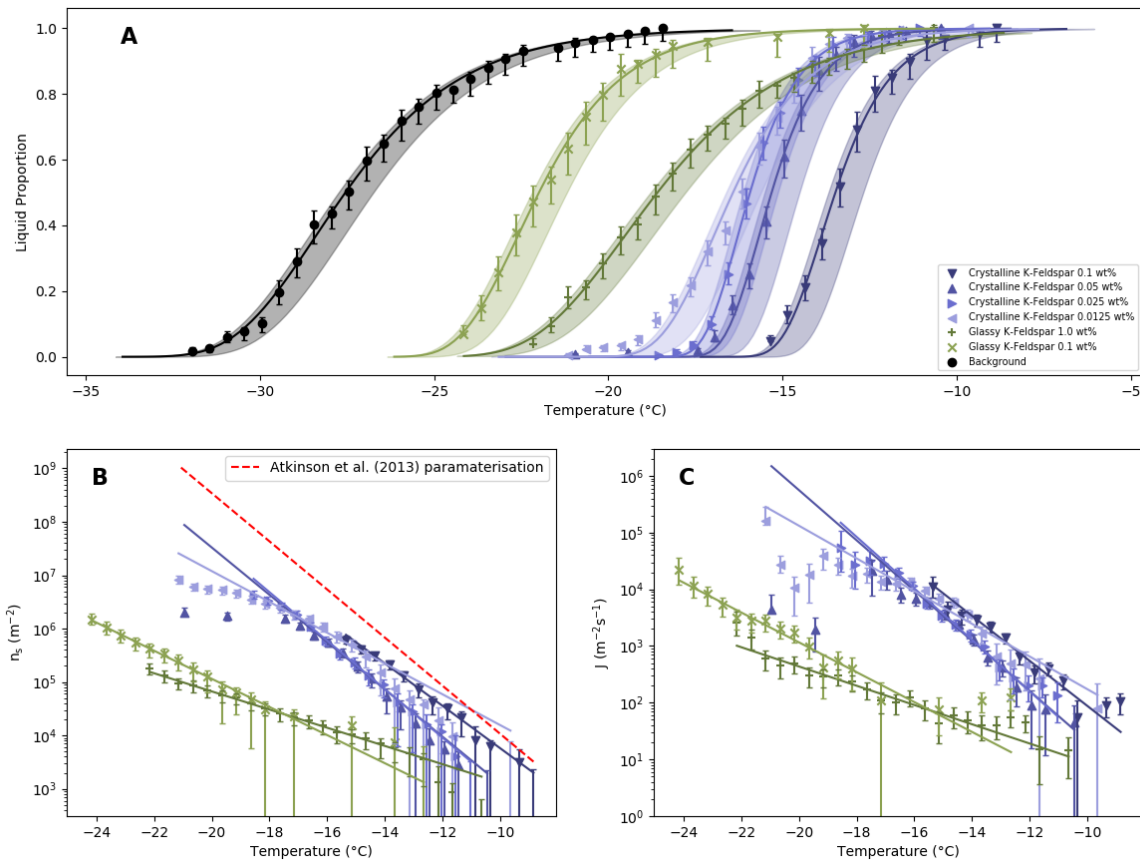


Figure 5. **A.** Liquid proportion ~~Frozen fraction~~ curves for 1  $\mu$ l droplets of water containing different fractions of glassy and crystalline K-Feldspar. The background freezing rate of the instrument is also shown ~~as the pure water frozen fraction~~. Temperature errors are shown by the shading. 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.

As mentioned by the other referees a little more discussion of the nature of the samples and of the preparation of the glass samples would be of useful

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  $\mu$ 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.