Authors' response to reviewers' comments for "Microfluidic Immersion Freezing of Binary Mineral Mixtures Containing Microcline, Montmorillonite, or Quartz" by Nadia Shardt, Florin N. Isenrich, Julia Nette, Christopher Dreimol, Ning Ma, Zamin A. Kanji, Andrew J. deMello, Claudia Marcolli

We thank the reviewers for their time and their suggestions that have significantly improved our manuscript. Below, we provide our responses and summarise the changes that we have made with page and line numbers referring to the uploaded document with tracked changes. Other minor revisions were also made to improve the manuscript, and we updated the TOC graphic.

Reviewer 2

Schardt et al. performed a study of the ice-nucleating activity of mixtures of three different mineral types, in addition to the activity of the individual minerals within a droplet microfluidic device. The main findings showed that K-feldspar microcline dominated the ice-nucleating activity in the binary mixtures when present, even at much lower concentrations than the other mineral in the mixture; While this is often generally accepted as being the case, this is the first time to my knowledge that it has actually been shown rather than being simply expected. An interesting finding was that a mixture of montmorillonite-microcline showed a slight decrease in ice-nucleating activity at cooler temperatures compared to microcline only and the authors provide a theoretical explanation for this phenomenon.

The experiments are well designed and performed and the results confirm some pre-existing notions while offering new interesting findings about montmorillonite-microcline that warrant further exploration. However, I am not convinced that there is enough here for publication as a research article in for ACP as is and may be more suitable for publication as an ACP Measurement Report or perhaps as a paper in AMT. What would elevate the manuscript for publication in ACP would be a further small subset of experiments to test the hypothesis about the effect of Na+ ions in solution from the montmorillonite influencing the microcline. This could, for example, be through testing of the leaching of Na+ from montmorillonite at different concentrations via methods such as ICP or atomic absorption spectroscopy and testing of the influence of these concentrations of montmorillonite on microcline and the influence of Na+ concentrations on microcline. Given this, I have a few major comments and some minor comments.

Major comments:

1. When each experiment was performed three times, does this mean that a new suspension was prepared and tested each time, or three repeats were performed on the same suspension? I'd be intrigued as to whether a new suspension of "mc 0.001 wt% + mm 0.1 wt%" would act in the same manner. It is also interesting that the bulk of the slope for this binary mixture is very similar to one of the mc 0.001 wt% repeats; there is more of a "tail" as the authors mention, but overall the main part of the line does not look vastly different to this particular mc 0.001 wt% experiment.

   Authors' response

   The three repeats for each experimental condition were prepared from the same starting suspension. We agree with the reviewer that additional experiments from independent suspensions of microcline and montmorillonite at those concentrations would be warranted to test our hypothesis more rigorously. One example where we do have multiple independent suspensions at the same concentration is that of 0.01 wt% microcline (pure microcline, mixed with 0.1 wt% quartz, and mixed with 0.1 wt% mm). In each of these experiments, the frozen fractions were indistinguishable, with the same temperature for the onset and end of freezing. However, as the reviewer mentioned, we cannot exclude the possibility that experimental

error or variability contributed to the observed "tail" of the mc+mm mixture, as shown by the predicted frozen fraction that assumes lower microcline nucleation temperatures.

Changes to manuscript

- Page 5 line 31: added "from the same starting suspension"
- Page 19 starting on line 20: added "Yet we cannot exclude the possibility that experimental variability in the determination of microcline's ice nucleation activity explains the observed tail of the microcline–montmorillonite mixture compared to the microcline–quartz mixture. As shown in Fig. 3, the trend of n_s vs. T for microcline derived from experimental frozen fractions does not collapse onto a single line over all studied concentrations, and in Fig. 6, the obtained fit for n_s to this data thus yields a frozen fraction at lower temperatures (dashed blue line) than those observed experimentally at a nominal microcline concentration of 0.001 wt.% (open diamonds). If the true activity of 0.001 wt.% microcline is represented by the dashed blue line, then the frozen fraction observed in Fig. 6a for microcline–quartz is explained by the inherent activity of a 0.1 wt.% quartz suspension, and the frozen fraction observed in Fig. 6b for microcline–montmorillonite is explained by the additive activity of each constituent, as depicted by the solid purple line calculated using Eq. (4)."

1. Page 15: This section is an interesting discussion and could explain some of the effects seen in the mm + mc curve. This is arguably the key finding of the paper,and would benefit greatly from exploration of this. For example, could the concentration of Na+ ions leached from the montmorillonite be estimated or measured and then experiments performed on microcline using aqueous solutions containing similar concentrations of Na+ or a range of concentrations to test the hypothesis?

Authors' response

We thank the reviewer for their suggestion for testing the hypothesis of ion exchange at the microcline surface. However, given the variability we now quantify in the nucleation site density of microcline and its importance for explaining the observed frozen fractions, further experiments would also need to be done to determine the variability in the observed "tail" of the microcline–montmorillonite mixture (as the reviewer alluded to in their first comment). Within the scope of the present paper, we do not aim to discriminate between the effect of ion exchange and the variability of the observed "tail".

1. Page 16, line 11: The ATD discussion should be in its own section. However, it is unclear why ATD is being discussed here. What is the context for its inclusion amongst a discussion about binary mixtures of minerals? I appreciate that ATD is in itself a mixture of minerals, but there is no apparent link or discussion between ATD and the other results shown here.

Authors' response and changes to manuscript

Upon the reviewer's suggestion, we have added a section heading for the results pertaining to ATD, and we now make predictions of frozen fraction for ATD based on the measurements performed on the pure minerals, with changes as outlined in our response to the first reviewer's first general remark.

Minor comments:

1. Page 2 line 7: Was XRD not performed on the quartz sample to ensure purity/composition?

   Authors' response
   In previous work from our group, the same quartz sample purchased from Sigma Aldrich was characterized by XRD to confirm the manufacturer's specification with 98.9% quartz (Kumar et al. Atmos. Chem. Phys., 19, 6035–6058, 2019).

1. Page 5, line 14: Some quartzes have been shown to exhibit changes in ice-nucleating activity even when suspended in water for a relatively short time (see Harrison et al. (2019; doi: 10.5194/acp-19-11343-2019)), while sonication is also a very energetic technique. Have the influences of these effects been assessed here to ensure there is no loss in quartz activity due to being in suspension for too long (particularly if also being heated by the sonication process)? Or the potential effect of sonication itself on activity – though I am unaware of any mention in the literature that sonication has an adverse effect.

   Authors' response
   All quartz samples, whether suspended alone or in a mixture, were treated in the same manner in terms of time spent in solution, so we assume that any potential impact of aging would be the same for all samples. We also note that the aging of quartz samples in water was reported by Kumar et al. (2019) to occur only in glass vials over a time period of days. In polypropylene Falcon tubes (as used in our study), the activity of quartz did not change after at least five days.

1. Page 5, line 20: What was the SEM analysis for? Determination of particle size distribution? EDS of the particles for composition analysis?

   Authors' response
   The SEM analysis was used in a qualitative manner to confirm that the particle sizes after filtration were indeed sufficiently small for improved uniformity in encapsulation between droplets. The quality and quantity of SEM images to determine particle size distribution was insufficient; rather, we used DVS to determine the BET surface area of the particles. The small sizes and morphologies of particles in the SEM images corroborates the high BET surface areas obtained.

1. Section 2.3: The CNN-Expert method seems to be the best way of analysing the data is a rapid but more accurate (than CNN only) manner, but not as good as "Expert only". Is the slight lack of accuracy compared to "Expert only" accounted for in the uncertainties in the data later on?

   Authors' response
   In our analysis, we assume the variability between replicate runs to be a greater source of variation in the results for frozen fraction than that arising from the slight difference between the CNN–Expert vs. the Expert only approaches for image analysis. While the Expert only is designated as the "true" classification, it may itself be subject to expert classification error (which is challenging to quantify in a rapid manner).

1. Page 10, line 8: Include reference to Harrison et al. (2019) when referring to variation in activity.

   Authors' response and change to manuscript
   We have added Harrison et al. (2019) to this sentence for improved completeness.

1. Page 10, line 25: As the authors discuss, it would make sense that the ns(T) values may be lower than expected since the larger particles have been removed compared to in the literature. Have the authors also considered that these very dense particles might also be settling in the syringe and tubing, thereby further reducing the size range of the particles that can actually enter the device for analysis?

Authors' response
We estimate that the sizes of particles where gravity separation would be relevant exceed those that are present after filtration. Given the time scale of the experiments performed, the actual size range of the particles entering the device would not be expected to change substantially.

1. Page 10, line 25: Also, it is very interesting to see the results for microcline compared to the literature, with the ns(T) values falling short of the "expected" activity. Both Peckhaus et al. (2016; doi: 10.5194/acp-16-11477-2016) and Tarn et al. (2018; doi: 10.1007/s10404-018-2069-x) saw similar behaviour when comparing microcline results from similar sized droplets to the literature and this phenomena likely warrants some attention in future. Further, Harrison et al. (2016; doi: 10.5194/acp-16-10927-2016) demonstrated that different microclines can have varying activity. Many microcline studies tend to specifically use one of a handful of samples to ensure results can be compared across techniques/experiments.

Authors' response
We thank the reviewer for discussing these results from the literature to interpret our reported results. Because of this variability in activity we designed our experiments to systematically measure each pure component (especially microcline) over a wide range of concentrations before performing experiments on binary mixtures. We provide a brief discussion of the variability in the manuscript, including the effect that the assumed specific area has on the calculated n_s.

1. Page 10, line 27: As noted in an earlier comment, some quartzes can lose activity after being suspended in water for even a relatively short period of time and this is worth bearing in mind here.

Authors' response
As we indicated in our previous response, there is no loss of activity in quartz expected when polypropylene Falcon tubes are used for sample handling.

1. Figure 3: Please add y-error bars to the ns(T) values, these should at least be calculated from the uncertainty in droplet volume, uncertainties in the measurement of concentration when preparing the suspensions and the BET values.

Authors' response
We thank the reviewer for the suggestion. We have chosen to illustrate the experimental reproducibility and the corresponding variation in experimentally-derived n_s values by plotting each experiment as an independent data series. A large portion of the uncertainty in the derived n_s values can be attributed to the stochasticity of nucleation, as investigated in the literature through Monte Carlo simulations. We used the recommendations by Alpert & Knopf (2016) to design our experiments with around 100 droplets and three replicates to reduce the uncertainty in the obtained frozen fractions and derived quantities. A further sensitivity analysis of the most important contributions to the uncertainty of n_s values would be an interesting future direction.

1. Page 12, line 8 (and Figure 4): It is unclear what the SEM analysis is for, I had assumed particle size distribution as mentioned in the text but this does not seem to have been measured.

Authors' response
As mentioned in our previous response to a similar note earlier, we used SEM as a complementary technique to qualitatively confirm the particle size as support .the BET measurements.

1. Page 13, line 1: This part on binary materials should have its own section with heading.

Authors' response and change to manuscript
We agree with the reviewer's suggestion and have added section headings "3.1 Freezing Temperatures of Pure Mineral Suspensions" and "3.2 Freezing Temperatures of Binary Mineral Mixtures".

1. Was there no background (pure water) assay performed for these experiments? The baseline data is all from Isenrich et al. (2022), which is quite unusual given that some of the results in this study encroach into the homogeneous freezing area.

Authors' response
We report the pure water data from Isenrich et al. (2022) as our background data, because it was performed contemporaneously as part of the same experimental campaign, and it is representative of the freezing behavior for pure water in the setup. We also performed another series of experiments on the homogeneous freezing of water with two droplet sizes and cooling rates to confirm the robustness of the instrument and observed the same nucleation rates across all tested conditions (*Phys. Chem. Chem. Phys.*, 2022, **24**, 28213-28221 DOI: 10.1039/D2CP03896J). To prevent contamination in the tubing between runs, the same tubing was only reused for experiments with the same mineral, and the lower concentration experiments were completed first. The tubing was also flushed with isopropanol after each day of experiments to avoid contamination.

Changes to manuscript
- Page 5 starting on line 24: added "To remove the possibility for contamination in the inlet PTFE tubing to the microfluidic device, the same tubing was only reused for experiments with the same mineral. The tubing was also flushed with isopropanol after each day of experiments. If multiple mineral concentrations were investigated on the same day, the lower concentration of each mineral suspension was investigated first to avoid potential contamination of subsequent experiments."
- Page 11 line 15: added "contemporaneously-measured pure water droplets ~~using the same experimental setup~~"

1. Page 15, line 7: "SWy-2 montmorillonite is a clay mineral that releases Na+ ions when suspended in water and these ions may exchange with the K+ ions at the surface of the microcline." – please provide a reference for this.

Authors' response
The cation exchange capacity of montmorillonite is indicated in the specification sheet of SWy-2 provided by the Clay Mineral Society, and the exchange with K^+ ions from the surface of the microcline is our hypothesized mechanism for the interaction between montmorillonite and microcline. Such an ion exchange mechanism has been hypothesized for other studied systems, such as microcline and dissociated species (Kumar et al. (2018)). Thus, we do not

add a reference for our hypothesis directly but clarify it to be so based on the literature discussed in the sentences that follow it.

Change to manuscript

- Page 19, line 4: added "we hypothesize that"

1. Page 16, line 14: The ATD has also not been processed in the same manner as the other minerals apparently, since a specific surface area has now been assumed based on another study for a particle size range that is completely different to that used for the other minerals (which had been filtered to 0.45 micron). Was the ATD also filtered? This becomes more confusing as it is revealed that the particle size has a large effect on the specific surface area, but it is unclear what particle sizes were used in these experiments and in that case why a normalisation to 22 m2/g is used.

Authors' response

We confirm that the ATD has not been processed in the same manner. We attempted to filter the ATD, but there was insufficient material remaining to quantify the composition by XRD. As a result, we performed experiments with un-filtered ATD as received by the provider (page 5 on lines 22–24). The ATD used was A1 Ultrafine, which has a documented size distribution with 95.5–97.5 % of particles being < 11 µm in size, and to represent this size distribution, we used 22 m^2/g as the specific surface area, according to the data reported by Ibrahim et al. (2018).

Changes to manuscript

- Page 22, moved the following sentences to line 7 instead of at the end of the paragraph: "The specific surface area has been shown to vary as a function of particle size; for example, Ibrahim et al. (2018) reported a value of 37.8 ± 1.7 m^2/g for the 0–3 µm nominal size range and a value of 2.8 ± 0.4 m^2/g for the 40–80 µm nominal size range. We assume a specific surface area of 22 m^2/g from Ibrahim et al. (2018) for the fraction of particle sizes between 5 and 10 µm to represent the specific surface area of the A1 Ultrafine ATD investigated herein, which is documented to have 95.5–97.5 % of particles being < 11 µm in size by the supplier."

1. Page 18, line 8: This should also be a new section.

Authors' response and change to manuscript

We thank the reviewer for their suggestion, and to improve the structure of the manuscript, we have moved this section to be placed before the presentation and discussion of ATD results and added a section heading "3.3 Freezing Temperatures of Arizona Test Dust (ATD) Suspensions".

1. Figure A1: Given that the feldspar sample contained 97 % microcline, should the literature parameterisations used for comparisons in the earlier figures not be scaled to this? I assume the literature parameterisation (e.g. Harrison et al. (2019)) is represented as 100 % microcline? Perhaps it would not make a substantial difference, but given the experimental values reported here are lower than the literature data this could be one of the reasons (in addition to those discussed elsewhere).

Authors' response

We agree with the reviewer that the 97% content of our microcline provides a negligible source of error compared to other contributions, i.e., variation in inherent sample activity from different sources and uncertainty in the specific surface area. It is also not fully clear

whether the literature parameterisations normalise for the purity of the samples reported, such as in Atkinson et al. (2013), where the purity of K-feldspar was reported to be 80.4 wt.%.

1. Page 19, line 34: "the freezing behavior of Arizona Test Dust (ultrafine fraction) also followed its mineralogical composition" – I do not think that this was particularly discussed in this way in the Results section, it was very unclear what the point or outcome of these ATD experiments was, particularly since none of the other mineral data were plotted.

Authors' response

Also raised by Reviewer 1, we agree with the reviewer's observation, and we have now strengthened the link between the results of the pure mineral experiments and the results obtained with ATD. We have fit experimental n_s vs. T for each pure mineral and made predictions of frozen fraction for ATD suspensions.

Changes to manuscript

- See changes listed in response to the first comment by Reviewer 1.