

We thank Reviewer 1 for his/her constructive comments. We reproduce reviewer's comments in *blue* and our responses in black.

General comments:

This paper examines immersion mode ice nucleation by a range of quartz and silica samples using differential scanning calorimeter technique which allows comparison of different nucleators and solute conditions, concluding that milling processes produce the sites that cause quartz to nucleate ice and that quartz doesn't nucleate ice better in the presence of ammonia, in contrast to feldspar minerals. The paper provides numerous sensible and well-supported suggestions for factors that may affect the effectiveness of quartz and silica and ice nucleators and discusses the complexity of assessing the role of quartz in atmospheric ice nucleation. The paper is admirably thorough and is well written. The conclusions are within in the scope of ACP and are of substantial interest. While I have a few minor comments that the authors may want to consider I support publication.

Specific Comments:

I think it is generally agreed that calculation of ice nucleation active site densities is helpful e.g. (Hoose and Möhler, 2012) and a recent intercomparison suggests that comparisons across different instruments is likely meaningful (DeMott et al., 2018). The data produced here and in other papers using DSC provides useful information for internal comparison but it is rather a shame that it does not lend itself to quantitative comparison with other techniques. Would it be possible to calculate n_s values from the available data? Some comment on this might be helpful.

Indeed, it is a drawback of the DSC method that ice nucleation active site densities cannot be directly derived. We attempted to quantify the ice nucleation activity in Kaufmann et al. (2016), by deriving an ice active particle fraction (f_{act}) from emulsion freezing experiments. However, there are significant uncertainties associated with the dust particle size distribution, the droplet size distribution and frozen water volume fractions in cases with overlapping heterogeneous and homogeneous freezing signals, resulting in f_{act} that might be up to a factor 6 higher or more than a factor 2 lower. An ice nucleation active site density as a function of temperature would still be more uncertain because the DSC does not register freezing events but just the heat flow due to freezing, which is shifted to lower temperatures compared with the freezing events. For TU Vienna quartz and SA quartz that we investigated in this study, active site densities have already been given in Zolles et al. (2015) and Whale et al. (2018), respectively. The focus of this study was to investigate how solutes affect the ice nucleation activity. DSC emulsion freezing measurements are very well suited for this purpose because they yield good statistics within one experiment. Adding active site densities would need an in-depth discussion of how they were derived from the DSC thermograms. Since active site densities of quartz samples investigated in this study have been reported previously and the manuscript is long already, we would like to refrain from adding this information.

Relatedly, the weight percents of quartz used are very high. A 10 wt% suspension is almost like mud and will flocculate and settle effectively immediately. I am curious as to why such high particle concentrations have been used?

As a standard, we used 5 wt% suspension concentrations. This concentration exhibits a low viscosity and can be well handled. We increased the suspension concentrations to 10 wt% in cases when 5 wt% did not lead to a discernable heterogeneous freezing signal. This was the case for the original amorphous silica sample (Alfa Aesar). For better comparison, we decided to also present the milled Alfa Aesar sample with a 10 wt%

suspension concentration. Moreover, all suspensions were strongly sonicated for 5 min before preparing the emulsions to minimize aggregation.

In addition, the presence of solutes may conceivably change the rate of flocculation and change how the solutions interact with the emulsifying oil. For the comparisons made in this study to be valid the droplets it is, I think, necessary that the droplet distribution across all DSC experiments is very similar. While I recognize that the original paper on the technique paper used up to 20 wt% I still think it would be helpful to have a figure or table somewhere demonstrating that droplet distributions for different suspension compositions are indeed similar, and perhaps some brief comment on how any variation in this distribution may affect results.

In Marcolli et al. (2007) we investigated whether the added dust particles influence the droplet size distribution. For Arizona test dust, we did not find a significant dependence up to 20 wt% suspension concentration. We therefore used all analyzed suspension concentrations to obtain a representative droplet size distribution. This is stated in Marcolli et al. (2007).

We regularly inspect the emulsions under the microscope to make sure that they are of uniform quality. We also did this after having added solutes and did not find any effect of the solutes on the droplet size distribution. Moreover, strong interactions of the added particles or solutes with the surfactant would become visible in the DSC thermograms as large spikes at warmer temperature due to large patches of water present in the emulsion that freeze at warmer temperature. We have added a sentence to the methodology section (lines 163-164) to make clear that we regularly monitor the quality of the emulsions: “Regular inspection under the microscope did not reveal an effect of dust particles or solutes on the droplet size distribution.”

The paper is quite long and much of the midsection is a rather turgid. Obviously, this paper is just one part of a very substantial of work, indicating sensible efforts have been made to divide up the vast number of results. However, the authors may want to consider presenting their results more concisely in places. This would aid readability.

We appreciate the reviewer’s comment and have made appropriate changes in the revised manuscript to be more concise in the *Discussion* section. Lines 326 – 330, 454 – 456 and 528 - 532 (from the 1st submission) have been deleted.

Pg 9 line 334-336- The surface area per droplet in Whale et al. is not as large as 10 cm^2 . The droplets used were smaller than those of Zobrist with a similar particle concentration. I suspect the silica used was simply different in some and that this accounts for the different freezing temperature observed.

Indeed, our formulation was imprecise, we therefore re-phrase: “Whale et al. (2018) found IN active site densities of silica particles from Sigma-Aldrich (silica gel) of $n_s \approx 10 \text{ cm}^{-2}$ at 251 K and $n_s \approx 0.1 \text{ cm}^{-2}$ at 261 K, corresponding to a slightly higher IN activity of these silica particles compared with those synthesized by Zobrist et al. (2008).” in the revised manuscript (lines 331 – 333).

Pg 3 line 77 and other places- There is some inconsistency in the citations to the other papers in the Kumar series, a’s and b’s aren’t always present.

All inconsistencies have been corrected in the revised manuscript (line 187 and 537).

Pg 3 line 105- Word missing somewhere in the sentence starting ‘Quartz,. . .’

We corrected by adding: “Quartz, the most common form of crystalline silica, ...” in the revised manuscript (line 105).

Pg 4 line 127- remove ‘only a mere. . .’

We removed it.

Pg 4 line 138- different number of significant figures on weight loss compared to elsewhere.

Weight loss data has been adjusted to 2 significant digits (line 138).

Pg 10 line 351-354- This sentence is a little difficult to follow.

We split this sentence in the revised manuscript (lines 348 - 351): “In Part 1 of this series, we showed that heterogeneous freezing onsets of microcline exhibit strong deviations from the water-activity-based description. Higher T_{het} compared to predicted values were observed for microcline suspended in very dilute $\text{NH}_3/\text{NH}_4^+$ containing solutions, while a substantial decrease in IN efficiency was observed in more concentrated solutions of inorganic salts including NH_4^+ containing salts and NH_3 .”

Pg 11 line 413- ‘Shortly’ is the wrong word here, ‘briefly’ maybe, although it would be better to just state the length of time.

We revised by just stating the length of time: “for the sample exposed to water for ~ 15 min” in the revised manuscript (lines 413 - 414).

Pg 12 line 436- ‘little’ is the wrong word. Should be ‘few’

We replaced “little” by “few” (line 436).

Pg 13 line 477- I’m not clear what is meant by ‘when quartz is ground in the atmosphere’. This should probably be explained.

We mean here “ground in the normal atmosphere” compared to grinding in a protected atmosphere devoid of oxygen. We therefore revised to “when quartz is ground in the normal atmosphere” (line 473).

Pg 17 line 630- I’m not sure ‘deteriorates’ is the right word.

We replaced “deteriorates” by “suppresses” (line 621).

References

- Kaufmann, L., Marcolli, C., Hofer, J., Pinti, V., Hoyle, C. R., and Peter, T.: Ice nucleation efficiency of natural dust samples in the immersion mode, *Atmos. Chem. Phys.*, 16, 11177-11206, doi:10.5194/acp-16-11177-2016, 2016.
- Marcolli, C., Gedamke, S., Peter, T., and Zobrist, B.: Efficiency of immersion mode ice nucleation on surrogates of mineral dust, *Atmos. Chem. Phys.*, 7, 5081-5091, doi:10.5194/acp-7-5081-2007, 2007.
- Whale, T. F., Holden, M. A., Wilson, Theodore W., O’Sullivan, D., and Murray, B. J.: The enhancement and suppression of immersion mode heterogeneous ice-nucleation by solutes, *Chemical Science*, 9, 4142-4151, doi:10.1039/C7SC05421A, 2018.
- Zobrist, B., Marcolli, C., Peter, T., and Koop, T.: Heterogeneous ice nucleation in aqueous solutions: The role of water activity, *The Journal of Physical Chemistry A*, 112, 3965-3975, doi:10.1021/jp7112208, 2008.
- Zolles, T., Burkart, J., Häusler, T., Pummer, B., Hitznerberger, R., and Grothe, H.: Identification of ice nucleation active sites on feldspar dust particles, *The Journal of Physical Chemistry A*, 119, 2692-2700, doi:10.1021/jp509839x, 2015.