Response to the Referee Comments on "A comparative study of K-rich and Na/Ca-rich feldspar ice nucleating particles in a nanoliter droplet freezing assay" by Andreas Peckhaus et al.

We would like to thank the two anonymous referees for the careful reading of our manuscript and numerous valuable comments and suggestions. We would also like to express a special gratitude to Prof. Gabor Vali for providing additional analysis of our data. Below we answer the referees' comments and give a reference to the revised sections of the manuscript, where necessary. Our answers follow the corresponding referee comments and are given in italic for clarity.

Response to Anonymous Referee #1

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The authors present a novel freezing assay for studying immersion freezing induced by various IN active particles. In this study, the IN ability of different feldspar samples was investigated, compared to other existing literature data as well as parameterized and interpreted using the so-called Soccer ball model. I recommend publication after the following comments have been addressed.

General comment:

The first question which came to my mind after reading the introduction: What is the motivation of your study? There are a lot of recent studies dealing with the topic of immersion freezing induced by feldspar particles and these results are summarized in the introduction but I am missing a motivation for your work. The functioning of the freezing assay, the collected data (i.e., detecting frozen fractions as function of T and t; good statistics due to large droplet ensemble; etc.) as well as the theoretical description are very impressive. So I recommend to modify the introduction and clearly state your motivation for doing these experiments.

We agree that this point has not been specifically addressed in the introduction. We have added the following sentence to the end of the introduction: "In spite of accumulating evidence of importance of K-feldspar for the atmospheric ice nucleation, systematic studies of natural feldspars are yet rare. Recently we have developed an apparatus capable of measuring the freezing of several hundred identical nanoliter droplets of mineral dust suspensions in both steady cooling and constant temperature regimes. This work is the first attempt to use this apparatus for a comprehensive characterization of several feldspar samples and assessment of stochastic vs. singular nature of ice nucleation induced by a highly effective ice nucleator. As will be shown below, low variability of droplet size and concentration, large number of individual droplets, automatic control of individual droplet freezing time and temperature used in our instrument improves the statistics and allows for parameterization of freezing efficiency of feldspar based on the classical nucleation theory."

Specific comments:

Abstract: Page 1, line 27: "FS04" has not been introduced. I would suggest to delete "FS04" here as it is not mandatory for the abstract.

"FS04" is now deleted from the abstract.

Page 2, line 23/24 and page 19, line 23: Deposition freezing: As there is no liquid phase involved I would call it deposition ice nucleation.

Agreed and corrected.

Page 2, line 29: What is the increased onset RH value (127%) referring to? RH of 105% or 135%?

This sentence is irrelevant for the discussion and has been removed from the text.

Page 3, line 12-13: Zolles et al. (2015) found indications in their study "that the higher INA of the K-feldspar sample is an intrinsic property and not a result of adsorbed organic/biological material." (Quotation from the original Zolles paper). Could you add this indication to your introduction?

We have added this point to the introduction.

Page 4, line 11: The abbreviation "CNT" hasn't be introduced before.

Corrected.

Page 4, line 13: There are two papers of Niedermeier et al. in 2011 and you cite both of them in your paper. Which one are you referring to here? Could you check throughout the manuscript as this citation issue occurs multiple times? Equation 2: The contact angle is defined between 0 and π. How can you integrate from minus to plus infinity? Why is there a 'n_{site}^{-1}' in the exponent?

We have corrected the references.

With respect to equation 2: the integration between minus to plus infinity is necessary to account for the continuity of a Gaussian probability distribution function p(Θ). Outside of the [0, π] interval, Θ is set to either 0 or π. Our approach follows that of Niedermeier et al., (2014).

In the original SBM formulation, surface area of an individual ice active site s_{site} appears in the equation for probability P_{unfr}, see equation 2 in (Niedermeier et al., 2014). We have replaced s_{site} with $S_p n_{site}^{-1}$, accounting for the fact that, formally, number of active sites per particle is proportional to the particle surface area. This explains n_{site}^{-1} in the exponent in the equation 2.

Page 6, line 3: Did you measure the freezing ability of the NanoPure water droplets without any inclusions to clearly see that homogeneous freezing occurs at lower temperature i.e., that the substrate itself does not influence your immersion freezing results?

Yes, we did. Figure 5 now contains the freezing curves for NanoPure water droplets on a silicon wafer.

Page 6, line 11-13: How fast do the droplets reach the temperature of the silicon substrate, i.e., how accurately does the temperature measured by the PT-100 represent the temperature of the droplets?

The maximum temperature lag ΔT due to a steady cooling can be estimated as $\Delta T = \frac{\lambda \cdot d^2}{\chi}$, where d is the droplet diameter (typically 100 µm) , χ is the thermal diffusivity of water, and λ is the cooling rate. A low estimate of the thermal diffusivity of water at -30°C, $\chi \approx 5 \cdot 10^{-8}$ m^2/s (Biddle et al., 2013), for the highest cooling rate used in this work (10 K/min) yields $\Delta T \approx 0.1K$. This value is within the temperature measurement accuracy. We conclude, therefore, that this effect should be negligible in our experiments.

Chapter 3.1.3: I am confused that the sample preparation was introduced before the samples themselves were introduced. I would suggest to move chapter 3.1.3 to chapter 4.

We agree with this suggestion. The sections have been rearranged accordingly.

Page 7, line 21: What is BCS 376?

We can only site (Harrison et al., 2016) *here: "BCS 376 microcline is a microcline sample from the Bureau of Analysed Samples with sample code 376".*

Page 8, line 15: What is 'W' in the given equation?

Indeed, W (weight concentration of the feldspar in suspension) was not introduced prior to the first use. It has been corrected.

Chapter 5.2 and Fig. 5: For the homogeneous freezing experiments there is no correlation between two freezing experiments i.e., these are statistically independent freezing events which I would consider to agree with the stochastic view on nucleation as all the droplets feature very similar freezing probabilities. But I don't understand the statement why a strong correlation like in Fig. 5D is in agreement with the stochastic view of nucleation. I think it shows that each droplet has its characteristic freezing probability (i.e., high probability to freeze within a given temperature range) and the droplets (strongly) differ concerning their freezing probabilities so that you can observe this high correlation. But this observation does not necessarily confirm the stochastic view on heterogeneous ice nucleation, it would also be in agreement with the singular view on nucleation. Did you perform freeze-thaw experiments also for lower and higher concentrated suspensions? I would assume that for higher (lower) concentrations the droplets' freezing probabilities would be very similar (more different) so that the correlation becomes weaker (stronger). What do you think?

Attributing a characteristic probability of a droplet freezing within a certain temperature range is the essence of a stochastic hypothesis. A singular hypothesis prescribes freezing of a given droplet at a same fixed temperature, over and over again. Therefore, the expected correlation between freeze-thaw cycles in the singular freezing case would be approaching unity and will be limited only by a limited repeatability of the temperature measurements.

We have performed freeze-thaw experiments with FS01 and FS02 samples in four different concentrations (0.8 wt%. 0.1 wt%, 0.025 wt%, and 0.01 wt%), but have not observed a clear relationship between the correlation coefficient and concentration.

Page 11, line 7-9: A linear decrease does not necessarily mean that the particles have to be uniform concerning their ice nucleation properties. Considering a droplet population, each droplet containing a large number of particles featuring a wide range of nucleation properties (i.e., contact angles), it might be that the effective contact angle distribution over the whole droplet population is narrow so that you can observe a linear decrease in the logarithm of the unfrozen fraction plot.

From the stochastic point of view, the overall freezing behavior of a large droplet ensemble will be equally influenced by both intra-droplet and droplet-to-droplet variability of feldspar properties. For a system containing two types of INAS with distinctly different distributions of contact angles (as in FS04), only one of these types will be activated at high temperature. If this distribution is narrow, it will exhibit an exponential decrease of unfrozen fraction. The second, low-temperature population of sites, would not be engaged at all.

Page 11, line 28-31: There is a difference concerning the cooling rate dependence found for kaolinite particles which you should point out. The temperature shift of 8K (4 orders of magnitude change in cooling rate) is presented in Murray et al. (2011). It is based on a calculation/parameterization and has not been directly observed. Wright et al. (2013) measured the cooling rate dependence for kaolinite and found that the median freezing temperature shifts about 3K when extending the experiment from 30min ($1 K min^{-1}$) to 50h ($0.01 K min^{-1}$), i.e., 2 orders of magnitude change in cooling rate. They use a different kaolinite sample but it also originates from CMS as the one Murray et al. (2011) used for their study.

This is a valuable addition and we have included it into the discussion.

Page 12-13/17 and Tables 2A and 2B: All FS02 samples (i.e., all concentrations) can be represented by a single contact angle distribution. But you determined several different (but similar) distributions for the FS04 samples (i.e. for 0.01wt%, 0.05wt% and 0.1wt%). What is the reason for that?

The FS02 and FS04 samples are distinctly different in that the FS02 is a mono-component whereas FS04 is not. Therefore, two different procedures were used for FS02 and FS04. For FS02, the initial values of $\mu_\theta = 1.32\ rad$ *and* $\sigma_\theta = 0.1\ rad$ *have been obtained from the fit of ISO liquid fraction decay curve at 256 K. Assuming that the same population of active sites is present in all suspensions, this pair of parameters has then been used to fit the other ISO decay curves, measured at different temperatures. For the FS04 sample, containing different populations of particles, the relative composition might be changing upon dilution. We have applied the fit to every suspension independently, which led to a slight variability of the fit parameters.*

In order to fit the ISO measurements of the FS02 sample the number of sites is increased tremendously. How reasonable are these high n_{site} values? You mention that caution is needed interpreting n_{site}. However, in order to calculate n_s (see Eq. (4)) it seems to be a very important parameter including physical meaning. Looking on Fig. 6A, it can be seen that the SBM fit for the 0.8wt% FS02 sample only partially represent the measured frozen fraction in the T range of 253K-256K, i.e., within that range where the ISO measurements were performed. Is it possible that this deviation leads to these high n_{site} values?

We would like to point out that n_{site} *is not an average number of all potential sites per droplet (which is* n_s^* *) but the number of sites engaged in a particular freezing scenario (temperature range, concentration, cooling rate). At the same time* n_{site} *is a variable fitting parameter. Any deviation of the system from ideality (skewness of the size distribution etc.) is compensated by an adjustable fit parameter. There is no way to decide what deviation is responsible for the shape of the measured freezing curve for FS02 0.8 wt%, but the high values of* n_{site} *indicate that the deviation is indeed present.*

In case of the FS04 sample the contact angle distribution is changed tremendously for the highest concentration as well as for the representation of the ISO data. Is it possible to represent the ISO data using the SBM parameters which you determined for the 0.8wt% sample from the frozen fraction vs. temperature curves (i.e., n_{site} = 3.5, mean of 0.75 rad and standard deviation of 0.12 rad)?

We refer to the discussion below. Technically it is possible, but the quality of the fit suffers significantly.

Page 13, line 9-10 and related to the comment above: Does this mean that you assume that the IN properties scale with wt% concentration? Looking at Table 2A and 2B this might be not valid for FS04 as the effective contact angle distribution changes with wt% concentration as well as then doing the ISO experiments. At the end this leads to different contact angle distributions for the same feldspar sample. The slopes of the freezing curves in Figure 4D seem to suggest that there is at least a bimodal contact angle distribution (you also mentioned this on page 14). Would it be possible to perform a bimodal soccer ball fit (see Augustin et al., 2013) for the FS04 sample using the fit parameters of the 0.8 wt% concentration in order to represent the first, high temperature branches of the 0.05 wt% and 0.1 wt% concentrations?

Indeed, in a number limited population of suspension droplets containing several sorts of IN active sites in different quantities, a dilution should lead to the scaling of IN properties. We have tried to show this using an asymptotic value of INAS density, n_s^**, as a measurable experimental parameter. A bimodal SBM fit of the entire curve set would definitely be conceivable, but is clearly outside the scope of this paper.*

Page 14, line 5-6: What do you mean here? Looking on equation (3), n_{site} should not have any unit, it is just a number?

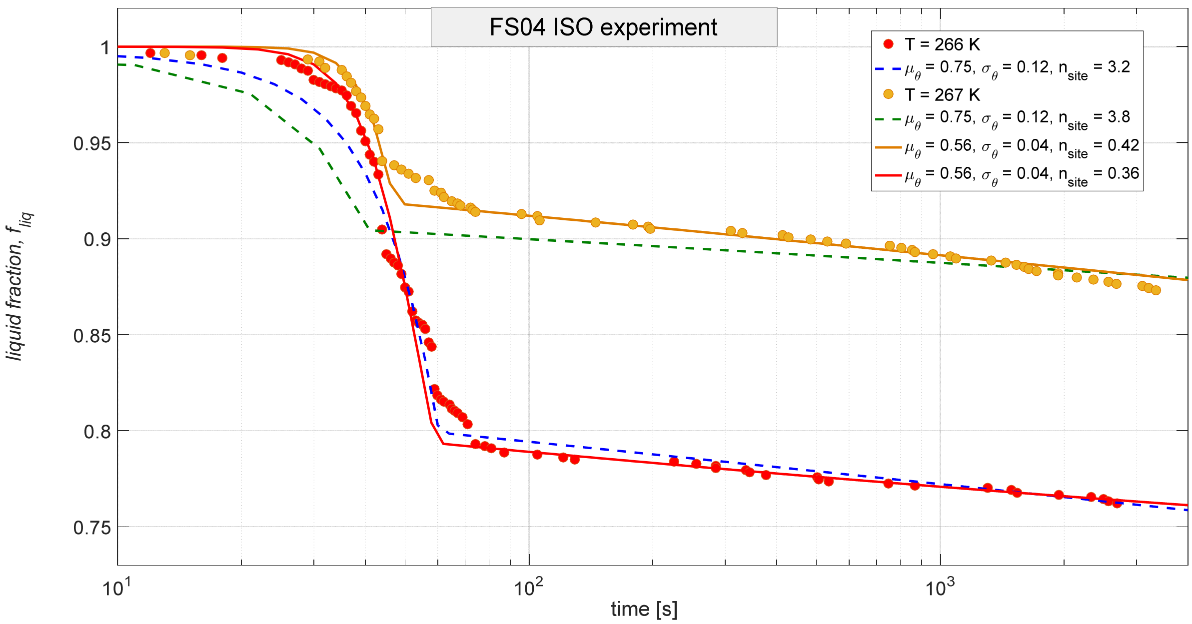
The reviewer's concern is unclear. n_{site} *does not have any unit in the cited lines of the manuscript.*

Page 14, line 21-30: How safe is the argument that the IN active site distribution is homogeneous? It might be that the IN site distribution is heterogeneous but due to the measurement procedure this might be masked as each droplet may feature few particles with very similar ice nucleation properties?

This argument is somewhat unclear to us. If every droplet features few particles with very similar ice nucleating properties, the distribution is homogeneous, isn't it?

I agree that in the ISO experiments the most efficient sites should be activated first and the less efficient ones should be "excluded". But I am still wondering whether it is possible to represent the FS04 data using the SBM parameters which you determined for the 0.8wt% concentration from the frozen fraction vs. temperature curves (see comment above)?

Yes, we have done this study and the figure below (analog to Figure 7B of the manuscript) illustrates the result. Using a pair of parameters $\mu_\theta = 0.56\, rad$ *and* $\sigma_\theta = 0.04\, rad$ *a good fit of both experimental curves, at 266 K and at 267 K, can be achieved (solid lines). With* $\mu_\theta = 0.75\, rad$ *and* $\sigma_\theta = 0.12\, rad$ *(the fit parameters obtained by fitting the freezing curve for W = 0.8 wt%), the 266K freezing curve can be fitted fairly well, whereas the 267K curve cannot be fitted quite as satisfactory. The strongest deviation is observed in the constant cooling ramp part of the curve, where the most active sites are activated. These sites are characterized by a low value of* μ_θ*, and therefore are not captured by a model with* $\mu_\theta = 0.75\, rad$*.*



Page 16, line 5-6: I don't understand this statement. Looking on Eq. (4) it is clearly seen that n_s is proportional to n_{site}?

Strictly speaking, this is true only for the low temperature side of the freezing curve, where $P_{unfr}(T, \mu_\theta, \sigma_\theta, t)$ *approaches unity or a constant. Where probability is changing strongly with temperature, there is no simple linear relationship between* n_{site} *and* $n_s(T)$*.*

Technical notes:

We have revised the manuscript to incorporate the technical notes listed below. We would like to thank the reviewer again for his valuable comments which helped us to improve the manuscript.

‘IN’ and ‘INP’ are used synonymously. I would suggest to only use one of them in the paper.

This is true. We have corrected it accordingly.

There are various cases where a citied study is put in brackets which should not appear e.g., page 16, line 26; etc. Please check throughout the manuscript.

Abstract: Page 1, line 31: It should read: “…the possibility of biological contamination of the sample has been ruled out.”

Page 2, line 31-32: I suggest the following changes here: “In a number of droplet freezing assay experiments (Atkinson et al., 2013; Whale et al., 2015; Zolles et al., 2015) K-feldspar particles have been investigated in the immersion freezing mode and it was found that K-feldspar particles…”

Page 5, line 31: Replace “Thus” by “The”.

Page 8, line 15: It should read: “Both methods delivered: : :”

Page 11, line 32: There is a ‘the’ missing in ‘on one hand’.

Page 13, line 14: It should read ‘been’ instead of ‘bee6n’

Page 14, line 19: Do you mean Fig. 6B here?

Page 14, line 22: identically instead of identical?

Page 15, line 21: Temperature cannot be warm or cold, only high and low.

Page 15, line 29: I would suggest to delete the articles ‘the’ in front of S_p and n_{site}.

Page 16, line 2: The right bracket behind Eq. (4) is missing.

Page 16, line 19: A word after ‘asymptotic’ is missing. Something like ‘value’?

Page 18, line 26. There is a whitespace missing between “the10-fold”.

Page 20, line 19: There is a ‘a’ missing in front of “number n_{site} of active sites…”

All of the above: corrected as requested.

References (sited by the referee and in our response):

Atkinson, J. D., Murray, B. J., Woodhouse, M. T., Whale, T. F., Baustian, K. J., Carslaw, K. S., Dobbie, S., O’Sullivan, D., Malkin, T. L., O’Sullivan, D., The importance of feldspar for ice nucleation by mineral dust in mixed-phase clouds., Nature, 498(7454), 355–358, 2013.

Augustin, S., Wex, H., Niedermeier, D., Pummer, B., Grothe, H., Hartmann, S., Tomsche, L., Clauss, T., Voigtländer, J., Ignatius, K. and Stratmann, F.: Immersion freezing of birch pollen washing water, Atmos. Chem. Phys., 13, 10989–11003, doi:10.5194/acp-13-10989-2013, 2013.

Biddle, J. W., Holten, V., Sengers, J. V and Anisimov, M. a: Thermal conductivity of supercooled water, , doi:10.1103/PhysRevE.87.042302, 2013.

Harrison, A. D., Whale, T. F., Carpenter, M. A. ., Holden, M. A., Neve, L., O'Sullivan, D., Vergara Temprado, J. and Murray, B. J.: Not all feldspar is equal: a survey of ice nucleating properties across the feldspar group of minerals, Atmos. Chem. Phys. Discuss., (February), 1–26, doi:10.5194/acp-2016-136, 2016.

Murray, B. J., Broadley, S. L., Wilson, T. W., Atkinson, J. D. and Wills, R. H.: Heteroge-neous freezing of water droplets containing kaolinite particles, Atmos. Chem. Phys., 11, 4191–4207, doi:10.5194/acp-11-4191-2011, 2011.

Niedermeier, D., Hartmann, S., Clauss, T., Wex, H., Kiselev, A., Sullivan, R. C., De-Mott, P. J., Petters, M. D., Reitz, P., Schneider, J., Mikhailov, E., Sierau, B., Stetzer, O., Reimann, B., Bundke, U., Shaw, R. A., Buchholz, A., Mentel, T. F. and Strat-mann, F.: Experimental study of the role of physicochemical surface processing on the IN ability of mineral dust particles, Atmos. Chem. Phys., 11(21), 11131–11144, doi:10.5194/acp-11-11131-2011, 2011a.

Niedermeier, D., Shaw, R. A., Hartmann, S., Wex, H., Clauss, T., Voigtländer, J. and Stratmann, F.: Heterogeneous ice nucleation: Exploring the transition from stochastic to singular freezing behavior, Atmos. Chem. Phys., 11(16), 8767–8775, doi:10.5194/acp-11-8767-2011, 2011b.

Niedermeier, D., Ervens, B., Clauss, T., Voigtländer, J., Wex, H., Hartmann, S. and Stratmann, F.: A computationally efficient description of heterogeneous freezing: A simplified version of the Soccer ball model, Geophys. Res. Lett., 41(2), 736–741, doi:10.1002/2013gl058684, 2014.

Whale, T. F., Rosillo-Lopez, M., Murray, B. J. and Salzmann, C. G.: Ice Nucleation Properties of Oxidized Carbon Nanomaterials, J. Phys. Chem. Lett., 3012–3016, doi:10.1021/acs.jpclett.5b01096, 2015.

Wright, T. P., Petters, M. D., Hader, J. D., Morton, T. and Holder, A. L.: Minimal cooling rate dependence of ice nuclei activity in the immersion mode, J. Geophys. Res. Atmos., 118(18), 10,510–535,543, doi:10.1002/jgrd.50810, 2013.

Zolles, T., Burkart, J., Häusler, T., Pummer, B., Hitzenberger, R. and Grothe, H.: Iden-tification of Ice Nucleation Active Sites on Feldspar Dust Particles, J. Phys. Chem. A, 119(11), 150129062629007, doi:10.1021/jp509839x, 2015.