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

Received and published: 24 February 2016

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?

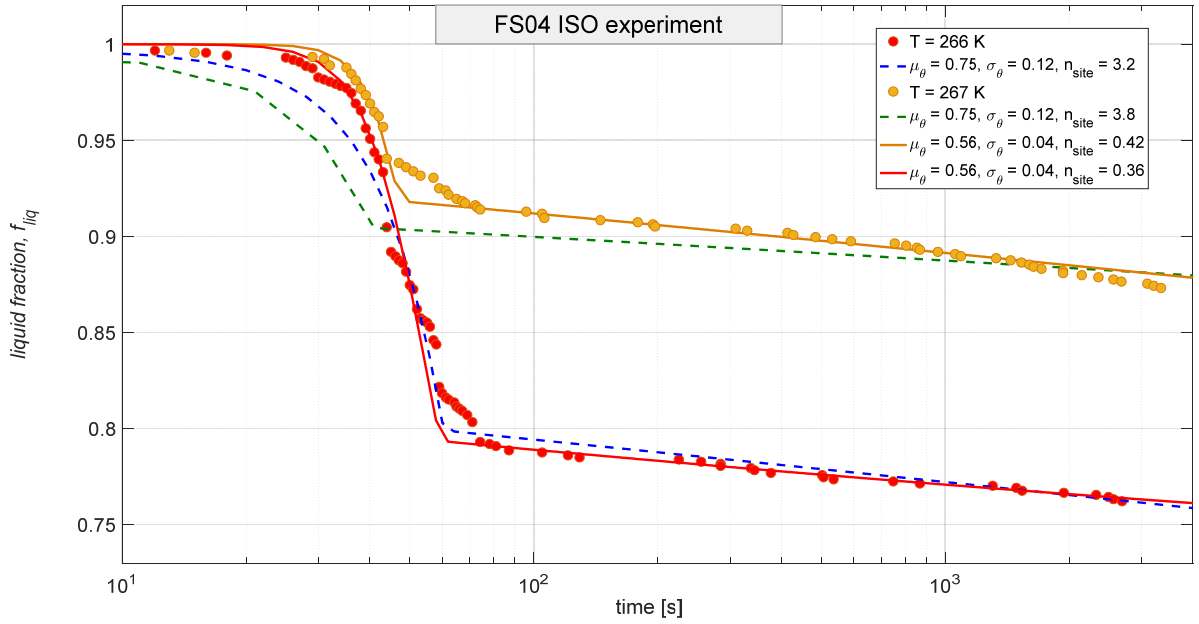
The reviewer's concern is unclear. n_{site} does not have any unit in the cited lines of the manuscript.

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.

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 comments and suggestions. We also express a special gratitude to Prof. Gabor Vali for providing additional analysis of our data.

Below we answer the referee's comments and give the references to the revised sections of the manuscript, where applicable. Since the review is organized in the form of a general discussion, our response also has a similar structure. The general discussion is followed by a point-by-point reply to the technical notes. For convenience, we use italic for our response.

Response to Anonymous Referee #2

Received and published: 18 March 2016

The manuscript under review introduces a new and powerful device for the examination of immersion freezing together with a thorough examination of the respective ice nucleation behavior of a number of different feldspar samples. It is an extensive study, discussing the influence of differences in the samples, sample aging, and different ways to run the experiments (isothermal measurements versus measurements done with varying cooling rates). Obtained results are modeled as well.

Overall, it is an interesting and timely work, and besides for two main issues regarding the contend, my main criticism is the large number of tiny flaws in both, language and organization, showing up in a large number of "Technical comments" I give at the end of this review. I want to point out explicitly here that a thorough language revision is needed (in excess of my comments and the editing that ACP offers for the final version prior to publishing).

We revised the manuscript incorporating all the technical comments and suggestions for language improvement. Above that, the manuscript has been proofread by a fellow scientist (native English speaker), to whom we are greatly indebted. Some parts of the manuscript, specified below, have been revised to improve the coherence of the text, as suggested by the referee. To our knowledge, we have done our best in matching the language standards of ACP.

I have two concerns with regard to the scientific content are: 1) A biological contamination is rationalized away when I think the results rather indicate that there might be such a contribution from biological components. 2) Section 5.5 (i.e., the derivation of the contact angle distribution and the respective discussion) seems muddled and incoherent (more on that below). But all in all, once the points I raise below are dealt with, the content of the work certainly merits publication in ACP and I am looking forward to seeing the final version published.

Concerning a possible contribution from biological compounds:
A reduction in ice nucleation upon treatment with hydrogen peroxide has been used by others (e.g., Tobo et al., 2014; O'Sullivan et al., 2014) to show that the related ice nucleation was caused by biogenic components of the examined samples (oxidation of organic matter). Pummer et al. (2012) examined ice nucleation active macromolecules (INM) from different pollen where none of the samples lost any ice nucleation ability upon heating up to 110 C (some samples were stable in their ice nucleation ability even after heating up to 170 C). The related INM were certainly not proteinaceous but were rather polysaccharides and were found to have a mass between 100 to 300 kDa (corresponding to some nanometer in size, following Erickson, 2009) and occur in large numbers on pollen grains (Augustin et al., 2013 estimate 20000 INM per grain of the pollen they examined), from which they can be easily washed off. From your observations (ice activity resistant to 90 C but not to H2O2 treatment), polysaccharides are a likely candidate. They might even occur accumulated, as they exist separately as freely movable molecules.

This is different from ice active protein complexes observed on some bacteria, which are ice active only when embedded in a cell membrane (at least a fragment), and where typically only one complex is present per cell. Hence n_m always also includes all of the mass of the cells and could be much higher if, as in the case of pollen, the INM appeared separated from their carrier. Concerning fungi, the n_m value you compare to in your estimation is the number of INM per mycelium mass (Pummer et al., 2015), so also here the density of INM when washed off their carrier (fungal spores in this case) can potentially be much higher. This strongly weakens your argument against a contribution from biological material.

Summarizing, an estimate like the one you present (the comparison to n_m for bacteria or fungi) compares apples and oranges, and I would claim that it proves nothing.

Based on all that, your examinations cannot rule out that biogenic compounds might be present on your sample FS04. Therefore, I strongly recommend you tune down all passages throughout the whole text that claim that the high ice nucleation efficiency of FS04 does not come from biogenic components, and instead rather point towards biogenic components as a possible cause of the observations.

We agree with the referee that the observed reduction of IN activity after treatment with H_2O_2 is a very strong indication towards the biogenic origin of the high-temperature active sites in FS04 sample. We also agree that bacteria or fungi are not the best choices for comparison in terms of INAS mass concentration, n_m. There are, however, natural systems better suitable for a comparison. In the work of O'Sullivan et al., (2014), the mass concentration of ice active sites for untreated fertile soil (figure 7 in their paper, soil "D") is given as high as $n_m = 3 \times 10^6\ g^{-1}$ at 261 K, which is two orders of magnitude lower than the value obtained in this study ($n_m = 2.7 \times 10^8\ g^{-1}$at 266 K). Soil contains up to 40% organic matter which is mostly responsible for its IN properties (Tobo et al., 2014). Augustin-Bauditz et al., (2016) has measured the freezing behavior of illite NX mixed with birch pollen washing water (BPWW) extract. From hygroscopic growth, they estimated the mass fraction of biological material in 0.5µm illite particles to be 9.7%. Although they could not measure at temperatures above -17°C, extrapolating their freezing curve to -10°C and calculating the mass concentration of IN active sites as $n_m(T) = -\frac{6 \cdot ln(1-f_{ice}(T))}{\pi \rho_p d_p^3}$ we obtain $n_m \approx 5 \times 10^7\ g^{-1}$.This is already close to the value we obtained for high-temperature active sites in FS04 at 266 K, but that would mean that FS04 must contain 10% birch pollen material by mass?! Additionally, to accept the biogenic contamination as an explanation for the high-temperature IN sites, we have to assume that the feldspar crystal used for the sample preparation was contaminated with INM with very homogeneous IN properties, as implied by a narrow distribution of contact angles established by fitting the isothermal freezing experiments at 266 K and 267 K. Finally, the modal value of contact angle distribution obtained with SBM fitting of immersion freezing curves for pure BPWW particles yielded a value 0.87 rad (Augustin et al., 2013), which is larger than any of our values for the high-temperature fraction of IN active sites in FS04 feldspar. The bulk of evidence drives us to the conclusion that at a realistic contamination level polysaccharides are not efficient enough to be responsible for the high-temperature nucleation of ice in FS04 suspension droplets. Since BPWW-like polysaccharides are the only "likely" candidate for such contamination (capable of preserving the IN activity after heating but degrading after H2O2 treatment), the biogenic nature of high-temperature active sites is highly unlikely. The proteinaceous nature has been ruled out by heating experiment.

As a compromise, we remove the statement about "ruling out" the possibility of the biogenic origin of the high temperature IN sites. The discussion has been modified accordingly.

Concerning section 5.5 - contact angle distributions:
This section is highly confusing, and I want to start out with saying that it has to be revised so much that it might be easier to write it from scratch.

You start out by saying: "The values of fit parameters obtained for the best fit are given in Table 2A." A little later, you say: "different combinations of n_site, mu_o and sigma_o could be found that would represent the experimental results equally well." The second sentence is a contradiction to the first one, where "the best fit" was mentioned. Additionally, now I wonder how these values presented in Tab. 2A were chosen, and what how other equally well fitting sets do look like.

The section 5.5. summarizes our attempts in testing the SBM ability to reproduce the experimental results obtained with the different methods. The apparently contradicting statements cited by the reviewer result from our initially cautious attitude towards the SBM. We were positively surprised finding out that some of the fit parameters (μ_θ and σ_θ) not only have a simple physical meaning, but also show low variability between the measurement methods, conditions, and instruments. On the other hand, the comparison of FS01, FS02 and FS05 clearly shows that the interpretation could be ambiguous: the freezing curve of a weaker INP FS05 was reproduced by the same μ_θ and σ_θ as for FS02 but by factor 3.5 smaller n_{site}. To our opinion, the value of this section is not in providing the final values of fit parameters, but in demonstrating the strong and the week sides of the SBM framework. For this reason, we prefer to keep our step-by-step treatment of the different samples and experimental conditions, and the resulting "mixed" values of fit parameters.

Then you show results based on the "best fit" for different cooling rates (I understand you take them from Tab. 2A?), and find that it fits OK but not perfect, claiming that the additional information obtained from the measurements made at different cooling rates does not help to constrain the fit parameters. But you did not test different sets, here. To be able to make this claim, you should have used a number of "best fits" from CR only, and see how good or bad these all fit the data from different cooling rates. And it might even be that then one of these "best fits" clearly stood out, in which case, and different from your claim, the additional information does help constraining the fit parameters.

Also, coming up with a log-normal instead of a Gaussian distribution for the contact angle distribution rather lowers the constraints on the results of the fits and does not really help here. If you used all information (see also below) you might just get one "really best" set of parameters for one sample, and if this does not explain all data well, you might wonder if the basic equation you are using needs to be amended. In this case, if it appeared, the use of a different shape of the distribution might help. But the way it was done here I suggest to not include the use of a further shape in your work (or alternatively do it more thoroughly).

Of course we have tested the different sets of CR freezing curves, otherwise, we would not have been able to plot the theoretical curves in Figure 8. What we show is that SBM does capture the observed trend: the less active suspensions exhibit a stronger shift of median freezing temperature than the more active INM. But no combination of fit parameters has would fit all cooling rates equally well, and no realistic parameter set could be found to reproduce the temperature shift of more than 0.5K over a ten-fold change in cooling rate. By using the asymmetrical contact angle distribution (log-normal) we tried to overcome this limitation, but have been only partly successful. We think this information might have a certain value for the general discussion and we prefer to keep it in the manuscript. As mentioned above, the achievement of an "ultimate best set" of fit parameters for a sample is not the goal we pursue in this paper. Such a set would be useless for atmospheric modelers due to a simple fact that there is no pure FS04 or FS02 feldspar mineral dust out there, and as we saw both experimentally and by means of numeric simulation, combining several INMs significantly change the freezing behavior of the mixture.

The next point I want to raise concerns n_site. Citing you, "each droplet contains on average a number n_site of IN active sites". Hence n_site depends on concentration and is not a parameter for which a value can be totally freely chosen. (Or, in other words, there is one more restricting equation.) You obviously kept it as a totally free parameter, otherwise values e.g., for FS02 in Tab. 2a for n_site would not have been 181, 8 and 2 as concentrations here were 80:5:1 (similar for FS04). This needs to be fixed.

We agree that this sentence is misleading since it implies an additional constraining condition. To our opinion, n_{site} should be interpreted as a number of individual sites required to achieve the best fit between the SBM model and experimental data within the probed range of experimental conditions. The range of conditions varies from experiment to experiment: for example, only part of the total IN active sites is actually "engaged" in an ISO experiment, and for high

concentrations and high temperatures, only the most efficient sites are going to be activated. The active sites with lower activity would be not activated and cannot be captured by the model. In such case, the proportionality between the number of INAS sites and total particle surface area S_p would be masked. We kept n_{site} as a free parameter in general, and the only free parameter when other fit parameters (μ_θ and σ_θ) were fixed, for example when the fit parameters obtained from the ISO experiments were used to fit the CR freezing curves. We find it encouraging, that the obtained values of n_{site} scale as 90:4:1 instead of 80:5:1 as would be expected from the concentration relationship.

I do, however, agree that the highest concentration of FS04 has to be treated separately. - But I wonder if parameters for that as given in Tab. 2A have any meaning. You elaborate nicely that this is obviously a second type of ice active site, and you are even able to separate it through the use of your isothermal measurements, but values given in Tab. 2A are a useless mixture between these two types for which I do not see an application. (You also claim (p. 14, line 20) that the shoulder, as which these active sites show up as, do not affect the fit algorithm. - Why not? Did you exclude them during the fitting process?) In any case: To prevent future readers from using these "mixed" values, I suggest to not show them at all and only discuss the second type of ice active sites (i.e., all that concerns the highest concentration of FS04) in the context of the isothermal results.

As explained above, we think that the "mixed" values nicely illustrate how the model descriptors change upon dilution. We prefer to keep these values in the present form.

In this section, you also say: "Thus, caution should be exercised when interpreting the fit results, as numerical features can be mistaken for physical relationships." and "To our opinion, such analysis demonstrates that fitting the freezing curves with freely variable three-parameter fit without providing additional constraint does not necessarily lead to a better understanding of IN nature." (Be careful with "freely variable three parameters", as I explained above.) Interestingly, however, you yourself use the obtained values several times to make some points about the samples, e.g., when you compare mu and sigma obtained for different types of ice nucleating materials, or when you ascribe a meaning to the broadness of the distribution (sigma) or say that all your samples (besides for the highest concentration of FS04) might have similar ice active sites. Or also when you finish this section by saying: "However, this comparison suggests that SBM framework correctly reproduces the relative ice nucleation efficiency of natural and artificial mineral dust aerosols." I agree with all your interpretations (and would even add that the low value of sigma for the sites only activating ice in the highest concentrated FS04 sample might point towards it being of biological origin). But if you do not trust the values you derive, you contradict yourself by making these interpretations.

Well, the safest way to avoid the ambiguity of interpretation would be to publish a set of solid experimental results and leave the numerical modeling for others. We have chosen to apply the SBM model ourselves and we think that in our case it brought us a step forward in, at least qualitative, understanding of how the freezing of suspension droplets works. At the same time, it never hurts to call for caution in applying numerical fits and interpreting the outcome. We have revised our statements to remove the apparent contradictions.

And now my suggestion for section 5.5: If I were to write this section, I would come up with ONE set of fit parameters for each of the four samples (and a fifth one for the high concentrated FS04) and then compare how well this fits all of the differently obtained data-sets. Isn't it this, in the end, why ONE sample is examined in different ways? To get as much information as possible from different perspectives and then see if it all fits together? The feeling arises that you do not use all information you have to constrain the fit parameters (e.g., different concentrations and cooling rates), and that, if you did use all of this, you might end up with the conclusion that the values you obtain do have some meaning beyond just being mere fitting parameters.

As mentioned above, our goal was to explore the relationships between the freezing behavior of a sample in the various types of experiments, not to produce an ultimate set of fit parameters. We think that this goal is better achieved by way of "case studies" and not by providing all possible cross-combinations of available constraints. We, therefore, restrain from changing the general structure of the section but revise the text to improve its coherence.

One additional point: sections 3.1.3 and 6.1, concerning the ageing of feldspar samples: As I understood, the samples aged as described in 3.1.3 were used later for immersion freezing measurements (described in 6.1), where the surface area of the particles needs to be known. How can you assure that you did not loose particles when exchanging the water? Discuss in the text how a possible loss of particles might relate to the observed change in median freezing temperature. Also: wouldn't a change in the type of the ice nucleating sites show up as a change in the contact angle distribution? Could you detect that?

The aged feldspar suspensions were centrifuged and water decanted carefully. The residual particles have been allowed to dry out in the clean environment at room temperature. The dry particles were weighted and re-suspended again in a known volume of water to ensure that no change in concentration is happening. Since no SBM modeling has been done for the aged suspensions, particle surface determination was not necessary.

Concerning the point of organization:

There is one particular point concerning the language: throughout the text, the articles "a" and particularly "the" are placed wrongly often, appearing where they should not appear but then missing in other locations, or using one of the two instead of the other. (This is so numerous that I refrained from listing all occurrences.) It can influence the meaning of a sentence, and disrupts the flow of the text, and I strongly recommend that the authors themselves should go over this carefully before resubmission (maybe asking a native speaker for help). I recommend this although I know that ACP offers a language correction before publishing the final paper, but for people at ACP, who know about language but not about the science behind the content, some of these misplaced articles might be difficult to correct.

While working on this review, I also realized that there is a long list of "Technical comments", including corrections of the language, adding to the pressing need to have a native speaker correct the text before re-submission. These comments were also necessary as references to figures, literature and such were not always correct. It would be good if in the future the author and also the co-authors paid more attention to these matters. (Examples concerning literature are: Citations were given for the wrong year, or the year given in the literature list was not in agreement with that in the text, or there were several citations by the same author from one year, but the corresponding "a" and "b" were not indicated in the text.) I mention occurrences I found while reading the text in my "Technical comments", but I did not check this thoroughly, as this is clearly a task for the authors.

We revised the manuscript incorporating all the technical comments and suggestions for language improvement. Above that, the manuscript has been proofread by a fellow scientist (native English speaker), to whom we are greatly indebted. We do not answer specifically to every technical comment on the list below, only to those that required a special attention.

Technical comments (I use "_" and "^" herein for sub- and super-script, respectively):

throughout the text: Consider using INP instead of IN - but in any case, use either one or the other (right now you use both in a non-consistent way). Also: IN appears in the abstract without being defined.

We use "INP" for "ice nucleating particle" and "IN" for "ice nucleating", in accordance with (Vali et al., 2015). Reference to IN meaning "ice nuclei" has been removed from the text.

page 1, line 19: Remove “(“ at beginning of line.
page 2, line 14-15: The paper you cite here (Kandler et al., 2011) appeared in 2009 - correct the year throughout the text or alternatively cite the 2011-paper you might be referring to.
page 2, line 24: Remove “(“ before Yakobi.
page 2, line 30: “changed” has to be “change”.
page 2, line 31: Insert “and was” between “and” and “found”.
page 2, line 33: “naturally” has to be “natural”.
page 3, line 21: Remove “(“ before Niedermeier and add “b” to 2011.
page 4, line 13: add “b” to 2011.
pate 4, equation 1: f_ice has to be defined somewhere
page 5, line 4-5: Either “…by the correlation coefficient rˆ2” or “… by rˆ2 (correlation coefficient)”.
page 8, line 11: SSA needs to be defined. In this case here, is it S_BET? If yes, use this symbol.
page 8, line 14-15: It is not clear which SSA you are using (S_BET or something else? - this would also not be clear if you had defined SSA as I ask you to do above - something else is missing). It is also not clear which two methods delivered similar results. (Also: add an “s” to “method”.) This needs to be elaborated.
page 9, line 1: Na+ rises steadily, too - please add that. Also, add “in the suspension” between “measured” and “over”.
page 9, line 3: The XRD analysis appears from nowhere, here. Add where and how this was made. It is not enough to only show the values in Table 1.
page 9, line 11: I assume you mean Steinke (2013)? (Or is the year given in the literature list (2013) not the correct one?) (And remove the “,” before the “(“.)
page 9, line 14: Change “have frozen” to “were frozen”.
page 9, line 27: Change “has frozen” to “froze”.
page 10, line 10: Do not change the tense, i.e., “show” has to become “showed”
page 10, line 23: Again, you mean “2011b”, right?

All of the above: corrected as requested

page 11, line 3: Rename “liquid fraction” to “fraction of liquid droplets”, here and also in the caption of Fig. 7, and remove the text “liquid fraction” from the y-axis of Fig. 7. The same also holds for “frozen fraction” on the y-axis of several other plots. One defines symbols to that they are used instead of the text, not together with it.

Done as requested.

page 11, line 2 to 18: I strongly suggest to change the sequence of the text given here. Put lines 6 to 9 first (small adjustments in the text will be needed), followed by the last sentence of the paragraph (The one starting with “In addition, biological IN…”). Then comes a new paragraph, starting with lines 3 to 5, describing your observation for FS02 and then the corresponding text dealing with a non-linear time dependence (again, check the flow of the text after the changes). The way it is now, you go back and forth between the non-linear and linear time dependence which is confusing.

We have rearranged the text flow according to this suggestion.

page 11, line 25ff: I like the relation of the temperature shift to a ten-fold-shift in cooling rate you give in one case, and wonder, why you do not give a similar “scaling” for the other temperature shifts you cite here. Alternatively, as I suggest above, summarizing the information in a table might also help the reader, maybe even better than any scaling could.

We have not conducted a dedicated study of cooling rate dependency. The main reason for that is relatively low variability of the ice nucleating efficiency of our samples. Besides, two recent studies provide a very detailed discussion on this topic: Herbert et al., (2014) and Wright et al., (2013). In this section we show that our observations are consistent with the literature data. We have chosen to reduce the discussion instead of providing even more sources.

page 11, line 26: Change “strongly vary” to “vary strongly”.

Done

page 11, line 31: “cooing” has to be “cooling”.

Corrected

page 11, 5.4: This section drags a bit. It goes on quite a bit about literature results, but it doesn’t become clear what you want the reader to take from it, nor how you think it relates to your own samples and why. Maybe you could add a table with all the literature results, which are difficult to grasp in the way they are given now, and only write a few lines about your results and related conclusions.

See above. We have reduced the discussion to the absolute minimum.

page 12, line 13: You certainly do not mean Fig. 2 here, do you? Correct this! And didn’t you bin the data for all cases for which you derived fit parameters? It is confusing here as you only mention panel A and D, so clarify this!

This is correct, it is figure 4 here. However, since our case studies are focused on FS02 and FS04, we show the binned data only for this two samples.

page 12, line 14: If what is now Fig. 6 will be mentioned here for the first time (which it is), swap Fig. 6 and 7. Alternatively, you could move section 5.5 to somewhere earlier in the text, so that upon the first mentioning of what is now Fig. 7 it is already clear where the lines come from.

We have rearranged the order of sections to comply with the order of figure numbers and their first mention.

page 12, line 17: Add “s” to the end of the word “experiment”.
page 12, line 22: Add “, and resulting fit parameters are given in Table 2B”
page 13, line 3: Remove “(“ before “Herbert”
page 13, line 14: Remove the “6” in “bee6n”.
page 14, line 19: Do you really mean Fig. 7 here? I think it is better visible in Fig. 4 and 6.
page 15, line 7: Again: 2011a or 2011b?
page 15, line 8: Hiranuma et al. is 2015 (again correct in the literature list but wrong here).

All of the above: done as requested

page 15, line 12 ff: Confusing sequence. Finish the first sentence after “Eq. (1)”. Remove the remaining rest of the sentence (explicit mentioning of FS01 and FS02 here is confusing, as this later on also includes FS04 and FS05). The next sentence then changes slightly and becomes: “Both, n_s(T) curves for FS01 and FS02 are very similar and are therefore shown together in Fig. 9.” page 15, line 15: You mentioned Atkinson et al. (2015) a number of times before, so “and elsewhere” is not correct. Either use the abbreviation you give here throughout the whole text, or not at all.

Done as requested.

page 17, line 15: Add “of the most highly concentrated suspension” following “suspension droplets”.

Done

page 17, line 22: Again: 2011a or 2011b?

Corrected throughout the text

page 17, line 25: The activation of these sites does NOT depend on concentration. The concentration influences at which temperature a DROPLET freezes, but not a single site! Rephrase!

Rephrased. The sentence now reads: “Presence of these sites will be detectable only in concentrated suspensions and setups, allowing measurements at high supercooling temperature”.

page 18, line 13: You could add to the end of the text here: ”…, as the feldspar is weathered to become clay.”

Added

page 18, line 14: The tile of this section only mentions the treatment with H2O2, but not the heat treatment. Correct this.

Corrected

page 18, line 25: The FS04 you are referring to here (the one kept at room temperature over night), is that a fresh one or a heated one? Add this information to the text.

It was a fresh sample. We now say so explicitly in the text.

page 19, line 7: Otherwise you mention a droplet volume of 0.2 nL, and here it is 0.6 nL. Correct this!

The droplet volume was 0.2 nL in all experiments.

page 20, line 4 ff: Also add the direction in which the shift of the median freezing temperature occurred (i.e., faster cooling -> lower T50).

Rephrased

page 20, line 7: exchange “by accelerating” to “when accelerating”.

Corrected

page 20, line 10: Change “have been found” to “were found to be”.

Corrected

page 20, line 12: Shouldn’t FS01 here be FS04?

Of course, thank you!

page 20, line 16: When referring to FS04 in parenthesis here, add that this was observed “, for the highest examined concentration”.

added

page 20, line 32: What do you mean by “for a particular INP”? Certainly not a single particle?

Particular INP type

page 21, line 3: Add “, beyond what was done in here” after “Further improvement of the CNT-based parameterizations” (the sentence as it is now gives the impression that this was examined in your study).

Modified

page 21, line 20 to 22: Just because it’s the final statement, I make suggestions for corrections for all of it:

- “by the wide range” has to be “by a wide range”
- add “a” between “volume, “ and “large”
- change “possible of conducting” with “it is possible to conduct”
- “type” (two words later) has to be “types”
- change “Such instrument, if” to “Such an instrument, when”

All of the above: done as requested

page 21, line 23: “Cheap” seems to be relative, here. At least put “comparably” before “cheap”, as I don’t think one can assemble and use a set-up like yours for less than 5000 Euro, which, for a university might already be quite a sum of money.

“Cheep” is, of course, a relative notion. What we had in mind was “cheap compared to CFDC or cloud chamber types of instruments”

Table 2B: Values for n_s* should be given here, too (similar to Table 2A).

The values of n_S^* now included into the table 2B.

Figure 4: Make sure that this plot covers two columns in the final version, and additionally increase the size of all numbers and letters for improved readability on a printout. - Check readability for all figures in general, in their final size, as occasionally still people want to read something on paper.
Figure 8: Why do you show data for all 4 samples, if you only present model results for 2 of them?

The fit parameters for the generic feldspars are very similar

Figure 9: Change the color of the shaded area, as it is the same than that of some FS02 data-points, which hence cannot be seen.

The issue seems to be PDF specific and will be resolved at the stage of final preparation

Literature (cited both by us and by the referee):

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(21), 10989–11003, doi:10.5194/acp-13-10989-2013, 2013.

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Erickson, H. P. (2009), Size and shape of protein molecules at the nanometer level determined by sedimentation, gel filtration, and electron microscopy, Biological Proce-dures Online, 11(1), 32-51, doi:10.1007/s12575-009-9008-x.

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Vali, G., DeMott, P. J., Möhler, O. and Whale, T. F.: Technical Note: A proposal for ice nucleation terminology, Atmos. Chem. Phys., 15(18), 10263–10270 [online] Available from: http://www.atmos-chem-phys.net/15/10263/2015/acp-15-10263-2015.html (Accessed 17 September 2015), 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.

A comparative study of K-rich and Na/Ca-rich feldspar ice nucleating particles in a nanoliter droplet freezing assay

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Abstract. A recently designed droplet freezing assay was used to study the freezing of up to 1500 identical 0.2 nL water droplets containing suspensions of one Na/Ca-rich feldspar and three K-rich and one Na/Ca-rich feldspar particles. Three types of experiments have been conducted: cooling ramp, isothermal freezing at a constant temperature, and freeze-thaw cycles. The observed freezing behavior ~~have~~has been interpreted with the help of a model based on the classical nucleation theory (Soccer Ball Model, SBM, Niedermeier, 2015). By applying the model to the different freezing experiments conducted with the same ice nucleating (IN) material ~~allowed to constrain,~~ the parameter space ~~and to derive~~can be constrained the unique sets of model parameters for specific feldspar suspensions~~.~~ can be derived. The SBM was shown to adequately describe the ~~shift of the freezing curves towards the lower temperature with dilution, the~~observed cooling rate dependence ~~and,~~ the ice nucleating active sites (INAS) surface density $n_s(T)$ in a wide temperature range, and the shift of the freezing curves towards lower temperature with dilution. Moreover, the SBM was capable of reproducing the variation of INAS surface density $n_s(T)$ with concentration of ~~IN~~ice nucleating particles in the suspension droplets and correctly predicting the leveling-off of ~~the~~ $n_s(T)$ at low temperature. The freeze-thaw experiments have clearly shown that the heterogeneous freezing induced even by very active ice nucleating species still possesses a stochastic nature, with the degree of randomness increasing towards homogeneous nucleation.

A population of the high temperature INAS has been identified in one of the K-rich feldspar samples ~~(FS04).~~. The freezing of 0.8 wt % suspension droplets of this particular feldspar was observed already at -5°C. These high temperature active sites could be completely deactivated by ~~treatment~~treating the sample with hydrogen peroxide but survived heating up to 90°C. Although the mass density of the high temperature ~~IN~~ice nucleating sites is comparable to that of the typical bacterial or fungal

INPs, the possibility of biological contamination of the sample ~~have~~has been ruled out. The freezing efficacy of all feldspar samples ~~have~~has been shown to reduce only slightly after ~~suspending~~suspension in water for over 5 months.

1 Introduction

Atmospheric aerosol particles influence the radiation budget of the Earth due to their absorption and scattering properties, they act as cloud condensation nuclei (CCN) due to the aerosol-cloud-interaction and promote ice formation in precipitation processes (Pruppacher and Klett, 2004). It is assumed that the formation of precipitation ~~in~~at mid-~~latitude~~latitudes proceeds predominantly via the ice phase (Baltensperger, 2010). A solid ice nucleating particle ~~known as IN~~(INP) is needed to trigger heterogeneous ice nucleation. For a quantitative description of heterogeneous ice nucleation, the concept of ice nucleation active site (INAS) surface density was introduced in order to assess the ice nucleating (IN) efficiency of aerosol particles, regardless of the experimental measurement conditions (Connolly et al., 2009). The ability of aerosol particles to act as ~~ice nuclei~~INP strongly depends on the material and the freezing mode (Hoose and Möhler, 2012). Especially mineral dust particles like kaolinite (Wex et al., 2014), illite (Hiranuma et al., 2014) and feldspar (Atkinson et al., 2013, denoted ATK2013 from now on) were identified as ~~potent IN~~efficient INP showing high INAS surface density in a particular temperature range.

Although a large amount of the earth's crust consists of feldspar mineral (~51%, Ronov and Yaroshevsky, 1969) only a minor fraction (~13% according to B. J. Murray et al., 2012) of this primary mineral contributes to the mineral-containing atmospheric aerosol particles. In particular, field campaigns showed that the mass fraction of K-feldspar collected on filter substrates in Taifou (Morocco) was 10 wt% in dust storm and 25 wt% in low-dust conditions (Kandler et al., ~~2011~~2009). Similar results were observed at Cape Verde with 20 wt% (“dust period”) and 25 wt% ("maritime period"). These field campaigns have been carried out in the vicinity of the Sahara Desert and may exhibit strong gradients of particle concentration with distance from the source (Nickovic et al., 2012). Mineral dust particles collected in Asia contained 11 wt% Na/Ca-rich feldspar and 8 wt% of K-rich feldspar (Jeong, 2008).

Despite their low mass abundance feldspar particles could play a crucial role in ice nucleation due to the fact that the freezing properties of a particle ensemble can be dominated by ~~IN~~INPs exhibiting the highest ability to initiate ice formation. Up to now, feldspar was studied with various experimental methods and in different freezing modes.

Deposition ~~freezing~~ice nucleation experiments carried out in an environmental scanning electron microscope (ESEM) have shown that K-rich feldspar (microcline) had the lowest onset freezing temperature and supersaturation with respect to RH_{ice} (onset RH_{ice}: 105% at -12°C, Zimmermann et al., 2008). In contrast, RH_{ice} for Na/Ca-rich feldspar (albite) showed only a weak temperature dependence ~~of RH_{ice}~~, whereas K-feldspar exhibited an increase of onset RH_{ice} with decreasing temperature. Diffusion chamber experiments have led to the conclusion that K-feldspar (orthoclase) is an effective deposition ~~IN~~INP at a temperature of -40°C (ice nucleation onset ~~RH_{ice}~~ observed at 135.0% ± 3.6% at the threshold of 0.1% of ice activated particles ~~(~~, Yakobi-Hancock et al., 2013). ~~Long term suspension of K-feldspar in water slightly increased the onset RH_{ice} value (127.1% ± 6.3%). It was concluded that the washing-out did not significantly changed the ability to nucleate ice.~~

In a number of droplet freezing assay experiments (~~Atkinson et al., 2013~~ATK2013; Whale et al., 2015; Zolles et al., 2015~~) the~~), K-~~-~~feldspar particles have been investigated in the immersion freezing mode~~ and~~. It was found that K-feldspar particles initiate freezing at higher temperatures than any other mineral dust particles. It was hypothesized that the fraction of K-feldspar in ~~naturally~~natural mineral dusts samples correlates with the ice nucleation efficiency (~~Atkinson et al., 2013~~ATK2013). Size-selected measurements of K-feldspar (microcline) aerosol particles carried out in the Leipzig aerosol cloud interaction simulator (LACIS) have revealed that the frozen fraction of droplets containing individual feldspar aerosol particles could ~~reached~~reach a plateau value well above -38°C (Niedermeier et al., 2015, NIED2015 in the following text). This behavior was interpreted in terms of a specific average number of ice nucleating sites per particle reaching unity inside the temperature range where the freezing curve starts to level off. Na/Ca-feldspar particles studied with a Cold Stage/Raman microscope setup featured ice activity in both deposition and immersion freezing modes, presumably due to the presence of K-feldspar impurities (Schill et al., 2015).

Several experiments addressed the influence of ageing on the ice nucleation efficiency of feldspar particles. Chemical treatment with sulfuric acid was shown to cause a reduction of ice activity of K-feldspar particles depending on the coating conditions (Augustin-Bauditz et al., 2014; Kulkarni et al., 2014). The ice activity of aged K-feldspar was similar to other chemically treated minerals, i.e~~.~~., Arizona test dust (ATD), kaolinite and illite NX. Mechanical milling of K-feldspar particles caused a slight increase in their ice activity, while enzymatic treatment significantly reduced their ice activity probably due to blocking of ice active sites (Zolles et al., 2015). Subsequent heating led to a restoration of the ice ~~efficiency.~~nucleation efficiency. Zolles et al. (2015) found indications "that the higher IN efficiency of the K-feldspar sample is an intrinsic property and not a result of adsorbed organic/biological material".

Laboratory studies of ice nucleation of feldspar in condensation and contact freezing mode are scarce. In particular, condensation freezing experiments conducted in the Manchester ice cloud chamber (MICC, Emersic et al., 2015) fall tube have shown the temperature dependence of n_s values being less steep compared to the immersion freezing experiments reported in ~~(Atkinson et al., 2013).~~ATK2013. In contact freezing experiments, K-feldspar particles have shown IN efficiency comparable to that of ATD and rhyolitic ash in the same temperature range (Niehaus et al., 2014). Note that in this study the particle size distribution was rather broad and therefore the results should be interpreted with caution.

In spite of accumulating evidence of the 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 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, a low variability of droplet size and concentration, a large number of individual droplets, an automatic control of individual droplet freezing time and temperature used in our instrument improves the experimental statistics and allows for parameterization of freezing efficiency of feldspar based on the classical nucleation theory.

This manuscript is organized as follows: In the methods section, the experimental setup and the model approach based on a so- called Soccer Ball Model (SBM, (Niedermeier et al., 2011 2011b, 2014, 2015) are described, followed by characterization of four feldspar samples (K-rich and Na/Ca-rich feldspar). In section 5 we present the results of cooling ramp experiments (CR), isothermal freezing experiments (ISO), and freeze-thaw cycle experiments. We show that both temperature and time dependent freezing behavior of selected feldspar samples can be described with the unique sets of fit parameters within the SBM approach. Using the fit parameters obtained for various feldspar samples we show that the observed temperature dependence of the INAS surface density is an inherent feature of the experimental method. Section 6 discusses the influence of aging and chemical treatment of feldspar. The concluding section is focused on the concentration and cooling rate/time dependence of immersion freezing of feldspar suspension droplets, discussed from the point of view of both singular and stochastic ice nucleation active sites ~~hypothesis.~~hypotheses.

2 Theoretical background

The parametric description of heterogeneous ice nucleation is based either on the stochastic or singular hypothesis (Niedermeier et al., 2011b; Vali, 2014). The stochastic approach assumes that a critical ice cluster needs to be formed before the freezing of the entire droplet can proceed. The heterogeneous IN causes a lowering of the ice germ formation energy and therefore ~~enhance~~enhances the probability of ice nucleation. For a given supercooling temperature, the probability of freezing event is a function of nucleation rate and time. In contrast, the singular approach assumes that the ice nucleation occurs on the specific active sites of the IN immediately as soon as a characteristic temperature has been reached (Fletcher, 1969). In ~~the~~this framework, of this approach ice nucleation probability is independent of time. Besides these two extremes, there exist several approaches that try to bridge the gap. In more detail, the time-dependent freezing rate (TDFR) model combines assumptions of the singular approach with a cooling rate dependence (Vali, 2014), multicomponent stochastic models make use of a simple linear expression of the temperature dependence of nucleation rate coefficient (Broadley et al., 2012) and ~~CNT~~classical nucleation theory (CNT) based approaches use a distribution of active sites or contact angles to represent the variability in ice nucleation behavior (Marcolli et al., 2007; Niedermeier et al., 2011 2011b).

Assuming the singular hypothesis, the ice nucleation active site (INAS) surface density as a function of temperature $n_s(T)$ can be expressed via the fraction of frozen droplets $f_{ice}(T)$ and the surface area S_p of ~~ice nucleating particles~~INPs per droplet (Connolly et al., 2009; Niemand et al., 2012):

$$n_s(T) = -\frac{\ln(1-f_{ice}(T))}{S_p} \quad (1)$$

The total particle surface area is either derived from surface area distributions or calculated from the mass of particles per droplet multiplied by the Specific Surface Area measured with BET approach (BET-SSA, Brunauer et al., 1938).

In this work we use the simplified version of SBM (Niedermeier et al., 2014, 2015) to show that both cooling ramp and isothermal experiments can be parameterized with a single set of CNT-based fit parameters. The approach is based on the assumption, that each droplet contains *on average* a number n_{site} of IN active sites, their ~~ice nucleating~~IN efficiency being characterized by the normally distributed contact angles θ. The distribution $p(\theta)$ is described by a mean contact angle μ_θ and standard deviation σ_θ. In ~~such~~this case, the probability P_{unfr} of a single suspension droplet to remain liquid after time t at given supercooling temperature T is given by

$$P_{unfr}(T, \mu_\theta, \sigma_\theta, t) = \int_{-\infty}^{+\infty} p(\theta) \exp\left(-J_{het}(T, \theta) S_p n_{site}^{-1} t\right) d\theta \quad (2)$$

Where $J_{het}(T, \theta)$ is the freezing rate coefficient at given temperature T and contact angle θ, and S_P is the total particle surface area per droplet (Pruppacher and Klett, 2004; Vali, 1999). Note that although $\theta \in [0, \pi]$ the integration is carried out on the interval $[-\infty, +\infty]$ to account for the continuity of a Gaussian probability distribution function p(θ). Outside of the $[0, \pi]$ interval, θ is set to either 0 or π. Assuming the random distribution of active sites between the droplets, the fraction of frozen droplets f_{ice} after time t can be calculated:

$$f_{ice} = 1 - \exp\left[-n_{site}\left(1 - P_{unfr}(T, \mu_\theta, \sigma_\theta, t)\right)\right] \quad (3)$$

In case of CR experiments, the cooling rate $c = dT/dt$ has to be introduced to relate the temperature and time: $T = T_{start} + ct$, where T_{start} is the start temperature of the cooling ramp (typically 273K). The parameters n_{site}, μ_θ and σ_θ can be obtained by fitting the Eq. (3) to the experimentally measured fraction of frozen droplets as a function of freezing temperature (in CR experiments) or freezing times in ISO experiments. As in (Niedermeier et al., 2014), the parameterization of relevant thermodynamic quantities ~~have~~has been adopted from (Zobrist et al., 2007). The goodness of fit is described by ~~r^2~~the correlation coefficient r^2.

Equation 3 can be used to explore the relationships between the apparent fraction of frozen droplets and material properties, the later described as a combination of μ_θ and σ_θ. Since the experimental parameter (particle number or mass per droplet) is represented by n_{site}, this equation provides also a basis for comparison between experiments conducted with the same material but under different experimental conditions (different droplet size and particle concentration). Moreover, it can be used to explore the relationship between the median freezing temperature and the cooling rate, which is often referred to as an indicator of either the stochastic or singular description of ice nucleation.

The INAS surface density can be derived from the CNT-based parameterization by substituting Eq. (3) into (1):

$$n_s(T) = \frac{n_{site}}{S_p}\left(1 - P_{unfr}(T, \mu_\theta, \sigma_\theta, t)\right) \quad (4)$$

This relationship is very helpful to understand the apparent behavior of the $n_s(T)$ curves obtained directly from the measurements via Eq. (1), as discussed below.

3 Methods

3.1 Experimental setup

The central part of the experimental setup is a cold stage (Linkham, Model MDBCS-196), which was used to carry out the cooling ramp and isothermal experiments (Fig. 1). Cooling is achieved by pumping liquid nitrogen from a reservoir through the copper sample holder. The cold stage can operate in the temperature range from 77 K to 400 K. Controlled heating and cooling ramps can be performed at rates between 0.01 K/min to 100 K/min. The temperature stability is better than 0.1 K.

A single crystal silicon substrate (Plano GmbH, 10×10 mm) was first cleaned with high grade acetone (p.a.), then rinsed several times with NanoPure water (Barnstead Thermolyne Corporation, Infinity Base Unit, 18.2 MΩ/cm). Finally, the silicon wafer was purged with nitrogen to remove residual water. ~~Thus cleaned~~This silicon wafer was then mounted into a square depression in the sample holder. ~~It was shown before (Steinke, 2013), that~~ A surface prepared in this way induces freezing of pure water ~~drops~~droplets only at temperatures very close to the temperature of homogeneous freezing of water, as discussed below in section 5.2.

The feldspar suspensions were prepared by adding the feldspar powder into 25 mL of NanoPure water and stirred for an hour. A piezo-driven drop-on-demand generator (GeSIM, Model A010-006 SPIP, cylindrical case) was used to print individual suspension droplets in a regular array onto the silicon substrate. Before dispensing, the substrate was cooled to the ambient dew point to reduce the evaporation of droplets. Up to 1500 suspension droplets of (215 ± 70) pL volume were deposited onto the silicon wafer resulting in droplets with (107 ± 14) µm diameter in spherical cap geometry with contact angle of 74°±10°. After printing, the droplet array was covered with silicone oil (VWR, Rhodorsil 47 V 1000) to prevent evaporation and any eventual interaction between the supercooled and frozen droplets. Measurements of the droplet geometry and volume are described in the Supplement.

The temperature of the droplets was measured with a calibrated thin film platinum resistance sensor (Pt-100) that was fixed directly on the surface of the silicon substrate by a small amount of heat conducting paste (vacuum grade) as shown on the inset of Fig. 1. The Pt-100 sensor was calibrated against a reference sensor in the temperature range from -40°C to +30°C prior to the experiment. The single point temperature measurement error was estimated to be ± 0.1 K.

A charge-coupled device (CCD)-camera (EO progressive) with a wide field objective (DiCon fiberoptics Inc.) was used to record the freezing of the suspension droplets. The substrate is illuminated by a ring light source mounted around the objective lens. Two polarizers (one in front of the light source and one in front of the objective) were used to enhance the brightness of the frozen droplets compared to the liquid ones. Video- and temperature recordings of the cooling and freezing

process were taken at a frame rate of 1 to 8 frames per second (fps), allowing for identification of individual freezing events with time resolution of 0.125 to 1 s and 0.1 K temperature accuracy. Freezing of individual droplets can be recognized by a pronounced increase of the light scattered from the frozen droplets (detected through the crossed polarizer in front of the objective lens). An automated video analysis routine allows for extraction of the fraction of frozen droplets as a function of temperature from the raw data. Subsequent data processing with a LabView routine allowed for calculation of a fraction frozen vs. temperature curve.

3.1.1 Cooling ramp experiments

Two types of freezing experiments have been performed with this experimental setup: In cooling ramp (CR) experiments, the temperature is linearly reduced with a constant cooling rate. Cooling ramp experiments from 273K to 233K were performed at three different cooling rates $c = dT/dt$ (-1 K/min, -5 K/min and -10 K/min) and the fraction of frozen droplets f_{ice} ~~is~~was recorded as a function of temperature with 0.1 K resolution. After each CR experiment, the substrate ~~is~~was heated to 274 K until every droplet has melted. ~~Thereby~~In this way, the same sample can be used ~~in the~~for several repeated CR experiments, allowing correlation analysis of subsequent freezing runs.

3.1.2 Isothermal experiments

In isothermal (ISO) experiments (also known as temperature jump experiments~~)~~), the temperature is reduced rapidly via initial ramp ~~(5~~(cooling rate from -5 K/min to -10 K/min) to a pre-set value and then held constant for about an hour, during which the individual droplet freezing times ~~being~~are recorded continuously. The set point temperature was chosen such that a maximum of 25% of the droplets froze during the initial cooling ramp. These ~~type~~types of experiments addresses both the influence of temperature and time on the ice nucleation process of feldspar particles immersed in water droplets.

4 Materials

4.1 Feldspar samples

The feldspar samples FS01, FS04 and FS05 were provided by the Institute of Applied Geosciences, Technical University of Darmstadt (Germany) and the feldspar sample FS02 was provided by the University of Leeds (UK). Samples FS01, FS04 and FS05 have been prepared by ball milling of single crystal mineral specimens. FS02 is the standard BCS 376 from the Bureau of Analysed Samples, UK. All samples were studied during the Fifth International Ice Nucleation (FIN) measuring campaigns at AIDA cloud chamber in the framework of the Ice Nucleation Research Unit (INUIT) project of German Research Foundation (DFG, see Acknowledgements) and the name convention has been preserved for consistency with the future publications. Table 1 gives an overview of the investigated feldspar samples.

~~3~~4.1.~~3~~1 Sample preparation for chemical ageing experiments

To ~~access~~assess the effect of ageing on the IN activity, the feldspar particles (FS01 und FS05) were left in water for over five months and the supernatant water was exchanged several times. Extreme care has been taken to avoid any contamination as a consequence of water exchange. The concentration of exchanged cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) have been measured regularly during the first month (see Supplement). For the cooling ramp experiments, the feldspar particles were centrifuged (Thermo scientific, 2000rpm for 20min), dried and re-suspended in 25 mL NanoPure water. Alternatively, fresh suspensions of feldspar (FS04) particles were heated to approximately +90°C for over an hour. Additionally, the FS04 feldspar sample has been suspended in 100 mL hydrogen peroxide aqueous solution (AppliChem GmbH, 30% p.a.) at +65°C und stirred for an hour or kept in hydrogen peroxide solution at room temperature overnight.

~~**4 Materials**~~

~~**4.1 Feldspar samples**~~

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4.2 Morphology and particle surface area

An environmental scanning electron microscope (ESEM FEI, Quanta 650 FEG) was used to record images and energy dispersive X-ray (EDX) spectra of individual feldspar particles deposited on graphite and silicon substrates. For each sample, over one hundred individual spectra have been recorded for the individual particles separated by at least 10 µm from other particles or agglomerates. The program Esprit 1.9 (Bruker) was used to quantify the chemical composition of the feldspar samples. SEM images of feldspar particles showed agglomerates consisting of several large rocky particles with the smaller particle fragments on their surface (Fig. 2). With respect to their morphology, both individual feldspar particles within ~~one~~a single sample, and ~~the~~those particles from different feldspar samples were very similar. The wide field images have been used to ~~access~~assess the size of the individual particles and to derive the average total particle surface area S_p contained by a single suspension droplet (see supplementary Fig. S1). An example of the size distribution of FS02 residual particles deposited on

silicon substrate is given in the Supplement (Fig. S2), and is in good agreement with the size distribution determined by laser diffraction method for the sample FS02 (~~Atkinson et al., 2013~~ATK2013).

The specific surface area (~~S_{BET}~~also often referred to as BET surface area, S_{BET}) has been measured with N_2 gas adsorption technique following the Brunauer-Emmett-Teller method (BET, Brunauer et al., 1938). The ~~SSA~~ S_{BET} of feldspar samples ranged from 1.79 to 2.94 m²/g (Table 1) which is lower than the BET surface areas reported by ~~Atkinson et al., 2013~~ATK2013, (3.2 m²/g for FS02 and 5.8 m²/g for Na/Ca feldspar particles respectively) and slightly higher than the BET surface area reported by (Schill et al., 2015) (1.219 m²/g for Na/Ca feldspar particles). The ~~SSA~~BET surface area was then used to calculate the "gravimetric" particle total surface area using the relationship $S_p = W \cdot V_{drop} \cdot S_{BET}$~~.~~, which accounts for the weight concentration of feldspar, W. Both ~~method~~methods delivered similar values of S_p, as demonstrated in Fig. S2.

4.3 Mineral composition

The mineralogical composition of the bulk samples FS01, FS04, and FS05 was determined by X-ray powder diffraction analysis (XRD). Relevant measurement parameters are shown in Table 1. Identification of the mineral phases was performed using the ICDD Database (ICDD, 2002).

The ternary phase diagram derived from EDX measurements of individual feldspar particles shows that particles of FS01, FS02 and FS04 have a similar chemical composition close to the end member microcline/orthoclase (Klein and Philpotts, 2013) (Fig. 3a). The compositional ~~distribution~~distributions of FS01 and FS02 are nearly overlapping, but ~~also~~ some particles richer in sodium and calcium were observed. The composition of FS04 was slightly closer to the end member microcline/orthoclase. Iron as a trace component was found in individual EDX spectra of FS02 and FS04, which can probably originate from trace impurities of aegirine (member of sodium pyroxene group) known to form in the alkaline igneous rocks also responsible for the formation of alkali feldspars (Deer et al., 1978), as in the region of Mount Malosa in Malawi. Note that the EDX spectra were measured on ~~the~~a single particle basis and therefore do not represent the weight average composition of the entire sample. The composition of the agglomerates may differ from that of the individual particles. In accordance with the solid solution series of plagioclase, the majority of FS05 particles are situated in the region of andesine (intermediate plagioclase, 30-50% anorthite, Klein and Philpotts, 2013) (Fig. 3b). However, individual particles were richer in sodium and closer to the end member albite. Based on the analysis of individual EDX spectra, the Al:Si ratio was found to be very close to 1:3. This ratio varies from 1:3 for albite to 2:2 for anorthite (end member of the plagioclase solution series). The EDX spectra of size selected FS05 particles (300 nm mobility diameter) do not significantly differ in their composition from larger coarse-grained particles. We therefore suggest that the FS05 sample predominantly consists of albite with minor heterogeneous inclusions of andesine. The observed steady rise of Ca^{2+} and Na^{+} concentration measured in the suspension over the period of four weeks supports this conclusion (see Supplement). In the following, we refer to FS05 as a "Na/Ca-rich feldspar" and to

FS01, FS02 and FS04 samples as “K-rich feldspar”. Overall, the EDX results mainly confirmed the composition of feldspar samples derived from XRD analysis (see Table 1).

5 Results and discussion

5.1 ~~Cooling ramp experiments~~

~~Suspensions of FS01, FS02, FS04 and FS05 were investigated in the concentration range from 0.8wt% to 0.01wt% (Fig. 4A-4D) at three different cooling rates: 1, 5 and 10 K/min. Supercooled water droplets containing feldspar particles froze well above the homogeneous freezing limit (which was found to be 237 K for 100 µm droplets on a pure silicon substrate, see Steinke, (2014). The concentrated suspensions (0.8wt%, dark coloured curves) have shown in general steeper freezing curves as compared to less concentrated suspensions. The freezing behavior of FS01 and FS02 was nearly identical. The freezing of Na/Ca-rich feldspar suspensions (FS05, Fig. 4C) occurred at lower temperature range (from 255.5K to 248K) as compared to K-rich feldspar suspensions. The concentrated (0.8wt%) suspension of FS04 was quite outstanding from the rest of samples as the droplets started to freeze already at 268K (Fig. 4D). All suspension droplets of FS04 have frozen at 255K. The effect of concentration was similar for all investigated feldspar sample suspensions. With decreasing concentration of feldspar suspensions, the frozen fraction curves covered a broader temperature range and the frozen fraction curves are shifted to lower temperatures. Additionally, the freezing curves of less concentrated FS04 suspensions (0.01 wt% to 0.1wt%) are very similar to those of FS01 and FS02 feldspar suspensions.~~

~~5.2~~ Freeze-thaw cycle experiments

To investigate the repeatability of droplet freezing, freeze-thaw cycle experiments with identical cooling rates have been performed. Every individual droplet has been assigned a rank number according to its freezing time in two successive CR experiments, with rank number 1 corresponding to the first droplet frozen and so on. The pairs of rank numbers of the individual ~~droplet~~droplets have been plotted on a 2D coordinate grid as shown in the Fig. ~~5~~4. Droplets that have ~~disappeared~~evaporated in the second temperature ramp experiment or could not be detected automatically were excluded from consideration. A perfect correlation between rank orders in two cycle experiments would imply that every droplet ~~has frozen~~froze exactly at the same temperature in both CR runs. On the other hand, no correlation between the freezing rank numbers would imply statistically independent freezing events or very steep temperature dependence of the heterogeneous nucleation rate coefficient (if the freezing times of individual droplets could not be distinguished within the time resolution of the video camera).

For NanoPure water droplets on a cleaned silicon wafer substrate, no correlation between the ranking order of freezing events could be observed, as shown by Pearson’s *r* coefficient equal to 0.14. However, a small fraction of droplet population near the beginning of a cooling cycle (Fig. ~~5a) show~~4a) showed local increase of correlation, which could probably be associated with contamination of the silicon wafer or impurities in the water or in the silicon oil. The freezing of these

contaminated droplets is also visible as a flat shoulder on the warm side of the frozen fraction curve for NanoPure water in the Fig. 5.

For concentrated FS01 suspensions, a higher correlation of freezing events was observed (r = 0.89, Fig. ~~5c~~4c). FS05 suspensions showed a lower correlation coefficient (r = 0.8, Fig. ~~5b~~4b). The highest correlation coefficient was obtained for concentrated FS04 suspensions (r = 0.92, Fig. ~~5d~~4d).

We have also 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.

These ~~observations~~results suggest that the correlation coefficient is related to the IN efficiency of the suspension material. INPs initiating freezing at a lower temperature also showed a lower correlation coefficient, while more efficient INPs ~~nucleate ice~~initiating freezing at a higher temperature, and in a ~~narrow~~narrower temperature range ~~showing~~, showed higher correlation coefficients. A similar conclusion was drawn for the ice nucleation of collected rainwater samples (Wright et al., 2013). Therein, a slight decrease of standard deviations of the median freezing temperatures at higher temperatures (i.e. reduced cooling rate dependence) has been reported. In ~~(~~the work of Campbell et al., (2015) a correlation plot was used for the characterization of silicon substrates roughened with diamond powder. It could be demonstrated that there was a strong correlation between freezing ranks of droplets in successive cooling runs on the scratched silicon substrates. Similar experiments, investigating the repeatability of freezing temperatures of single droplets of distilled water and two soil dust samples were carried out with a microliter droplet freezing assay (Vali, 2008). The derived Spearman rank correlation coefficients for pairs of runs were higher than 0.9, indicating a high repeatability of freezing temperatures. The standard deviation of the mean freezing temperature, evaluated from the freeze/thaw cycle experiments on individual droplets containing ATD (Wright et al., 2013), soil dust (Vali, 2008) and Nonadecanol (Zobrist et al., 2007) was found to be less than 1 K. For volcanic ash (Fornea et al., 2009) and black carbon (Wright et al., 2013~~)~~), this value was larger ~~(~~by a few degrees~~)~~.. These experiments corroborated the small variability ~~of~~in freezing temperatures of individual droplets. ~~The presented~~Our correlation plots demonstrate both the ~~random variability~~randomness of freezing temperatures in successive cycle experiments, as well as the variability of surface properties across the population of feldspar particles~~, while in~~. In contrast, for the cycle experiments ~~on~~with individual droplets, the variability of surface properties ~~can~~could be neglected (Niedermeier et al., ~~2011~~2011b). The strong correlation between freezing events observed in our freeze-thaw cycles confirms the idea that the heterogeneous nucleation of ice is stochastic in nature, but its average observable characteristics (like fraction of frozen droplets) are governed by temperature dependent efficiency of individual IN active sites.

5.2 Cooling ramp experiments

Suspensions of FS01, FS02, FS04 and FS05 were investigated in the concentration range from 0.8wt% to 0.01wt% (Fig. 5A-5D) at three different cooling rates: 1, 5 and 10 K/min. Supercooled water droplets containing feldspar particles froze well

above the homogeneous freezing limit (which was found to be 237 K for 100 µm droplets on a pure silicon substrate, see Figure 5). The concentrated suspensions (0.8wt%, dark coloured curves) have shown in general steeper freezing curves as compared to less concentrated suspensions. The freezing behavior of FS01 and FS02 were nearly identical. The freezing of Na/Ca-rich feldspar suspensions (FS05, Fig. 5C) occurred at lower temperature range (from 255.5K to 248K) as compared to K-rich feldspar suspensions. The concentrated (0.8wt%) suspension of FS04 was quite outstanding relative to other samples, as the droplets started to freeze already at 268K (Fig. 5D). All suspension droplets of FS04 were frozen at 255K. The effect of concentration was similar for all investigated feldspar sample suspensions. With decreasing concentration of feldspar suspensions, the frozen fraction curves covered a broader temperature range and the frozen fraction curves are shifted to lower temperatures. Note that the freezing curves of less concentrated FS04 suspensions (0.01 wt% to 0.1wt%) are very similar to those of FS01 and FS02 feldspar suspensions. The raw measurement data have been averaged within the 0.5K temperature intervals (Fig. 6 shows the case of FS02 and FS04).

5.3. Isothermal experiments

For a droplet population containing single component INPs kept at constant temperature, the classical nucleation theory (CNT) predicts an exponential decay of the number of *liquid* droplets with time. To see if such behavior can be observed under realistic experimental conditions, we have conducted a series of isothermal experiments where droplets were cooled down rapidly (typically at rate of 10 K/min) and then kept at constant temperature T_{ISO} for an hour. These experiments have been conducted for concentrated (0.8 wt%) suspensions of FS02 at T_{ISO} = 253K, 254K, 255K, and 256K, and FS04 at T_{ISO} = 266K and 267K. The resulting unfrozen decay curves are shown in Fig. 7 together with the SBM simulations that are discussed in the next section.

~~For droplets of FS02 suspensions, decay of the liquid fraction $f_{liq}(t)$ is clearly deviating from the linearity (in log-log scale) indicating broad distribution of the active sites responsible for ice nucleation (Fig. 7A). The deviation from linearity is more pronounced for lower temperatures, as more and more ice nucleating sites become active.~~

~~A different behavior is seen~~ For the FS04 suspensions. The $f_{liq}(t)$ curve shows a nearly linear (in log-log scale) decrease with time (Fig. 7B), with the decay rate becoming less steep at lower ~~temperature~~temperatures. A linear decrease is usually attributed to a single component IN population with a uniform and narrow distribution of active sites and/or contact angles on the particle surface: AgI (Murray et al., 2012), kaolinite (Murray et al., 2011) and illite NX (Diehl et al., 2014). In ~~contrast,~~addition, biological IN were found to exhibit a constant nucleation rate indicating a narrower distribution of active sites and/or contact angles on the IN species (Yankofsky et al., 1981).

For droplets of FS02 suspensions, decay of the fraction of liquid droplets $f_{liq}(t)$ clearly deviates from the linearity (in log-log space) indicating a broad distribution of the active sites responsible for ice nucleation (Fig. 7A). The deviation from linearity is more pronounced for lower temperatures, as more and more ice nucleating sites become engaged.

Such non-linear time dependence ~~have~~has been reported for a number of mineral dust particles immersed in water droplets. In droplet freezing assay experiments, ~~FS02~~ suspensions of feldspar identical to our FS02 sample (Herbert et al., 2014), ATD suspensions (Wright et al., 2013) and less concentrated illite NX suspensions (Broadley et al., 2012) featured a non-linear time behavior. Studies in the Zurich Ice Nucleation Chamber (ZINC) have also found that size-selected kaolinite particles (Fluka, 400nm and 800nm) showed also a non-exponential decay with increasing residence time and temperature (Welti et al., 2012). Non-exponential time dependence was associated with a ~~multi-component~~heterogeneous system featuring a high degree of interparticle variability. Other authors ascribe the deviation from the single-exponent to the diversity of active sites and the finite number of droplets (Wright et al., 2013). ~~In addition, biological IN were found to exhibit a constant nucleation rate indicating a narrower distribution of active sites and/or contact angles on the ice nucleating species (Yankofsky et al., 1981).~~

5.4. Cooling rate dependence

For all investigated concentrated feldspar suspensions, a weak cooling rate dependence of the median freezing temperature ($T_{0.5}$) was observed (Fig. 8). For FS01, FS02 and FS05 the median freezing temperature was shifted by ΔT = 0.6 - 0.7 K toward lower temperature, as cooling rate $c = dT/dt$ increased from -1K/min to -10K/min. However, for concentrated FS04 suspensions (0.8 wt~~%~~%), the $T_{0.5}$ decreased by only 0.2 K.

~~Depending on the mineral dust type~~The experimental and ~~the concentration~~numerical studies of ~~suspension, the reported influence of~~ the cooling rate effect on the median freezing temperature ~~can strongly vary. A 0.1 wt% ATD suspension showed a temperature shift value of ΔT = 1.3K for a change in cooling rate from 0.01K/min to 5K/min (~~$T_{0.5}$ have been reviewed recently by Wright et al., (2013~~). This corresponds to a temperature shift of ΔT = 0.5K per ten-fold change in the cooling rate. In contrast, the kaolinite (Murray~~) and Herbert et al., ~~2011),~~(2014). For mineral dusts (ATD, montmorillonite ~~and flame soot~~) the median freezing temperature becomes lower by 0.5 K to 1.5 K per ten-fold increase in the cooling rate. For kaolinite suspensions (~~Wright et al., 2013) showed a very strong cooling rate dependence. For kaolinite suspensions (sample provided by~~ Clay Minerals Society, CMS) a temperature shift of 8 K (three orders of magnitude change in cooling rate) ~~and ΔT =~~has been predicted based on the parameterization of experimental data (Murray et al., 2011), but the measured temperature shift revealed only 3~~°C for montmorillonite suspensions (~~ K temperature shift when decreasing cooling rate by two orders of magnitude ~~change in cooing rate) were obtained. For illite NX suspensions a complex cooling rate dependence was observed: on one hand, concentrated illite NX suspensions (0.89 wt%) exhibited a temperature shift of 1-2 K for a change in cooling rate from 1 K/min to 5 K/min. On the other hand, a negligible cooling rate dependence for low concentrated illite NX suspensions was observed. These apparently contradicting observations could be explained consistently in the framework of a stochastic multicomponent model (Broadley et al., 2012).~~ (Wright et al., 2013).

Unlike mineral dusts, biological INP showed a weaker cooling rate dependence. For Snomax~~®~~®, a weak increase of the $T_{0.5}$ value with decreasing cooling rate was found ~~(~~by Wright et al., (2013~~). The cooling rate dependence of $T_{0.5}$ for Snomax~~

was quantified in microliter droplet freezing assay () and Budke and Koop, (2015): an). The increase in cooling rate by two orders of magnitude from 0.1 K/min to 10 K/min led to a temperature shift of ΔT = 0.55K and ΔT = 0.64K for highly concentrated (Class A type) and less concentrated (Class C type) Snomax® suspensions, respectively. This is consistent with our observation of reduced cooling rate dependence for droplets containing highly effective IN particles.

5.5 SBM-based fit of experimental data

To demonstrate the common features and differences in freezing behavior of all feldspar suspensions, we have applied the SBM-based fit to the experimental freezing curves of all feldspar samples obtained for various concentrations. The raw measurement data (as shown in Fig. 2A and 2D) have been averaged within the 0.5K temperature intervals. TheseThe binned data have been fitted with Eq. (3) with adjustable fit parameters $n_{site,}$ μ_θ, and σ_θ (Fig. 6). Binning improves the efficiency of minimization algorithm that has been programmed in Matlab. The fit parameter values of fit parameters obtained for the best fit are given in Table 2A.

For isothermal experimentexperiments, the fit routine has been modified to fit the entire decay curve of the liquid droplet fraction. This was achieved by allowingsetting the cooling ramp relationship to $T = T_{start} + ct$ in the time interval $t_{start} \leq t \leq t_{ISO}$ until. Once $T_{ISO} = T(t_{ISO})$ has been reached and then fixing, the relationship is set to $T(t) = T_{ISO}$. In this way, the fit routine was forced to find the set of fit parameters capable of reproducing both frozen fraction at the end of the cooling ramp $f_{liq}(t_{ISO})$ and time evolution of the decay curve at constant temperature $f_{liq}(t), t > t_{ISO}$. The resulting "composite" fit curves are shown in Fig. 7A and 7B for FS02 and FS04, respectively, and resulting fit parameters are given in Table 2B.

By allowing all three Ideally, a single set of SBM parameters being freely adjustable, different combinations of $n_{site,}$ μ_θ and σ_θ could be found that wouldshould represent the experimental resultsfreezing behavior of a given INP obtained in different experiments (CR with different cooling rates, CR with various concentrations, and ISO freezing experiments) equally well. ThereforeIf this is not the case, a constraining condition is required to obtain self consistenta meaningful set of fitting parameters. Such conditionA suitable constraint can be found in different ways: by analysinganalyzing the cooling rate dependence of $f_{ice}(T)$ or by finding the unique set of fit parameters adequately describing both CR and ISO experiments with the same INPs. .

First, we compare the observed shift of the median temperature with the theoretical values calculated with the help of Eq. (3), with $T_{0.5}$ being the temperature where $f_{ice} = 0.5$ and $\Delta T_{0.5}(c) = T_{0.5}(c) - T_{0.5}(-1\,K/min)$ (solid lines in Fig. 8). The values of n_{site}, μ_θ and σ_θ have been taken from the SBM fit of the CR freezing curves, as described above in this section. The absolute values of $\Delta T_{0.5}(c)$ are satisfactory reproduced by the model for FS01 and FS02 at $c = -5\,K/min$ and for FS04 at $c = -10\,K/min$ but are 0.2K off for FS01, FS02, and FS05 at $c = -10\,K/min$. The shift of the median temperature is less pronounced for better ice nuclei (compare $\Delta T_{0.5}(-10\,K/min) = -0.2K$ for FS04 vs. $\Delta T_{0.5}(-10\,K/min) = -0.5K$ for

"generic" feldspars FS01, FS02, and FS05 and this feature is clearly captured by the SBM (Fig. 8). Although the trend in the cooling rate dependence is adequately predicted, we note that the $\Delta T_{0.5}(c)$ calculated with Eq. (3) ~~is insensitive to the variation of input parameters (see also the discussion in (Herbert et al., 2014): therefore it is not possible to achieve~~cannot predict more than $\Delta T_{0.5} = -0.5K$ for a ten-fold change in the cooling rate~~.~~ without relaxing the constraint on μ_θ and σ_θ (see also the discussion in Herbert et al., 2014). However, ~~the cooling rate dependence seems to be sensitive to the symmetry of the contact angle distribution $p(\theta)$: by assuming the log-normal instead of Gaussian distributed contact angles but otherwise preserving all model parameters a~~a slightly better agreement with the measurements of $\Delta T_{0.5}$ at $c = -10\,K/min$ could be achieved by assuming the log-normal $p(\theta)$, but otherwise preserving all model parameters (dashed line in Fig. 8). We conclude therefore that ~~cooling rate dependence of the~~SBM does capture the observed trend (the less active suspensions exhibit a stronger shift of median freezing ~~curve is adequately described by SBM~~ temperature) but ~~can hardly~~cannot be effectively used to constrain the fitting routine.

The allowed variability of fit parameters can be reduced if we consider that the same IN material has been used in CR experiments with different weight concentrations W. In this case, the values of μ_θ and σ_θ can be kept constant in the simulation of the freezing curves, and only n_{site} should be varied. The initial pair of μ_θ and σ_θ can be determined either by fitting the freezing curve measured for the lowest concentration or by assuming the fit parameters obtained from the ISO experiments (if available), as it has been done here for FS02.

The same ~~considerations have bee6n~~approach has been used to constrain the fit of isothermal data for FS02 and FS04, obtained for different values of T_{ISO}. For FS02, the initial values of $\mu_\theta = 1.32\,rad$ and $\sigma_\theta = 0.1\,rad$ have been obtained from the fit of composite liquid fraction decay curve at 256 K. This pair of parameters ~~have~~has then been ~~then~~ used to fit the other ISO decay curves and the freezing curves measured in the CR experiments with various concentrations. Within this approach, a high quality fit ($r^2 > 0.95$) of all frozen fraction curves (Fig. 6A) and liquid fraction decay curves (Fig. 7A) could be achieved. ~~Note that the number of IN sites per droplet n_{site} required to achieve the fit convergence, increases with the rising concentration of FS02 suspension, which make sense as the number of sites per droplet is increasing with mass concentration of the particulate matter in the suspension. Note also, that obtained~~Note that the pair of fit parameters for FS02 is very close to the values $\mu_\theta = 1.29\,rad$ and $\sigma_\theta = 0.1\,rad$ obtained in (~~Niedermeier et al., 2015~~NIED2015) by fitting the frozen fraction curves measured in the diffusion channel LACIS for the ~~same~~similar feldspar specimen (FS01).

The fit of the ISO measurements of FS02 has ~~delivered~~yielded a higher number of IN active sites n_{site} for higher T_{ISO} (Table 2B). This ~~contra-intuitive~~counterintuitive observation ~~can~~could be possibly explained by the relationship between T_{ISO} and the final fraction of frozen ~~droplet~~droplets achieved at the end of the ISO run. For higher T_{ISO}, the final fraction of frozen droplets is lower, and the fit algorithm "compensates" for the reduction of available sites by increasing their total number. This effect was not very pronounced in case of FS04 (see Table 2B), probably because the final fraction of frozen ~~droplet~~droplets for both used T_{ISO} values used was very similar. This observation, however, hints that n_{site} should not be treated blindly as a number of active sites *activated* during the cooling ramp or isothermal freezing, but rather as a number of active ~~site~~sites

required by the numerical algorithm to reproduce the freezing curve. Thus, caution should be exercised when interpreting the fit results, as numerical features can be mistaken for physical relationships.

Almost the same distribution of contact angle ($\mu_\theta = 1.33\ rad, \sigma_\theta = 0.1\ rad$) as for FS02 was obtained by fitting the concentrated FS05 suspensions. This is a somewhat unexpected result since freezing curves are visibly shifted towards the lower temperature (by at least 2K, see Fig. 4A and 4C). ~~If one would trust the physical~~Straightforward interpretation of fitting parameters~~, the similarity of contact angle distributions~~ would mean that the difference between K-rich feldspar (FS01, FS02) and Na/Ca-rich feldspar (FS05) is not in the activity of IN sites but in their number per unit particle surface (~~n_{site}~~compare $n_{site} = 47$ for FS05 against $n_{site} = 181$ for FS02, with only 20% difference between total particle surface S_p). ~~However~~On the other hand, the same difference in median freezing temperature ~~shift~~ can be ~~obviously~~ compensated by increasing the standard deviation from $\sigma_\theta = 0.1\ rad$ for FS02 to $\sigma_\theta = 0.14\ rad$ for FS01 (compare $n_{site} = 30$ for FS01 and $n_{site} = 181$ for FS02, which have a very similar freezing behavior). ~~To~~In our opinion, such analysis demonstrates that fitting the freezing curves *with ~~freely variable~~a three~~-~~ adjustable parameter fit* without providing additional constraint does not necessarily lead to a better understanding of IN nature. Therefore, the intercomparison of the freezing behavior, either of different specimens or observed ~~in~~within different experimental setups, based on such a fit, should be done with extreme caution.

The sample FS04 ~~is~~stands out clearly ~~standing out of~~within the ~~analysed~~analyzed group of feldspars in several respects. For this specimen, it was not possible to fit all freezing curves obtained at various concentrations with a fixed pair of fit parameters μ_θ and σ_θ. The $\mu_\theta = 0.75\ rad$ found for freezing curve measured for the 0.8 wt% suspension indicates a very high IN efficiency. However, for the diluted suspensions (0.1 wt% to 0.01 wt%) the fit parameters that secured the best fit appeared to be close to the values obtained for three other feldspar specimens (see Table 2A). Such behavior could only be interpreted in terms of bimodal population of active sites in the FS04 sample, with the sites belonging to the very active second mode present in scarce numbers and thus ~~visible~~visibly dominating the freezing curve of concentrated suspension droplets. In diluted suspensions, the presence of the second mode is visible as a shoulder on warmer side of the freezing curves for 0.1 wt% and 0.05 wt% suspensions (see Fig. ~~7B~~6B). This shoulder, however, does not affect the fit algorithm. Note that we have not constrained the fitting parameters in any way here, applying the fit algorithm to every freezing curve independently, which caused a slight variation of μ_θ and σ_θ.

The two-component hypothesis of FS04 freezing behavior is strongly supported by the data of isothermal decay experiments and corresponding fit. The fit parameters that provided the best fit of liquid fraction decay curves were identical, apart ~~for~~from the 15% difference in the n_{site} value, so that the only experimental value actually different in the simulation is the T_{ISO} (266K and 265K). The value of $\mu_\theta = 0.56\ rad$ is even lower than the mean contact angle obtained from the fit of the freezing curve $\mu_\theta = 0.75\ rad$ and the standard deviation $\sigma_\theta = 0.04$ indicates a homogeneous population of IN active sites. The difference in μ_θ between the CR and the ISO fits should be attributed to the fact that in the CR experiment the whole distribution of freezing sites is involved in ice nucleation, and therefore the contact angle obtained in the fit represents the whole distribution of active sites. ~~On the contrary~~In contrast, in the ISO experiments only the most efficient sites are activated

so that the less efficient sites are excluded from the freezing process. The homogeneity of the active sites distribution is consistent with the linearity of the decay curve in the log-log scale (Fig. 7B).

Such low values and narrow distributions of contact angles (and hence, high IN activity) have been previously obtained in SBM ~~fit~~fits for freezing curves of biological INPs. For example, the INPs generated from Czech and Swedish birch pollen washing water (BPWW) have been characterized by $\mu_\theta = 1.01$ rad, $\sigma_\theta = 0.08$ rad, and $\mu_\theta = 0.83\,rad, \sigma_\theta = 0.0005\,rad$, respectively (Augustin et al., 2013). For Snomax® particles, the best INP known up to date (Wex et al., 2015), SBM parameters of $\mu_\theta = 0.595\,rad, \sigma_\theta = 0.04\,rad$ have been calculated based on the same approach (Hartmann et al., 2013). Within this reference framework, the IN efficiency of ~~high~~the highly active mode of FS04 is higher than that of the BPWW and at least as high as that of the Snomax®.

Overall, the IN activity of feldspars investigated in this study is situated at the upper end of ice activity scale. For ATD, the range of SBM ~~parameter~~parameters was found between $\mu_\theta = 2.13\,rad$, $\sigma_\theta = 0.33\,rad$, and $\mu_\theta = 2.48\,rad$, $\sigma_\theta = 0.39$ rad (Niedermeier et al., ~~2011~~2011b). The mean and standard deviation of the contact angle distribution of Illite NX was found to be ~~1.9 rad~~$\mu_\theta = 1.9\,rad$ and ~~0.29 rad~~$\sigma_\theta = 0.29\,rad$, respectively (Hiranuma et al., ~~2014). Note, however, that these fit data were not constrained by isothermal freezing experiments. However,~~2015). This comparison suggests that the SBM framework correctly reproduces the relative ice nucleation efficiency of natural and artificial mineral dust aerosols.

5.6 Surface density of IN active sites

The CR experiments performed with varying concentration allowed us to calculate the INAS surface density via Eq. (1~~) in the temperature range from 238K to 260K for FS01 and FS02 (Fig. 9~~). Both $n_s(T)$ curves for FS01 and FS02 are very similar and are therefore ~~put~~shown together in ~~one plot~~Fig. 9. In the temperature range between 252K and 260K (occupied by the 0.8 wt% suspension data) our $n_s(T)$ values are only slightly lower than those reported for FS02 in ~~(Atkinson et al., 2013, denoted~~ ATK2013~~ in the plot and elsewhere).~~. The data of ATK2013 is shown in the form of an exponential ~~parametrization~~parameterization and is used as a reference for all other $n_s(T)$ plots (black solid line in Fig. 9 to Fig. 11). Size-selected measurements of FS01 particles in LACIS also showed a similar slope of $n_s(T)$ curve but the values are shifted towards higher n_s, located at lower ~~temperature~~temperatures (orange open triangles, ~~Niedermeier et al., 2015, denoted~~ NIED2015~~ in the plot and in the following discussion~~). Both our $n_s(T)$ curves for FS01 and FS02 suspensions and the data from NIED2015 showed a leveling-off of $n_s(T)$ values with decreasing temperature. A qualitative explanation that was suggested in NIED2015 is that at ~~colder~~lower temperature the surface density of INAS is approaching asymptotic value n_s^*, equal to the maximum surface density of *all possible* INAS for the given particle population. The leveling off has not been reported in ATK2013, obviously because the suspension was not diluted sufficiently to reach the temperature range where the leveling-off would be expected.

The $n_s(T)$ can be easily related to the SBM fit parameters obtained from the CR and ISO experiments via Eq. (4). The shaded area in the Fig. 9 shows the range of $n_s(T)$ that we obtain by assuming the fit parameters from Table 2A: $\mu_\theta =$

$1.32\,rad$, $\sigma_\theta = 0.1\,rad$, $c = -1\,K/min$, $n_{site} = 2$, and varying weight concentration of feldspar in the droplet suspension from 0.01 wt% to 0.8 wt% (and therefore varying the total particle surface area since $S_p = W \cdot V_{drop} \cdot S_{BET}$). Note that varying ~~the~~ S_p has essentially the same effect on ~~the~~ $n_s(T)$ as varying ~~the~~ n_{site} since these two quantities appear as a ratio in the Eq. 4. The fact that all experimental data fall inside the shaded area demonstrates that the range covered by n_{site} variation corresponds to the variation range of total particle surface at different weight concentrations. One can immediately see that the SBM simulation captures the leveling-off of $n_s(T)$ at lower temperature.

As pointed out in NIED2015, the asymptotic value n_s^* is the limit of $n_s(T)$ when the probability of the suspension droplet to freeze at T, $P_{freeze} = 1 - P_{unfr}(T, \mu_\theta, \sigma_\theta, t)$, approaches 1 (recall Eq. (4~~).~~)). It is therefore clear that the suspension droplet is bound to freeze when $n_s(T)$ reaches the value n_s^*, and further increase of the IN active site efficiency (described in the model by decreasing the value of contact angle) would not result in the further increase of the freezing probability (or the fraction of frozen droplets). The value of n_s^* is therefore a true suspension property as compared to n_{site}, which is just a number required by the minimization algorithm to fit the experimental freezing curve. For combined FS02 and FS01, the upper ~~boundary value~~bound of n_s^* was found to be 2.1×10^7 cm^{-2}, corresponding to the surface area occupied by a single IN active site $S_{site} \approx 5\,\mu m^2$, a square patch with the side length of 2.2 µm, which is at least 6 orders of magnitude larger than the cross ~~section~~ sectional area of a critical ice nucleus at low temperature (Pruppacher and Klett, 2004).

We observe that the data of NIED2015 ~~are laying~~lie outside the shaded area in Fig. 9. The values of $n_s(T)$ reported in NIED2015 have been obtained for single, size selected feldspar particles, with the modal electrical mobility diameters ranging from 0.2µm to 0.5µm. If we use the geometric surface area (based on the aerodynamic diameter, as specified in NIED2015) of a 0.5µm particle as ~~the~~for S_p in Eq. (4), and use the constant temperature, and a residence time of 1.6 s (as in LACIS ~~condition~~), we obtain the blue broken line that agrees with the data of NIED2015 quite well. The ratio of ~~asymptotic~~ n_s^* values is evidently equal to the ratio of S_p values in NIED2015 and in this study (red broken curve in Fig. 9). Thus, we arrive at the conclusion that the apparent INAS surface density in the plateau region is a function of the particle surface area per droplet, which is not obvious considering that per definition the INAS surface density is defined as a number of frozen droplets *normalized* by the particle surface.

For the ~~asymptotic of~~ INAS surface density ~~for~~asymptote with NIED2015 data, we calculate $n_s^* = 4.7 \times 10^8\,cm^{-2}$, and the corresponding surface area occupied by a single IN in this case is reduced to $\approx 0.21\,\mu m^2$, a square patch with the side length of $\approx 460\,nm$, still "oversized" ~~for~~compared to a single critical ice germ. The fact that the asymptotic "surface area per active site" is much larger than the cross ~~section~~ sectional area of a critical ice germ supports the idea that "ice active sites" ~~should be some~~are local features (of morphological or chemical nature) and not the homogeneous patches ~~of~~on the particle surface.

The $n_s(T)$ curves of FS05 suspensions are shifted ~~to~~toward the lower temperatures compared to FS01 and FS02 (Fig. 10) but otherwise showed the same behavior (exponential growth in the range from 250 K to 257 K and gradual leveling-off at lower temperature). Together with our values, both measurements reported recently in ATK203 and (Schill et al., 2015) fall

nicely into the range of n_s values predicted by Eq. (4~~)~~), by assuming the fit parameters of: $\mu_\theta = 1.33\,rad,\ \sigma_\theta = 0.1\,rad,\ c = -1\,K/min$, and $n_{site} = 5$, and varying weight concentration of feldspar in the droplet suspension from 0.01 wt% to 0.8 wt%. The upper ~~boundary value~~bound of n_s^* was found to be $1.8 \times 10^7\ cm^{-2}$, very close to that of FS01 and FS02.

The outstanding nature of FS04 becomes more evident on the $n_s(T)$ plot (Fig. 11). The bimodal behavior is clearly visible with the first mode being active already at 268K, 5K below the melting point. The second mode is located at lower temperature and ~~is~~ almost ~~coinciding~~coincides with the $n_s(T)$ curve of FS01 and FS02 (shown as red broken line in Fig. 11). Both modes show the leveling-off starting below 266 K for the high-temperature mode and below 248 K for the low-temperature mode.

The coexistence of two independent sets of IN active sites can be reproduced by Eq. (4) by using two separate sets of fitting parameters (Table 2A) for calculation of $n_s(T)$. The $n_s(T)$ range covering the low-temperature mode is obtained by assuming the fit parameters: $\mu_\theta = 1.3\,rad,\ \sigma_\theta = 0.12\,rad, n_{site} = 10$, and varying the weight concentration of feldspar in the droplet suspension from 0.01 wt% to 0.1 wt%, whereas the high temperature mode is represented by fit parameters: $\mu_\theta = 0.75\,rad,\ \sigma_\theta = 0.12\,rad$, and varying the n_{site} from 0.2 to 10. Note that the $n_s(T)$ curve calculated with the fit parameters obtained from the isothermal freezing experiments ($\mu_\theta = 0.56\,rad,\ \sigma_\theta = 0.04\,rad$, Table 2B) is only reproducing the rising slope of the measured curve. This means that the overall shape of the high-temperature part of the curve (above 255K) is influenced both by IN active sites from both active and less active modes, and is responsible for the higher value of μ_θ than the one obtained from the isothermal freezing experiment.

A formal comparison of the asymptotic INAS surface densities n_s^* for two modes -- $2.4 \times 10^7 cm^{-2}$ for the low temperature mode ~~vs.~~versus $1.0 \times 10^4 cm^{-2}$ for the high temperature mode -- suggests that the highly active sites constitute roughly 0.1% of all sites in our suspension droplets. Multiplying the n_s^* for the high temperature mode with the total particle surface area per droplet, we obtain $n_s^* \times S_p = 0.29$, implying that only 30% of all suspension droplets of the most highly concentrated suspension contain at least one high temperature active site at all. One can obtain approximately the same number by noting that only 75% of all droplets froze in the ISO experiment after cooling the droplet assay down to 266 K and waiting for an hour (see Fig. 7B). Since the amount of feldspar in our suspension droplets (0.8 wt%) corresponds roughly to 3.7×10^3 individual feldspar particles of 0.5 µm diameter, one could estimate that only one in ≈ 12000 feldspar aerosol particles of this size would contain a single, highly active ~~ice nucleating~~IN site. This estimation might be helpful in understanding the nature of these sites, as discussed below.

A two-step ice nucleation behavior was previously ~~obtained~~observed for pure, size-selected ATD particles (Niedermeier et al., ~~2011~~2011a) and birch pollen washing water residual particles (Augustin et al., 2013) in LACIS, for soil dust particles (O'Sullivan et al., 2015) and Snomax® (Budke and Koop, 2015; Wex et al., 2015) particles in droplet freezing assay experiments. These measurements highlight that there could be multiple, distinct populations of ~~ice nucleating particles (~~INPs~~)~~ present in a particular material. ~~The activation~~Presence of these ~~individual~~ sites ~~critically depends on concentration~~will be detectable only in concentrated suspensions and setups, allowing measurements at high supercooling temperature. To our

knowledge, ~~however,~~ multiple ice nucleating species in a single-component mineral dust aerosol (like illite, ~~kaoline~~kaolinite, montmorillonite, etc.) have not been observed before.

6 Influence of ageing

6.1 Aging in aqueous suspension

To examine the influence of aging on the ice activity of feldspars, K-feldspar (FS01) and Na/Ca-feldspar (FS05) particles were soaked in water for over five months and the supernatant water was exchanged twice. Soaking in water resulted in a decrease of the median freezing temperature by 2 K for FS01 and by 3 K for FS05 0.8 wt% suspensions. (Fig. 12). The reduction of ~~ice nucleating~~IN efficiency is thought to be correlated with the release of soluble components from the framework of the mineral (e.g. alkali metal ions, hydrated ~~aluminium~~aluminum and silicon species), which might be ~~repartioned~~repartitioned as amorphous material on the surface of feldspar particles (Zhu and Lu, 2009; Zhu, 2005) ~~und~~and inhibit ice active sites. The stronger reduction in T_{50} values observed for FS05 might be a consequence of a higher dissolution rate of the Na/Ca-feldspar particles (Parsons et al., 1994; Zhu, 2005). The time evolution of the leaked cation concentration (K^+, Na^+, Ca^{2+}, and Mg^{2+}) have ~~been~~was measured during the first month by liquid ion chromatography and is shown in the supplementary Fig. S6. We have observed a steady rise of cation ~~concentration~~concentrations, during the whole period of observation, according to the $\sim t^{0.5}$ law, well known in petrology for the dissolution rates of tectosilicates as they are weathered to become clays (Parsons, 1994). This behavior clearly differs from the cation release from illite clay mineral in aqueous suspension, where no further increase of the cation concentration was observed after initial fast release occurring on the order of several minutes (Hiranuma et al., 2015). The depletion of framework cations in the surface crystalline layers of feldspar might be another explanation ~~of~~for the observed reduction of ice ~~activity.~~nucleation efficiency. Due to the constant release of the framework cations, the IN activity of the ageing feldspar should gradually reduce over long time ~~period~~periods, as the feldspar is weathered to become clay.

6.2 Treatment with heat and hydrogen peroxide

We have ~~undertaken an attempt~~attempted to shed some light onto the anomalously high ~~ice nucleating~~IN efficiency of concentrated FS04 by treating it both thermally and chemically. Our primary suspect was contamination with biological IN particles, known to be the most active ~~ice nucleating particles~~INP in immersion mode. To this ~~matter~~end, we have conducted the CR experiments with the 0.8wt% suspensions heated up to 90°C for an hour. Heating is a common procedure to test for proteinaceous ice nuclei that are expected to degrade progressively with increasing temperature (Pouleur et al., 1992; Pummer et al., 2012). ~~Thus~~Heat- treated FS04 showed a slight decrease of the T_{50} value from 264.7K to 263.9K in 1K/min CR experiment, but the $n_s(T)$ curve preserved ~~it~~its bimodal shape and position (Fig. 13). This clearly demonstrates that proteinaceous IN could not be responsible for the high ice activity of FS04 particles. Another test is the removal of thermally

stable, carbonaceous IN by digestion with hydrogen peroxide solution (O'Sullivan et al., 2014; O'Sullivan et al., 2015). This treatment, performed at 65°C for one hour, has indeed resulted in the significant reduction of the ice activity of FS04. Keeping the freshly prepared FS04 sample in hydrogen peroxide over night at room temperature lowered the T_{50} even further (Fig. 12C and Fig. 13). A weak cooling rate dependence of chemically treated FS04 particles was observed, with ~~the10~~the 10-fold change in responsible for $\Delta T \approx 0.5K$. This is more than ~~the~~ ΔT observed for untreated suspensions by a factor of 2 (open symbols in Fig. 12 and Fig. 5) and is characteristic for generic feldspars FS01 and FS02. By looking at $n_s(T)$ curves of thermally and chemically treated FS04, it becomes clear that the treatment has reduced its IN activity down to that of the generic K-feldspar (FS01 and FS02). A further reduction was not observed and is not expected since the generic K-feldspar particles showed no detectable change in ice activity after a thermal treatment (O'Sullivan et al., 2014; Zolles et al., 2015). Based on these results alone, organic IN cannot be ruled out as a reason for the ~~anomalous~~anomalously high freezing efficiency of FS04.

Let us ~~calculate~~estimate the amount of "contamination" required to produce the observed enhancement of INAS surface density at high temperature. The feldspar powder used for preparation of FS04 suspension was produced by ball milling of a single crystal specimen. Due to the usual ~~precaution~~precautionary measures taken to avoid the contamination during and after the preparation, it is logical to assume that the contamination could ~~be~~have been introduced on the surface of the specimen prior to milling, and the amount of contamination should be proportional to the surface area of the original specimen. In the previous section, we came to ~~a~~the conclusion that only every third droplet in our experiment contained a highly active ice nucleating "entity". Since the mass of feldspar per 0.~~6~~2 nL droplet at 0.8 wt% concentration is $V_d \times 0.008 \times \rho_{FS} = 1.2 \times 10^{-8}\ g$, we can estimate the mass concentration of active sites $n_m = 2.7 \times 10^8\ g^{-1}$, which is, for example, two orders of magnitude higher than the mass concentration of ice active sites in untreated fertile soil (see Fig. 7 in O'Sullivan et al., 2014). Soil particles contain up to 40% organic matter which is thought to be responsible for their IN properties (Tobo et al., 2014). Augustin-Bauditz et al., (2016) has measured the freezing behavior of illite NX mixed with birch pollen washing water (BPWW) extract. BPWW contains resuspendable IN active macromolecules, most probably polysaccharides (Pummer et al., 2012), which, unlike ice nucleating proteins, preserve their IN efficiency upon heating. In the work of Augustin-Bauditz et al., (2016), they estimated the mass fraction of biological material in 0.5µm illite particles to be 9.7%. Although they could not detect freezing events above -17°C, extrapolating their fraction of frozen droplets curve to -10°C and calculating the mass concentration of IN active sites as $n_m(T) = -\frac{6 \cdot ln(1-f_{ice}(T))}{\pi \rho_p d_p^3}$, we obtain concentration of macromolecules $n_m \approx 5 \times 10^7\ g^{-1}$. This value is close to what we obtained for high-temperature active sites in FS04 at 266 K, but that would imply that FS04 sample contains 10% polysaccharides by mass, which is hardly possible. Additionally, to accept the biogenic contamination as the explanation for the high-temperature IN sites, we have to assume that the feldspar crystal used for the sample preparation was contaminated with INM with very homogeneous IN properties, as implied by a narrow distribution of contact angles established by fitting the isothermal freezing experiments at 266 K and 267 K. Finally, the modal value of contact angle distribution obtained with SBM fitting of immersion freezing curves for pure BPWW particles yielded a value 0.83 rad (Augustin et al., 2013)~~equal to $n_m = 2.7 \times 10^8\ g^{-1}$. Such value is characteristic for ice active fungal species~~

~~(Pummer et al., 2015) or most active component of Snomax® at 267K (Wex et al., 2015). Suppose the specimen was a cube with a side of 1cm prior to milling, which is a typical size of low cost single crystal specimen of feldspar. Assuming that all high active INP were located on the surface of such a specimen, we obtain a surface density of INPs $\approx 1.2\ \mu m^{-2}$, more than one ice nucleating particle per square micron. To our knowledge, such contamination is impossible, and we therefore arrive at the conclusion that the active sites responsible for the high-temperature freezing mode are inherent for the feldspar itself. The question of the nature of this ice nucleating substance remains open~~, which is larger than any of our values for the high-temperature fraction of IN active sites in FS04 feldspar. These arguments bring us to the conclusion that at a realistic contamination level polysaccharides are not efficient enough to be responsible for the high-temperature nucleation of ice in FS04 suspension droplets. Since BPWW-like macromolecules are the only "likely" candidates for such contamination (capable of preserving the IN activity after heating but degrading after H_2O_2 treatment), the biogenic nature of high-temperature active sites seems to be unlikely. The origin of these sites, however, remains uncertain.

Several studies addressed the influence of ageing processes on the IN activity of feldspar particles. In more detail, diffusion chamber studies showed no statistically significant change in ice nucleation ability of unwashed and washed feldspar (orthoclase) particles in deposition mode freezing experiments (Yakobi-Hancock et al., 2013). Enzyme-treated K-feldspar ~~treated with enzyme~~ nucleated ice at much lower temperatures, but after heating, the ice activity has been restored to the original level. For Na/Ca-feldspar particles (albite and andesine~~)~~), no distinct change after thermal and chemical treatment was noticed (Zolles et al., 2015). A strong reduction of ice activity of K-feldspar particles (microcline) immersed in water droplets was achieved by treatment with sulfuric acid (Augustin-Bauditz et al., 2014). It was suggested that the treatment with sulfuric acid irreversibly modified the lattice structure of K-feldspar, as was also suggested by the ice nucleation experiments with bare and sulfuric acid coated K-feldspar particles (Kulkarni et al., 2012). To be more specific, in the deposition freezing experiments a reduced ice activity for coated feldspar particles was found, while no significant difference between bare and coated K-feldspar particles was observed in immersion freezing experiments. This behavior was explained in terms of dissolution of coating material under water-supersaturated conditions. ~~This~~These results, however, ~~are hardly comparable~~cannot be directly compared with our observations since coatings have not been applied in our study.

7 Conclusions

A newly developed Cold Stage apparatus was used to study the freezing behavior of up to 1000 identical feldspar suspension droplets, each with ~~the~~a volume of 0.2 nL. The setup features a motorized droplet injector positioning stage, liquid N_2 temperature control, and automated freezing detection system based on a wide field video camera equipped with polarization optics. Suspensions of three K-rich feldspars (microcline) and one Na/Ca-rich feldspar (albite with andesine inclusions) have been examined with different concentrations ranging from 0.01 wt% to 0.8 wt% and cooling rates from -1 K/min to -10 K/min. All concentrated feldspar suspensions have shown a steep temperature dependence of the INAS density, whereas diluted

suspensions showed a flattening with decreasing temperature approaching asymptotically a limiting value n_s^*. The K-rich feldspar samples, FS01 and FS02, and Na/Ca-rich feldspar, FS05, showed a weak cooling rate dependence ~~on the order of 0.6K shift of~~: median freezing temperature decrease on the order of 0.6K over ~~the~~a ten-fold ~~change~~increase in the cooling ~~range, whereas~~rate. In contrast, the median freezing temperature of the FS04 suspension ~~was shifted~~increased by only 0.2K ~~by~~, when accelerating the cooling from -1K/min to -10K/min.

The setup has proven to be perfectly suited for isothermal freezing experiments, ~~that~~which we have conducted with FS02 at four constant temperatures from 253K to 256K, and with FS04 at two constant temperatures of 266 K and 267 K. The liquid fraction decay curves ~~have been~~were found to be clearly nonlinear in the log-log coordinates for the FS02 and quite linear for FS04. Since the non-linearity of the decay curves is normally associated with the heterogeneity of the sample, one would expect stronger heterogeneity of FS02 as compared to ~~FS01.~~ FS04.

To explore the relationship between stochastic and singular nature of ice nucleation, several freeze-thaw experiments with cooling rate of -5 K/min have been conducted. The degree of correlation between two subsequent freezing runs~~,~~ expressed as Pearson's correlation coefficient, have been shown to increase gradually from 0.14 in the case of pure water droplets on a silicon substrate to 0.92 for the best ~~ice nucleating~~ IN material in this study (FS04~~).~~) observed at the highest examined concentration. The fact that the correlation does not become ideal, even for the best IN, clearly demonstrates the stochastic nature of ice nucleation.

We have used a CNT-based theoretical framework (the so-called Soccer Ball Model, SBM, Niedermeier et. al., 2015) to provide a consistent interpretation of the observed freezing behavior. This framework is based on the assumption ~~of number $n_{site}(T)$ of~~ that the active sites are randomly ~~dispersed~~distributed over the surface of all ~~ice nucleating particles~~INPs inside a single suspension droplet. The IN efficiency of these sites is characterized by a Gaussian distribution of contact angle θ with mean value μ_θ and standard deviation σ_θ. We show that it is possible to adequately describe the freezing curves obtained for different concentration and cooling rates in the CR experiments, and the isothermal decay of fraction of liquid droplets with time using a unique set of SBM parameters μ_θ and σ_θ and varying n_{site} according to the weight concentration of feldspar in suspension. Moreover, it was possible to use the same parameters to reproduce the experimental data obtained for the same feldspar specimen by different methods: LACIS, droplet freezing assay from ATK2013, and the data of Schill et al., (2015). Most noteworthy, however, is the observation that this approach seems to be capable of reproducing the variation of INAS surface density $n_s(T)$ with concentration of IN in the suspension droplets and correctly predicts the leveling-off of the $n_s(T)$ at low ~~temperature~~temperatures. The asymptotic ~~value~~active site density n_s^*, achieved by $n_s(T)$ as the freezing probability of every droplet in the ensemble approaches unity, can be interpreted as a method independent property, inherent ~~for~~to the suspension only~~, and,~~. Together with the mean value of contact angle, ~~provide~~this asymptotic value provides a basis for the parametrization of IN properties that is required ~~in~~within the atmospheric modeling.

It should be stressed, however, that a consistent interpretation of the freezing behavior for a particular INP type is only possible ~~in~~through a combination of different experiments (cooling ramp, isothermal decay, freeze-thaw cycles) and thorough characterization of particle morphology (BET SSA, chemical composition, and size distribution). The fit parameters

obtained by fitting the temperature jump ~~followed by~~and subsequent isothermal decay experiments allowed us to constrain the variability of fit parameters describing the CR freezing curves and therefore the $n_s(T)$ curves. Further improvement of the CNT-based parametrizations, beyond what was done in here, can be ~~done~~achieved by accounting for the contact angle variability and the particle surface variability separately, and by assuming asymmetry of the contact angle distribution. Although the mechanistic understanding of IN active sites is still missing, this framework is worth developing further to be prepared for the future when the nature of the IN active sites will be characterized quantitatively via nanoscale measurements or ab-initio calculations.

One of the K-rich feldspar specimens (FS04) has shown an anomalously high ~~ice nucleating~~IN efficacy, initiating the freezing already at -5°C. The INAS surface density of this feldspar clearly demonstrated a bimodal distribution of active sites, with a high temperature mode occupying the temperature range from 255K to 268K, and ~~the~~a low temperature mode in the range below 255 K, identical to the generic feldspar suspensions (FS01 and FS02). A proteinaceous origin for these highly active IN entities could be ruled out, since heating the suspension to 95°C yielded no observable change in the IN efficacy. Treatment of 0.8 wt% ~~suspensions~~suspension of FS04 with 30% hydrogen peroxide (H_2O_2) solution resulted in the deactivation of the ~~anomalous~~ high-temperature IN mode and reduction of ice nucleation activity down to that of the generic K-rich feldspar. ~~The proteinaceous origin of the these highly active IN entities could be excluded by heating the suspension to 95°C without any observable change of the IN efficacy.~~ Applying the SBM fit to the temperature jump – isothermal decay experiments, ~~the~~a value of $\mu_\theta = 0.56\ rad$ was obtained, which was previously found for ~~bacterial~~proteinaceous INP (Snomax), ~~the most active ice nucleating particle so far.~~but is lower compared to $\mu_\theta = 0.83\ rad$, measured for polysaccharides washed down from birch pollen grains. The number of high temperature active sites per mass of feldspar ($n_m = 2.7 \times 10^8\ g^{-1}$) was found being too high to be explained by surface contamination of the feldspar specimen prior to milling. ~~We therefore arrive at a conclusion~~We argue that the presence of high temperature IN sites should be an inherent property of this particular feldspar specimen. Their nature, however, remains ~~unclear~~uncertain.

We conclude by suggesting that the droplet freezing assay presented in this paper is a useful tool for studying immersion freezing induced by ~~the~~a wide range of IN active materials, due to ~~its~~the low variability of droplet volume, a large number of individual droplets that can be observed simultaneously, and possibility ~~of conducting~~to conduct different ~~type~~types of freezing experiments with the same sample. Such an instrument, ~~if~~when complemented by a careful ~~characterization of particle~~ surface and chemical characterization of an INP sample, ~~could provide~~provides a fast and comparatively cheap method ~~of~~for INP characterization.

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Table 1: The mineral composition and specific surface area (N_2 BET SSA) of feldspar samples.

Sample	Source	Mineral composition (XRD)	BET SSA [m²/g]
FS01	Minas Gerais, Brazil, supplied by IAG TU Darmstadt	76% K-feldspar (microcline) 24% Na/Ca-feldspar (albite)	1.79
FS02	Bureau of Analyzed Samples, UK, standard BCS 376 (provided by University of Leeds, UK)	80% K-feldspar* 16% Na/Ca-feldspar* 4% quartz	2.64
FS04	Mt. Maloso area (Malawi), supplied by IAG TU Darmstadt	80% K-feldspar (microcline) 18% Na/Ca-feldspar (albite) 2% quartz	2.94
FS05	IAG TU Darmstadt, in-house collection	>90% Na/Ca-feldspar (albite)	1.92

*mineral phase was not specified

Table 2A. SBM parameters obtained by fitting the CR freezing curves. The total particle surface area per droplet S_p is given for 0.8 wt% concentration and could be recalculated for all other mass concentrations. Pearson's *r* correlation coefficient was calculated from the freeze – thaw experiments. Note that n_S^* given here represents the upper bound value for the suspension series.

	FS01	**FS02**			**FS05**	**FS04**			
$\boldsymbol{W}$ $[\boldsymbol{wt\%}]$	0.8	0.8	0.05	0.01	0.8	0.8	0.1	0.05	0.01
$\boldsymbol{S_p}$ $[\boldsymbol{cm^2}]$	2.5×10^{-5}	3.7×10^{-5}			2.7×10^{-5}	4.2×10^{-5}			
$\boldsymbol{n_S^*}$ $[\boldsymbol{cm^{-2}}]$	2.1×10^{7}				1.8×10^{7}	1×10^{4}	2.4×10^{7}		
$\boldsymbol{n_{site}}$ [#]	30	181	8	2	47	3.5	63	25	6.8
$\boldsymbol{\mu_\theta}$ $[\boldsymbol{rad}]$	1.3	1.32			1.33	0.75	1.32	1.3	1.35
$\boldsymbol{\sigma_\theta}$ $[\boldsymbol{rad}]$	0.14	0.1			0.102	0.12	0.15	0.12	0.1
$\boldsymbol{r^2}$	0.99	0.96	0.99	0.95	> 0.95	0.99	0.95	0.98	> 0.99
$\boldsymbol{Pearson's\ r}$	0.89	-	-	-	0.8	0.92	-	-	-

Table 2B: SBM parameters obtained by fitting the ISO decay curves.

	FS02				**FS04**	
T_{ISO} $[K]$	256	255	254	253	267	266
S_P $[cm^2]$	3.7×10^{-5}				4.2×10^{-5}	
n_S^* $[cm^{-2}]$	1.1×10^8	4.0×10^7	1.8×10^7	1.1×10^7	1.0×10^4	8.6×10^3
n_{site} [#]	4400	1565	705	410	0.42	0.36
μ_θ $[rad]$	1.32				**0.56**	
σ_θ $[rad]$	0.1				0.04	
r^2	0.99	0.98	0.98	0.94	0.99	0.98

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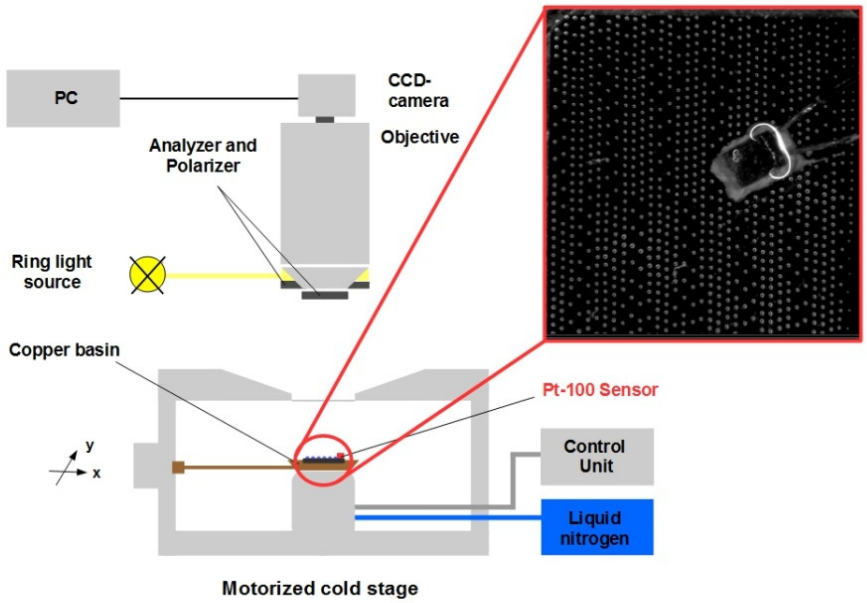

Figure 1: Schematic drawing of the nanoliter droplet freezing assay setup (side view). The inset shows the top view of 10×10 mm Si-wafer with ≈ 1200 droplets immersed in silicon oil. The square shape near the center of the wafer is the Pt-100 temperature sensor.

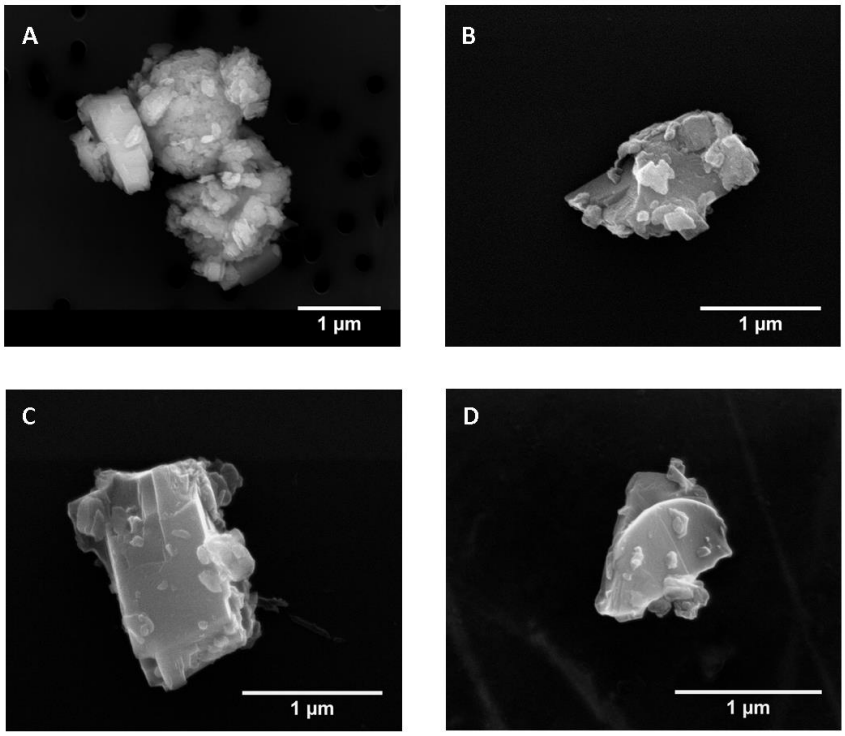

Figure 2: SEM images of A) FS01, B) FS02, C) FS04 and D) FS05 particles.

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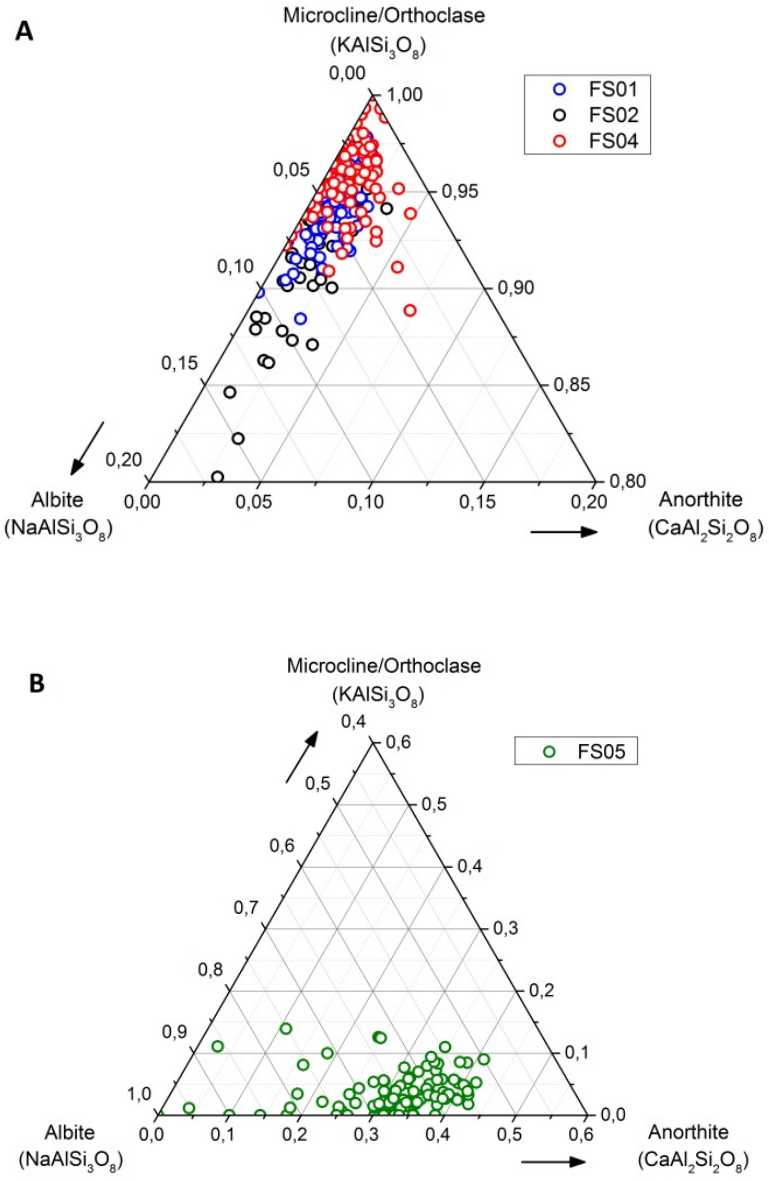
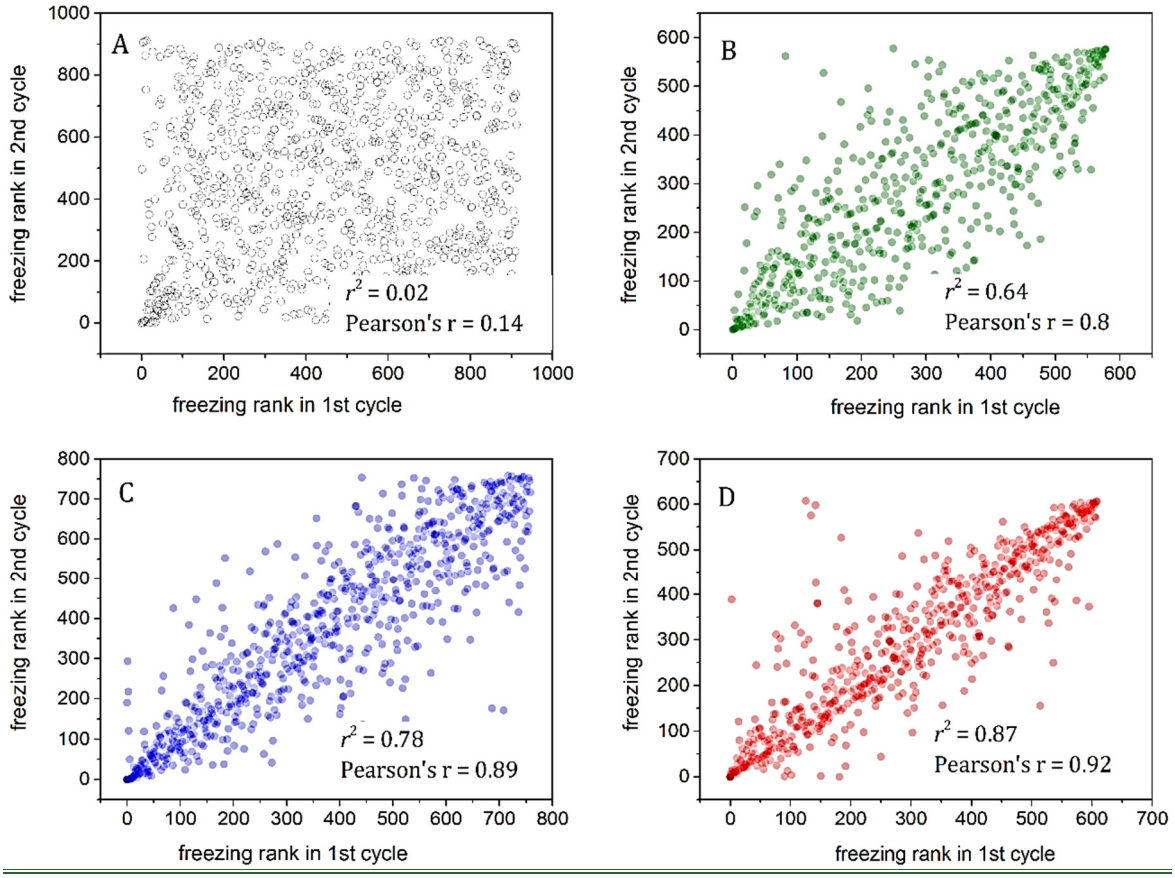
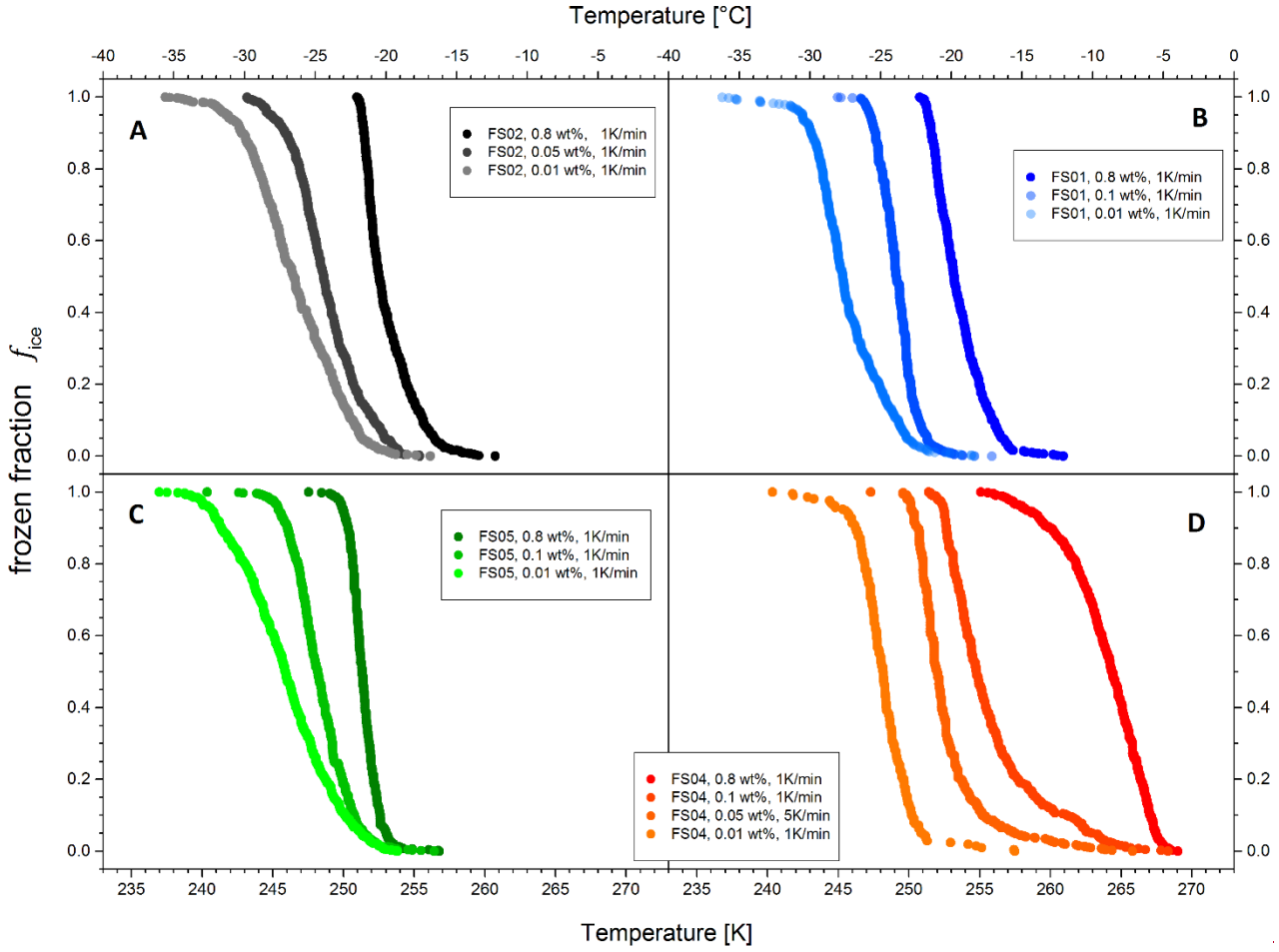


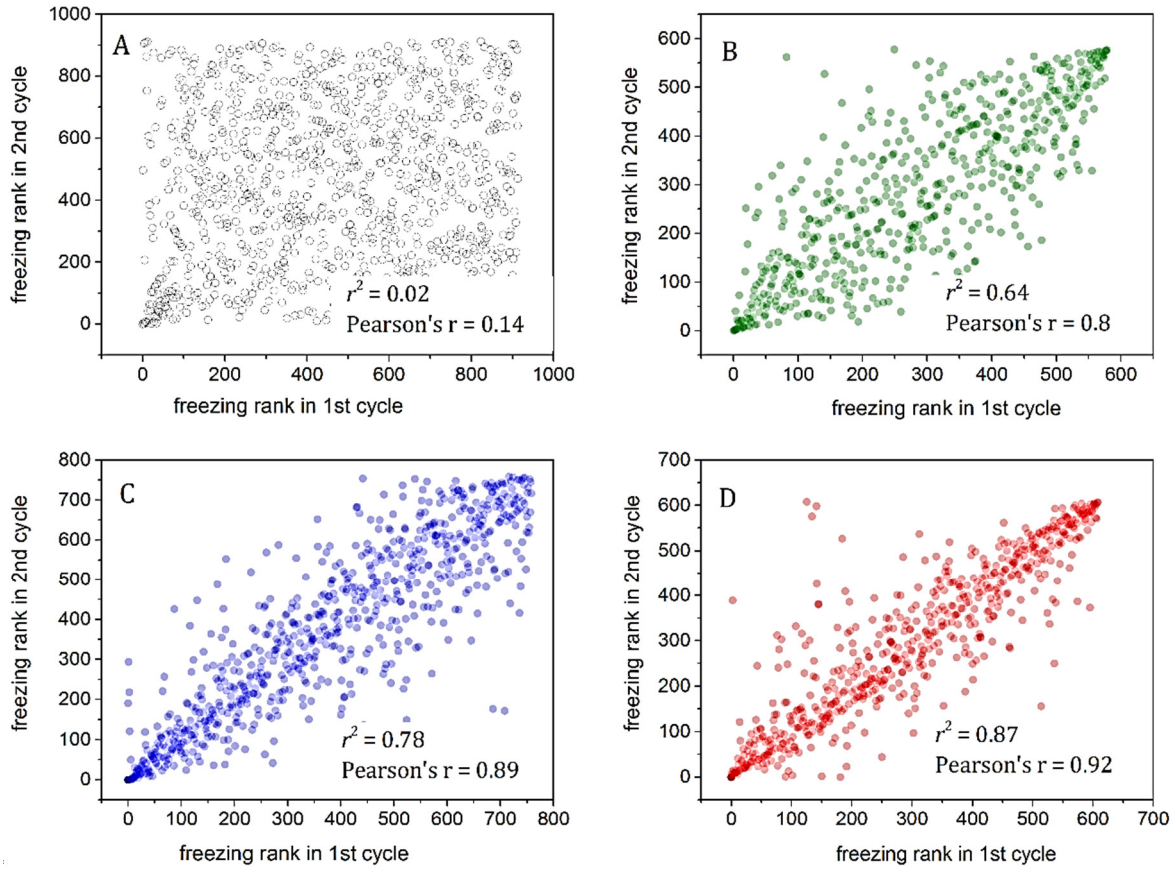
Figure 3: EDX data of individual feldspar particles plotted on the ternary phase diagram based on elemental mass percentages. A) Ternary phase diagrams of K-feldspar particles (FS01, FS02 and FS04) and B) Na/Ca-feldspar particles (FS05). Note the different scales of the ternary axis.


A
freezing rank in 2nd cycle
freezing rank in 1st cycle
r^2 = 0.02
Pearson's r = 0.14
B
freezing rank in 2nd cycle
freezing rank in 1st cycle
r^2 = 0.64
Pearson's r = 0.8
C
freezing rank in 2nd cycle
freezing rank in 1st cycle
r^2 = 0.78
Pearson's r = 0.89
D
freezing rank in 2nd cycle
freezing rank in 1st cycle
r^2 = 0.87
Pearson's r = 0.92

Figure



~~**Figure 4.** Frozen fraction curves of feldspar suspensions with various concentrations for A) FS02, B) FS01, C) FS05, and D) FS04.~~**4** ~~Note the initiation of freezing at 268 K for FS04 0.8wt% suspension droplets.~~



~~Figure 5~~: Correlations plots of freeze-thaw cycle experiments of feldspar suspensions (0.8wt%, 5 K/min). A) NanoPure water, B) FS05, C) FS01, and D) FS04. In the bottom right corner of every panel the adj. r^2 and the Pearson's r correlation coefficients describe the degree of correlation.

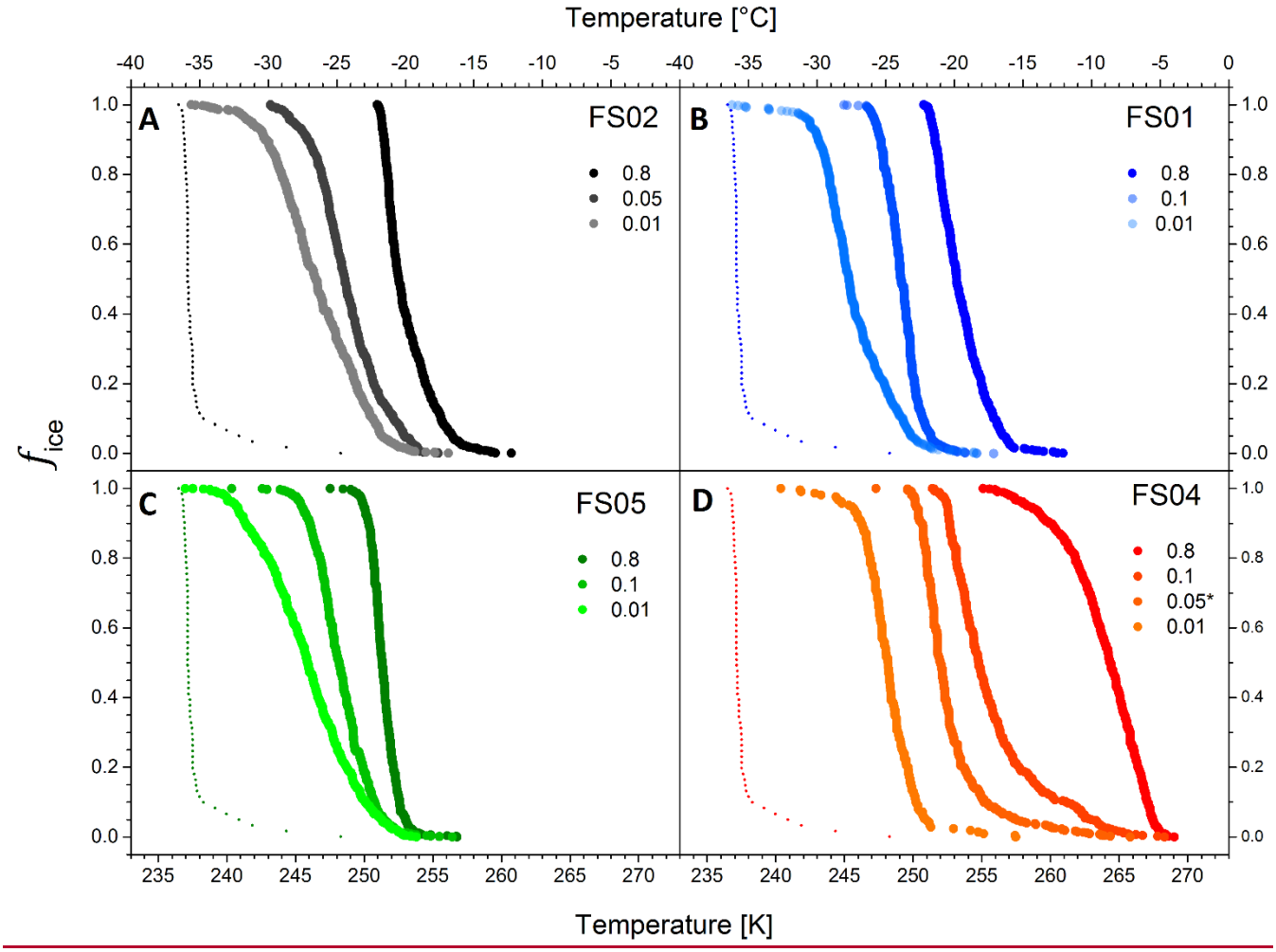
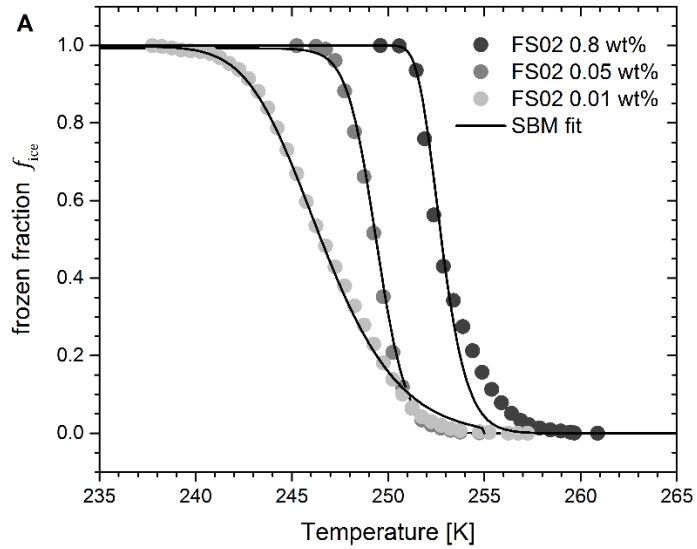
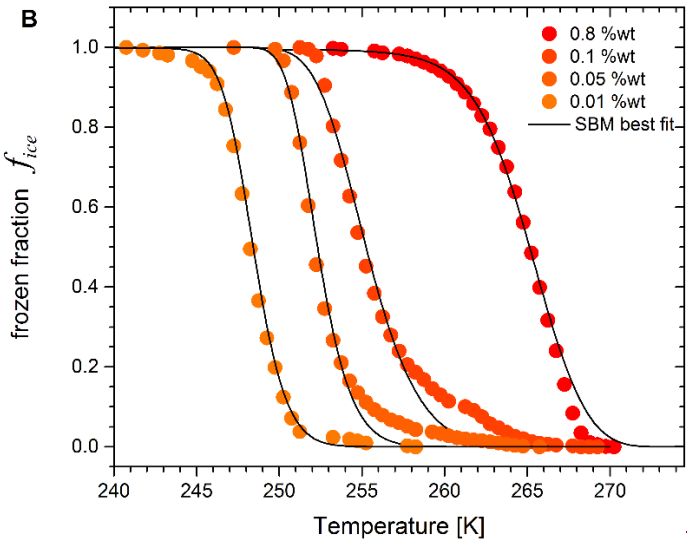
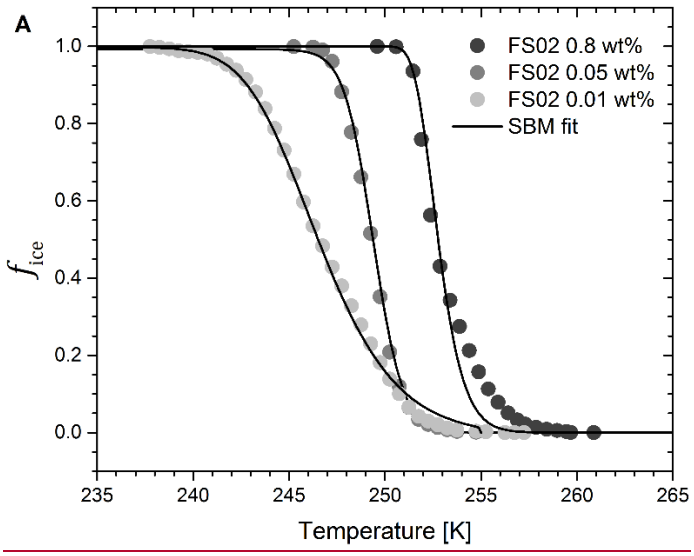


Figure 5. Frozen fraction curves of feldspar suspensions with various concentrations for A) FS02, B) FS01, C) FS05, and D) FS04 samples. Suspension concentration is given in the legend of each plot in wt %. Frozen fraction curves for Nanopure water droplets on a clean silicon wafer is given as dot line on each plot. All curves were measured with a cooling rate of -1 K/min, except for FS05 0.05 wt%, for which the cooling rate was -5 K/min (marked with an asterisk). Note the initiation of freezing at 268 K for FS04 0.8wt% suspension droplets.


A
FS02 0.8 wt%
FS02 0.05 wt%
FS02 0.01 wt%
SBM fit
frozen fraction f_{ice}
Temperature [K]


B
0.8 %wt
0.1 %wt
0.05 %wt
0.01 %wt
SBM best fit
frozen fraction f_{ice}
Temperature [K]

5



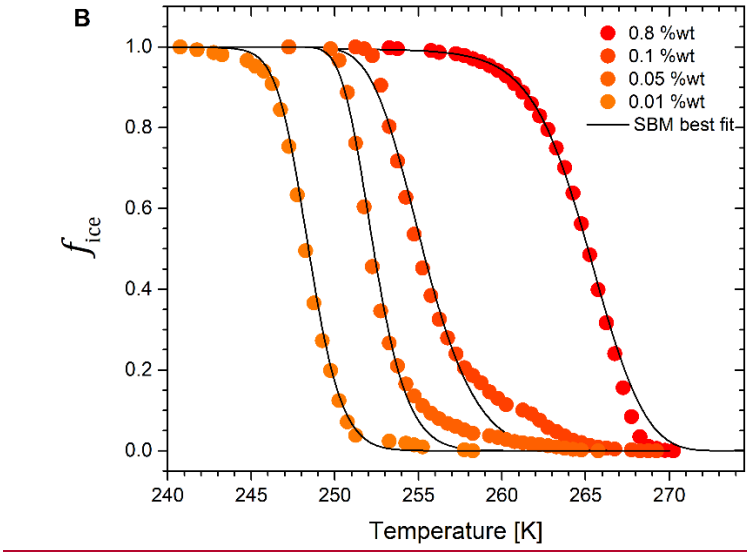
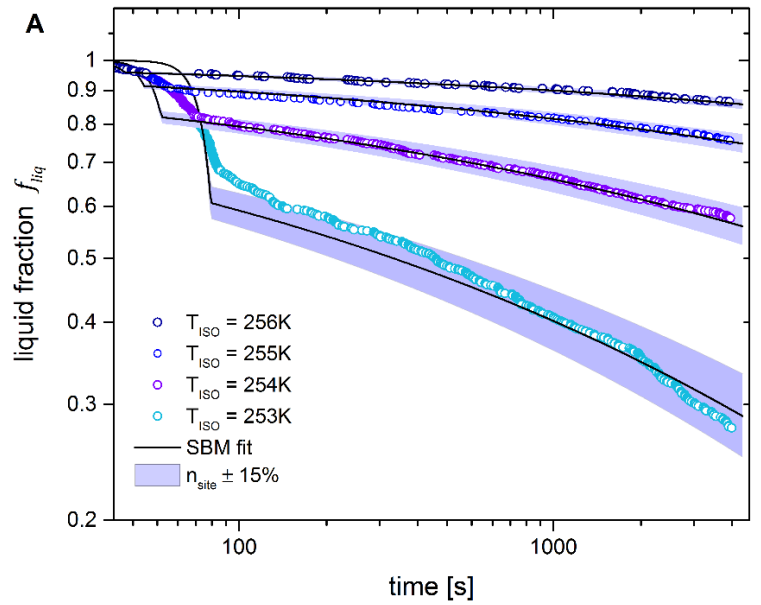
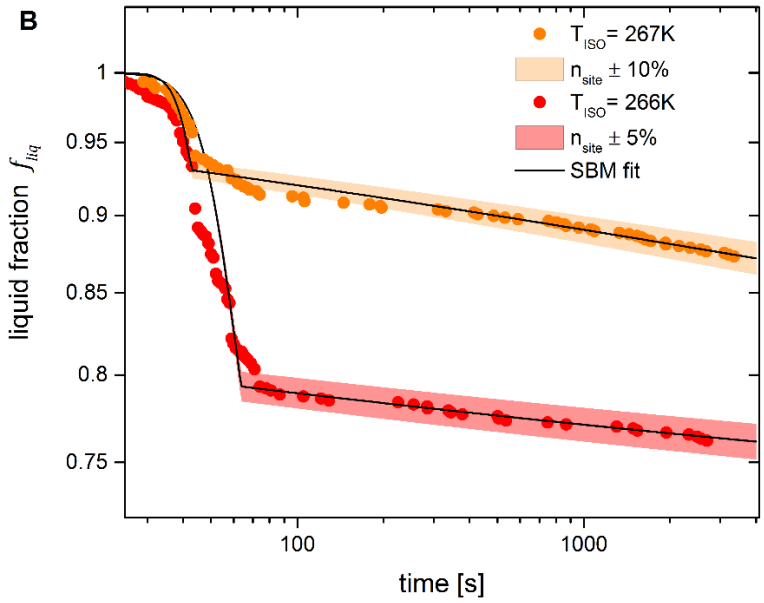


Figure 6. Freezing curves of FS02 (A) and FS04 (B) binned into 0.5K temperature intervals (filled symbols) and SBM best fit (solid curves). Fit parameters are given in Table 2A.


A
liquid fraction f_{liq}
time [s]
T_{ISO} = 256K
T_{ISO} = 255K
T_{ISO} = 254K
T_{ISO} = 253K
SBM fit
n_{site} ± 15%


B
liquid fraction f_{liq}
time [s]
T_{ISO}= 267K
n_{site} ± 10%
T_{ISO}= 266K
n_{site} ± 5%
SBM fit

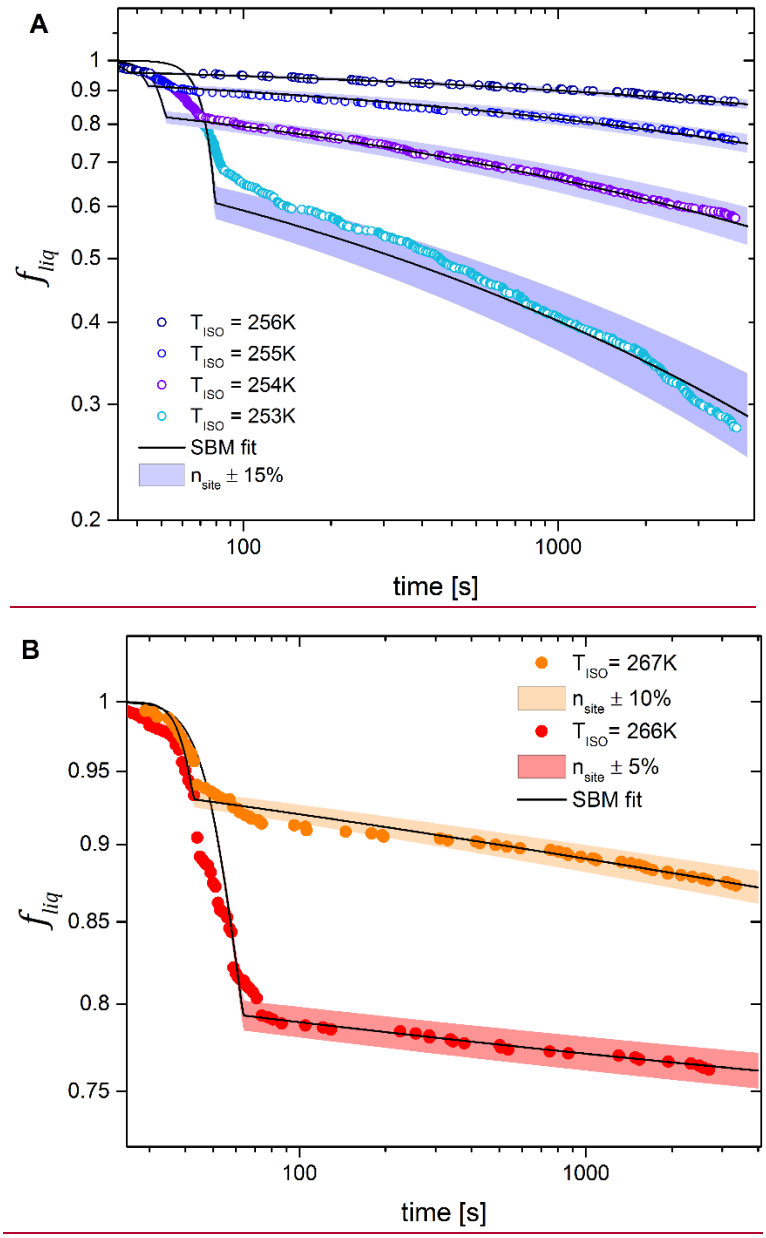


Figure 7. Decay of the ~~liquid~~ fraction of liquid droplets with time for FS02 (A) and FS04 (B) for different T_{ISO} (log-log scale). Solid lines show composite SBM fit with parameters given in Table 2 (see section 7 for detailed discussion). Shaded areas indicate the variability $n_{site} \pm \Delta n_{site}$ of a best fit value, with actual Δn_{site} given in the legend.

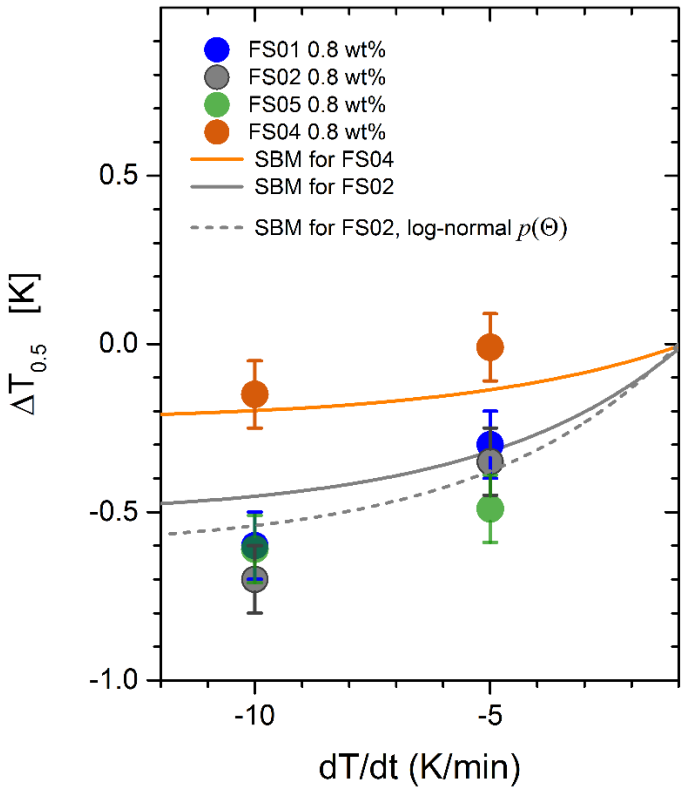


Figure 8: The shift $\Delta T_{0.5}$ of the median temperature $T_{0.5}$ relative to the $T_{0.5}$ at $1\ \mathrm{K/min}$ for different cooling rates $\mathrm{c} = \mathrm{dT/dt}$. Solid lines represent expected $\Delta T_{0.5}(c)$ calculated with fit parameters given in Table 2. Dashed line is the theoretical temperature shift calculated with the same SBM parameters for FS02 but assuming the log-normal distribution of contact angles *p(θ)*.

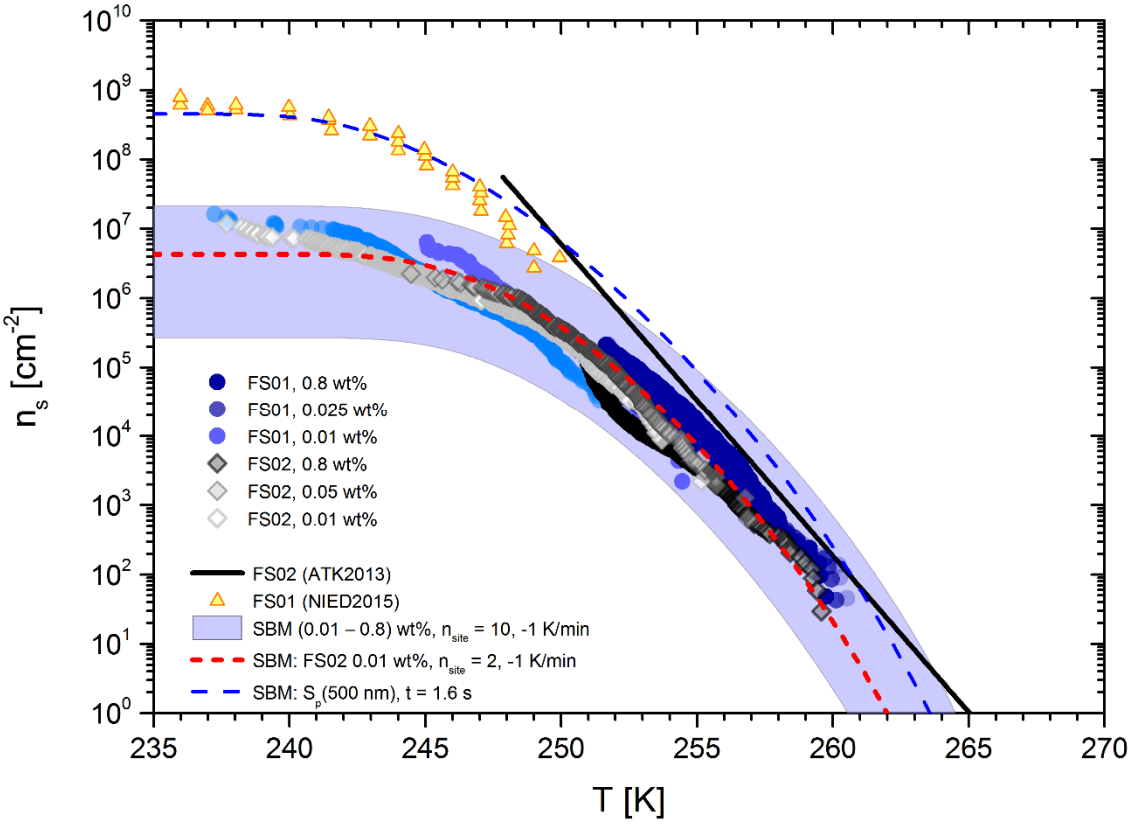


Figure 9: $n_s(T)$ curves of K-feldspar particles FS01 and FS02. Shaded area shows the range of $n_s(T)$ values predicted by equation 4 with fixed parameter set $\mu_\theta = 1.32$ rad, $\sigma_\theta = 0.1$ rad, $n_{site} = 10$, and suspension between 0.01 wt% and 0.8 wt%. Red broken line corresponds to the best fit parameter set for FS02 (Table 2A) with 0.01 wt% and $dT/dt = -1K/min$. The blue broken line is calculated with the same parameter set but assuming a single FS01 particle with Stokes diameter 500 nm per droplet and fixed temperature lasting for 1.6 sec (LACIS conditions) instead of constant cooling rate.

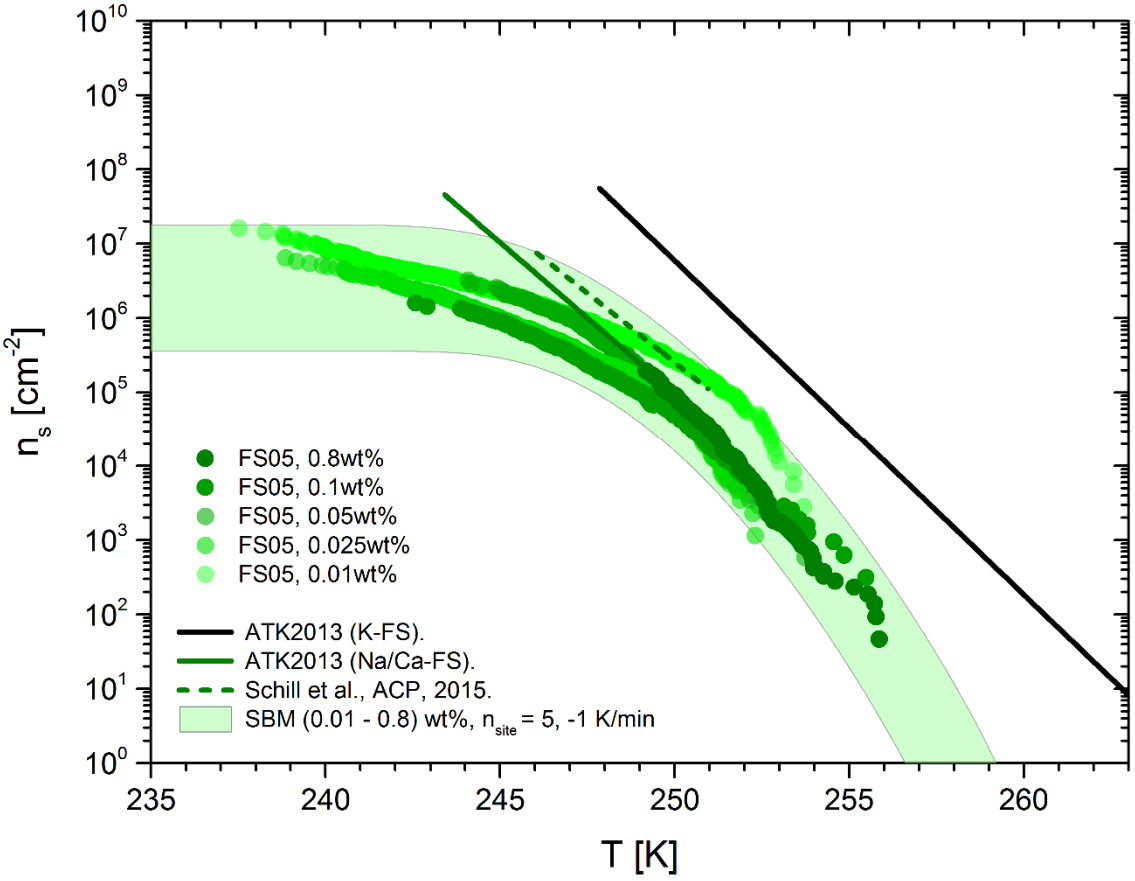


Figure 10: $n_s(T)$ curves of Na/Ca-feldspar suspensions FS05. Shaded area shows the range of $n_s(T)$ values predicted by equation (4) with fixed fit parameter set $\mu_\theta = 1.33\,rad$, $\sigma_\theta = 0.102\,rad$, $n_{site} = 5$, and concentration of feldspar suspensions varied between 0.01 wt% and 0.8 wt%. Black and green solid lines are exponential fits of data from ATK2013 for K-rich and Na/Ca-rich feldspar suspension droplets, respectively.

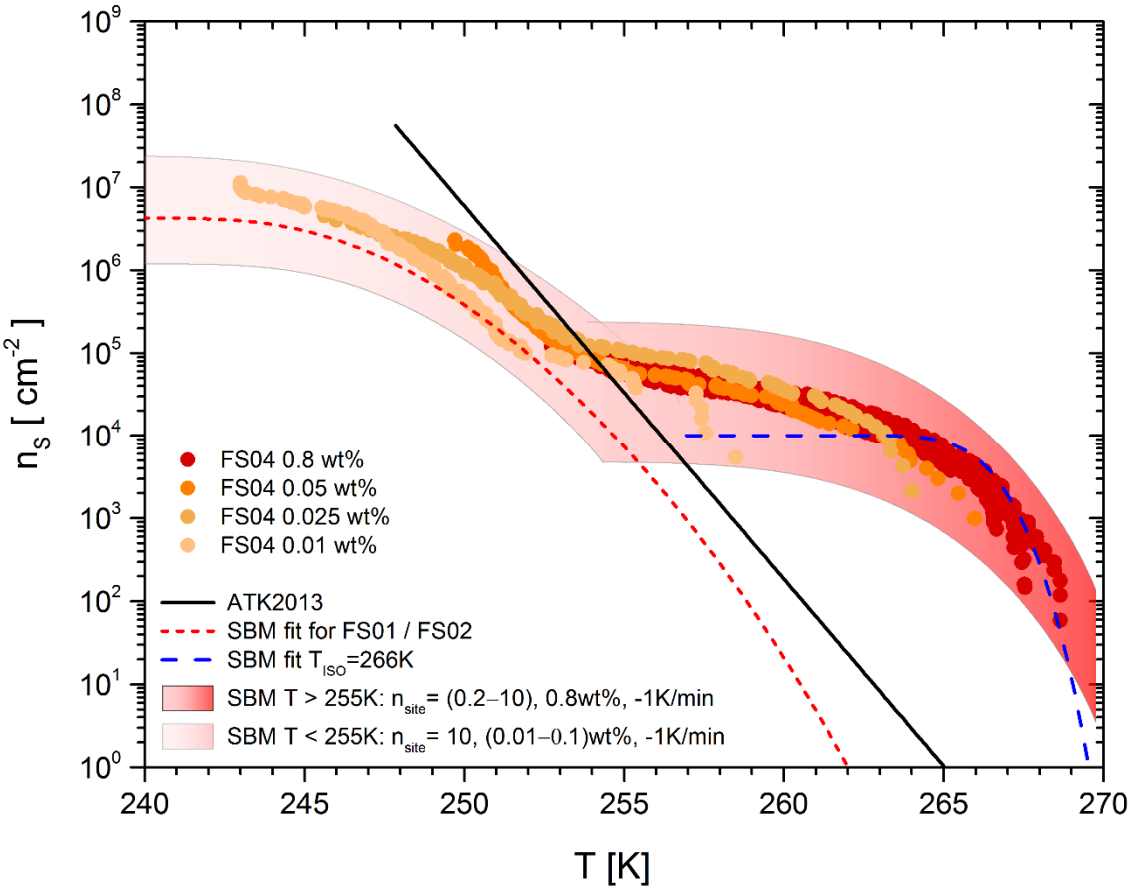


Figure 11: $n_s(T)$ curves of K-feldspar particles (FS04). Shaded areas shows the range of $n_s(T)$ values (for details see text). Black solid line is a fit of data from ATK2013 for FS02. Red broken line is a fit to our FS02 data (as in Fig. 9). Blue broken line is the $n_s(T)$ curve predicted by Eq. (4) with parameters obtained from the isothermal freezing experiments (Table 2B).

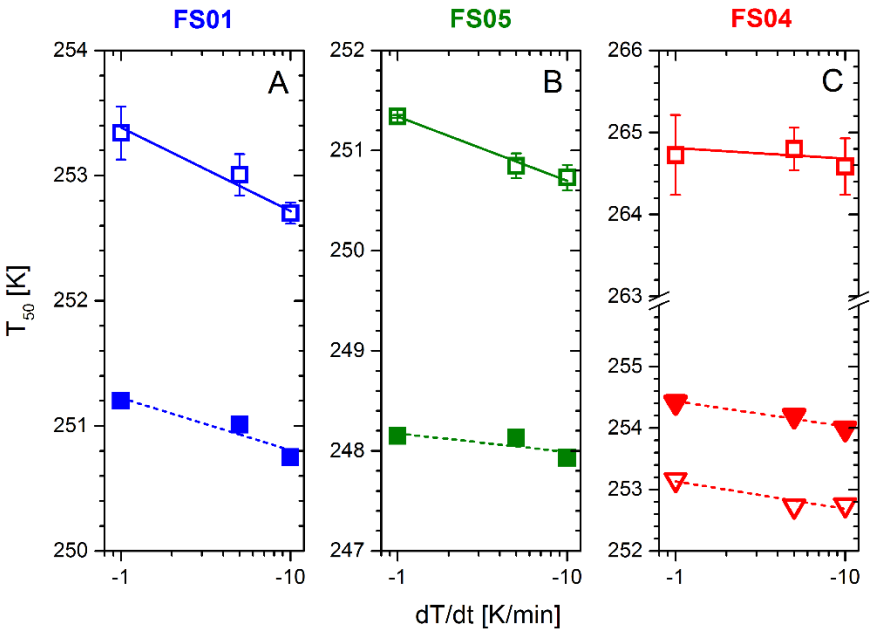


Figure 12: A, B) Median freezing temperature $T_{0.5}$ for the aqueous suspensions of FS01 und FS05 aged for over five months (blue and green filled symbols). C) Median freezing temperature $T_{0.5}$ of FS04 0.8 wt% suspension treated with 30% H_2O_2 for an hour (filled triangles) and overnight (open triangles). $T_{0.5}$ for the freshly prepared ~~suspension~~suspensions is shown as open square symbols in all three panels. Straight lines are non-weighted linear regressions of the averaged $T_{0.5}$ values for three different cooling rates.

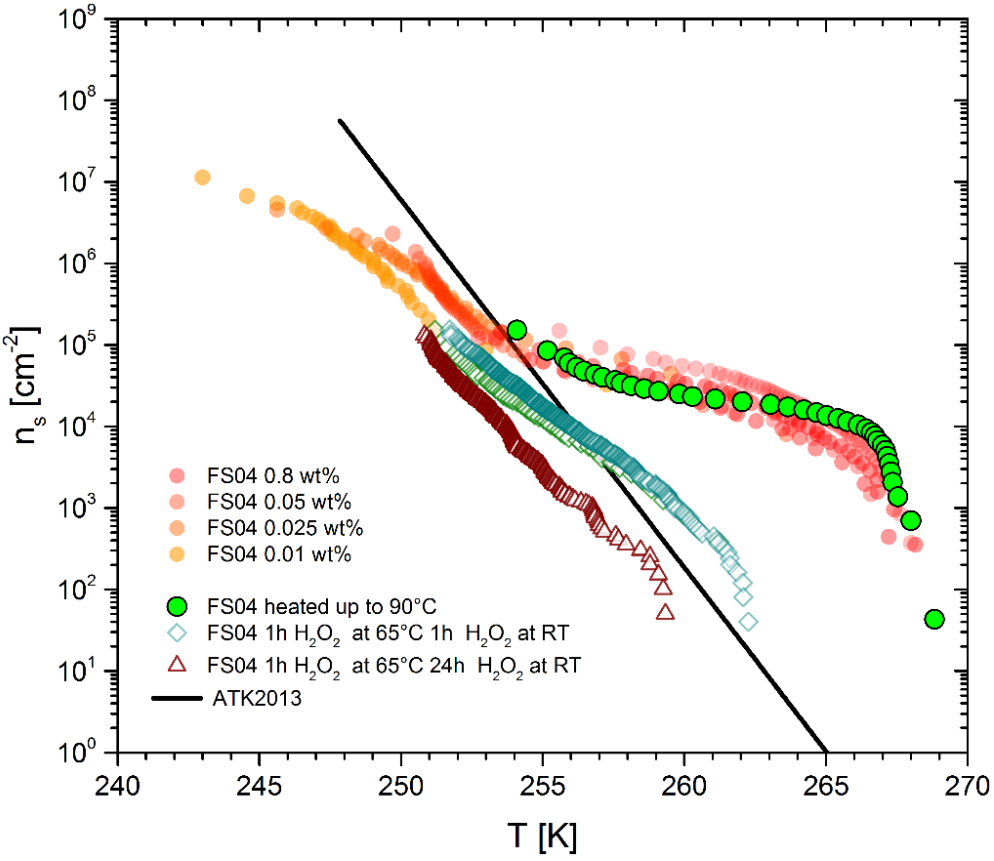


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Figure 13: $n_s(T)$ curves of K-feldspar particles (FS04) after heating to 90°C and chemical treatment with hydrogen peroxide.