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 r^2" or "… by r^2 (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.

Augustin-Bauditz, S., Wex, H., Denjean, C., Hartmann, S., Schneider, J., Schmidt, S., Ebert, M. and Stratmann, F.: Laboratory-generated mixtures of mineral dust particles with biological substances: characterization of the particle mixing state and immersion freezing behavior, Atmos. Chem. Phys., 16(9), 5531–5543, doi:10.5194/acp-16-5531-2016, 2016.

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.

Herbert, R. J., Murray, B. J., Whale, T. F., Dobbie, S. J. and Atkinson, J. D.: Representing time-dependent freezing behaviour in immersion mode ice nucleation, Atmos. Chem. Phys, 14, 8501–8520, doi:10.5194/acp-14-8501-2014, 2014.

O'Sullivan, D., B. J. Murray, T. L. Malkin, T. Whale, N. S. Umo, J. D. Atkinson, H. C. Price, K. J. Baustian, J. Browse, and M. E. Webb (2014), Ice nucleation by soil dusts: Relative importance of mineral dust and biogenic components, Atmos. Chem. Phys., 14, 1853–1867, doi:10.5194/acp-14-1853-2014.

Pummer, B. G., H. Bauer, J. Bernardi, S. Bleicher, and H. Grothe (2012), Suspendable macromolecules are responsible for ice nucleation activity of birch and conifer pollen, Atmos. Chem. Phys., 12, 2541-2550, doi:10.5194/acp-12-2541-2012.

Pummer, B. G., C. Budke, S. Augustin-Bauditz, D. Niedermeier, L. Felgitsch, C. J. Kampf, R. G. Huber, K. R. Liedl, T. Loerting, T. Moschen, M. Schauperl, M. Tollinger, C. E. Morris, H. Wex, H. Grothe, U. Pöschl, T. Koop, and J. Fröhlich-Nowoisky (2015), Ice nucleation by water-soluble macromolecules, Atmos. Chem. Phys., 15, 4077–4091, doi:10.5194/acp-15-4077-2015.

Tobo, Y., Demott, P. J., Hill, T. C. J., Prenni, A. J., Swoboda-Colberg, N. G., Franc, G. D. and Kreidenweis, S. M.: Organic matter matters for ice nuclei of agricultural soil origin, Atmos. Chem. Phys., 14(16), 8521–8531, doi:10.5194/acp-14-8521-2014, 2014.

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.