<u>Response to Reviewer 1: Reviewer comments are reproduced in bold font and author comments in regular typeface.</u>

Review of "Ice nucleation properties of K-feldspar polymorphs and plagioclase feldspars" by André Welti and co-authors for Atmospheric Chemistry and Physics

General comments:
Welti et al. present a study about the immersion freezing behavior of a variety of different feldspar samples which builds on recent investigations by Augustin-Bauditz et al. (2014), Peckhaus et al., 2016), Harrison et al. (2016), and Whale et al. (2017). The samples were chosen carefully to provide a variety of crystal structures, chemical compositions, and ordering of the crystal lattice. They include five polymorphs of K-feldspar and four plagioclase feldspars. The immersion freezing experiments were performed with droplets containing single, size-selected particles and care was taken to minimize the amount of multiply-charged particles in the sample aerosol. Furthermore, the study includes X-ray fluorescence measurements giving information about bulk chemical composition and scanning electron microscopy images of particle morphology.

What differentiates the present paper from the earlier studies is the discussion of the effect of particle size and the degree of order in the crystal network on the ice nucleation efficiency of the samples. The authors' conclusions concerning these factors are generally comprehensible and well substantiated by the presented results. However, in some cases, which are pointed out in the specific comments, I am missing a more precise explanation. The figures are mostly clear, but I would like to suggest some alternatives for presenting the data (see specific comments). Language-wise, the paper is concisely written but some minor adjustments would increase readability (see technical corrections).
Overall, the paper is interesting, understandable, and fits within the scope of Atmospheric Chemistry and Physics. I recommend publication after minor editing.

We thank the reviewer for the comments and suggestions. We address the specific comments individually below.

Specific comments:
1) Size dependence of ice nucleation behavior

The authors often refer to the "pronounced size dependence of ice nucleation activity" as if this is a rarely observed feature. Normally, the ice nucleation behavior scales with the surface area of the immersed particles, meaning that the efficiency increases with increasing particle size. The authors should clarify to what extent the size dependent ice nucleation behavior of their samples deviates from the standard. In my opinion, this is best done by calculating the ice nucleation active surface site density $n_s(T)$ for differently sized particles. In contrast to the chosen T_{50} approach, this method would have the benefit of providing an overview over the whole investigated temperature range. I hence suggest to replace Fig. 5 with a multi-panel figure (like Fig. 3) showing $n_s(T)$ of the different particle sizes for all investigated samples (see, e.g., Fig. 5 in Hartmann et al., 2016).

We prefer to leave Figure 5 as is, but now add a figure in the appendix for the INAS densities since converting the frozen fraction to INAS densities involves accounting for the surface area, which is easily calculated given the particle size information in the manuscript. Concerning the extent of size dependence, we observe that all samples show a size dependence, mostly even stronger than linearly scaling with surface area with decreasing particle size. One microcline sample shows almost linear scaling of the frozen fraction with surface area. As all samples have this strong size dependence, we indeed consider it "pronounced". To be more specific we changed the sentence to (<u>page 1 line 21-23</u>): "A pronounced size dependence of ice nucleation activity for the feldspar samples is observed, with the activity of smaller sized particles scaling with surface area or being even higher compared to larger particles. The size dependence varies for different feldspar samples."

Furthermore, the authors state that "microcline exhibited immersion freezing even for 50 nm particles" whereas for orthoclase "ice nucleation requires active sites present on 400-800 nm sized particles" and relate this observation directly to the effect of these particles on atmospheric ice nucleation. Concerning the potential of these species as atmospheric INP, one must always combine their efficiency and their abundance. Larger orthoclase particles might be needed to trigger ice nucleation as efficiently as smaller microcline particles, but maybe many more orthoclase particles are emitted into the atmosphere?

This is true, we agree, we have clarified this in the text, that atmospheric abundance of ice nucleation species needs to be considered in order to determine atmospheric relevance (see page 1 line 26-27)

Besides, the fact that ice nucleation was not observed for 100 or 200 nm orthoclase particles is related to the detection limit of the instrument. If the authors had investigated more droplets, they would eventually have observed ice nucleation triggered by the small orthoclase particles. This should be made clear in the manuscript.

We disagree with this reasoning, the argument of the detection limit applies to both, the orthoclase and the microcline experiments, the detection limit did not change between these two. i.e. we did not have to increase the amount of microcline in a single droplet, or increase the number of droplets observed in order to observe ice nucleation in the 50 nm microcline sample. The fact that 50 nm microcline (amazonite) demonstrated ice nucleation activity similar to that of 800 nm orthoclase, shows that even for the same detection limit, the 50 nm particles are potent INPs compared to the 100 or 200 nm orthoclase particles. i.e. by changing the number of droplets, or detection limit, this would not change the conclusions that 50 nm microcline particles are much more active than the 100 nm orthoclase particles.

2) Difference to earlier studies
This refers to P3L14-18, where I think the authors should clarify the innovation of their study more. Like this, it sounds as if they might expect an effect of methodology on the results, as the other studies were performed with droplets containing numerous particles each. Please state that by using single particles, you are focusing on a different temperature range than the other studies (except Augustin-Bauditz et al., 2014).

We have now clarified that we are able to focus on lower temperatures (< 253 K) with the single immersed particles (see page 3 line 30-31 in revised manuscript). However, the observed size dependence also indicates that except for cases where activity scales linearly with surface area (only one Microcline in this study), the particle size distribution used in drop freezing experiments (which make an assumption of linear scaling of activity with surface area) can potentially have an influence on the measured activity.

3) Multiply-charged particles
The authors should be more precise concerning the amount of multiply-charged particles in the cases where the CPMA was not used. This issue could be addressed by including actually measured size distributions in Fig. 2 instead of the schematic ones. Alternatively, the authors could include the following statement on P4L28-29: "The use of the CPMA for the selection of larger particles (400 nm, 800 nm) was not necessary as the fraction of larger particles was reduced to … % by the cyclones and the impactor upstream of the DMA."

We agree with the reviewer and now include specific numbers for the diameters and fraction of multiply charged particles in section 3.1 of the revised manuscript (see page 5 line 10 -22). We also include a figure in Appendix C to show the contribution of the multiply charged particles to the frozen fractions for the 50 nm sample, where the highest multiple charged particle fraction is calculated.

4) Figure 4

I see more benefit from one figure showing *FF* over *T* for 800 nm particles of all samples. This would be more suited for comparing the ice nucleation signatures of the different feldspars than just showing the range in which freezing occurred. Error bars could be omitted (because they are already shown in Fig. 3) and symbol size reduced for clarity.

Even without the error bars, such a figure becomes messy and actually rather difficult to read, as there is a huge amount of data overlap. It results in not being able to see the frozen fraction curves for many samples because of the temperature overlap. As such we keep Figure 4 as is. Furthermore, not having error bars if we plot frozen fraction vs. temperature would not allow for a realistic comparison of differences (or similarities) between the samples.

Technical corrections:

P1L9: Replace "Na/Ca-rich feldspar" with plagioclase to be consistent with the title. The composition is explained below anyhow.

We agree, done (page 1 line 9 revised manuscript)

P1L11: Replace "are" with "were" in "Samples are selected…".

Done (page 1 line 11)

P1L18-20: This sentence would benefit from being split into two.

We agree, done (page 1, line 18-19).

P1L24-25: Either omit the "s" at "temperatures" or at "depends".

We changed "depends" to "depend" (page 1 line 26).

P1L29: There is also contact freezing in which the contact causes nucleation, not an immersed particle.

We have now adjusted page 2 line 2 -5 to reflect contact nucleation as a mechanism in this explanation of freezing of supercooled drops.

P2L12: Within a sentence "e.g." should be preceded by a comma. A comma should also follow in case you are using American English. This also applies to "i.e.". Generally, check your manuscript for consistency with either British or American English. E.g., see "favouring" on P11L10 or "generalise" and "analysed" on P12L8 and L13.

We inserted the comma before "e.g." (page 2 line 17) but not after as we are using British English as is evident by the words specified by the reviewer.

P2L13: Less efficient in comparison to which other species?

Compared to other mineral species such as muscovite and kaolinite – we have now clarified this aspect on page 2 line 18 of the revised manuscript.

P2L14: Change "for example" to "e.g.".

Done, now page 2 line 19

P2L22: Capital “X” in “x-ray”.
Done, now page 2 line 27

P3L21: Mention that XRF is a bulk, not a single particle technique.
We now mention this on page 4 line 3, in addition we note that we explicitly state that XRF is a bulk composition measurement when discussing the data in section 5.2, already in the original manuscript.

P3L28: Omit comma following “polymorphism” and add “s” to “occur”.
Done, now page 4 line 10

P3L30-31: Add comma behind “sanidine”. Be consistent using either “temperature” or “temperatures”.
Comma added, and “temperatures” corrected to “temperature”, page 4 line 12 in revised manuscript.

P4L1-2: I suggest to remove the brackets and structure the sentence as follows: “sanidine in volcanic and very high-temperature metamorphic rocks, orthoclase in … rocks and microcline in … rocks.”
Done! Page 4 line 14-16 revised manuscript.

P4L2: “feldspar”: This should be plural.
Changed to plural and added comma before feldspars (page 4 line 16)

P4L3: Why is Table 3 referred to before Table 2 is mentioned? Should the labels be switched?
Thank you for pointing this out. We now refer to section 5.2 (page 4 line 17) instead of Table 2.

P4L3-10: I appreciate the discussion of the atmospheric relevance of the samples. However, I feel that the last sentence in this paragraph might better be shifted before “We note…” to introduce the reader to this topic.
This has now been done. The last sentence “Samples used in this study..” has now been moved further up in the paragraph (Page 4 line 17-19 in revised manuscript). “We note” has now been changed to “As such..” (page 4 line 19)

P4L12: Change “are” to “were”.
Done, page 4 line 26

P4L21: Change “multiple charged” to “multiply-charged”, also in the other instances. Also, “single charged” should become “singly-charged”.
This is a matter of preference, as such there is no rule saying multiple should be multiply etc. As such we retain the current structure. However, we note the lack of plurals on page 5 lines 4-5, and have corrected those.

P5L12: Remove hyphen in “ice-layer”.
Done (now page 5 line 31)

P5L18: Insert hyphen in “in line”.
Done (now page 6 line 4)

Fig. 3: Please state how you derived the error bars.
We have added a description of the error bars in the caption of Figure 3 and refer the interested reader to the work of Lüönd et al. (2010).

P6L13: How were the 25 % derived? Which particle size are you referring to?
Thanks for catching that, we were referring to the 800 nm particle curves in Figure 3. We have now corrected this (page 6 line 29).

P6L22-25: Could you state the parameters of the amazonite contact angle distribution? Should amazonite be capitalized on P6L22?
The parameters are the mean contact angle, and the variance of the distribution. However, the contact angle distribution referred to in page 7 line 11 is from a different paper (Ickes et al., 2017) and bears no inclusion here for just a single sample and is also not the focus or objective of the paper. We corrected the capitalization of amazonite on page 7 line 8 (revised manuscript) the reviewer is correct, this does not require capitalization. Thanks!

P6L26: Here you could refer to the Fig. showing $n_s(T)$ which I suggested as a replacement for Fig. 5.
We now refer to the INAS figure A1 in the appendix A (page 6, line 12-13).

P7L7-9: This statement would be more convincing if you provided actual numbers for the remaining multiply-charged particles in the 400 and 800 nm aerosol.
We have now provided the fraction of multiply charged aerosol for all the sizes in section 3.1 (see page 5 line 10-21). However, we would like to re-iterate that the fraction of multiply charged particles have no bearing on this statement, as the convergence is occurring at the higher surface areas (i.e. larger particles sizes) where we have the fewest percentage of multiple charged particles (see section 3.1 of revised manuscript).

P7L10-11: I advise not to use T_{50} for comparison to other studies. In this regard, my suggestion from above, i.e., showing $n_s(T)$, would be helpful.
We have included $n_s(T)$ (we use the term INAS density) in the appendix following the Reviewer recommendations. It is not clear from the Reviewer's comment why in addition a comparison using T_{50} cannot be presented.

P7L23-25: "it remains unknown what particle property other than chemistry and crystallography or morphological features … could be active sites": This conclusion cannot be made at this point in the manuscript since you only discuss these factors in Sec. 5. Please reword. On P7L25, do you mean "as discussed"?
Agreed, we have rephrased the statement, which is meant to introduce and explain the structuring of the discussion and not to draw any conclusions (see page 8 line 10-12).

P8L8: "sanidine" should also be followed by a comma.
Done (page 8 line 27)

P8L11: Sometimes you use "(see Figure…)", sometimes only "(Figure…)". Be consistent.
This is not accidental; there is no need for consistency here, because the two indicate different things. When we say "see Figure xx" we are suggesting that a reader should look at the Figure while reading that sentence, and when we just say (Figure xx) we are informing the reader where the relevant information is available.

P8L13-14: What is the difference between a defect-free and an ordered crystal? Please clarify.
The degree of order and disorder in feldspars is determine by the distribution of silicon and aluminum distribution within the tetrahedrons, in sanidine the distribution is random, where as in an ordered crystal (microcline), the distribution of these atoms are regular. Defects can occur in both, ordered or disordered crystals, since a defect would imply a point defect or a line defect. In the former, this can be because of a

vacancy at a point where there should be an atom, or the presence of an atom at a location where there should be empty (interstitial space). Line defects can occur if atoms are misaligned

P8L29: I think, it might be helpful to indicate the perthitic structures in Fig. 6, maybe with the help of overlaid boxes.
We think this could reduce the aesthetic of the images. But we add a description to the caption in Figure 6 and refer to it at the said location now page 9 line 20-23

P9L29: "Contrary to the Pb content, …": Are you referring to microcline not quite fitting the linear relation in Fig. 7? This should be discussed in the previous paragraph.
Done (see page 10 line 15-16 and line 23-24).

P10L4: Move "(increase entropy)" behind "structuring of water".
Done (page 11 line 8)

P10L6-7: The explanations of kosmotropic and chaotropic in brackets should be moved to P10L2, where the terms are first mentioned.
Done (now page 11 line 6)

P10L10-11: I suggest to move this statement towards the beginning of Sec. 5.2. Otherwise the reader might wonder for quite some time how valid your conclusions about the bulk chemical composition are for the investigated submicron particles.
Done. We moved this sentence to page 10 line 9-10 at the beginning of section 5.2. In addition, we also refer to the INAS densities in appendix A to demonstrate the similarity in composition with particle size.

P10L28: Insert comma between "cold" and "low".
Done, (page 12, line 1).

P11L9: Missing bracket after "sanidine".
Done – thanks (page 12 line 14).

P11L25-26: Either change "temperatures" to "a temperature" or "that" to "those".
We restructured this sentence to "above homogeneous freezing temperatures" so that the plural use is more obvious (page 12 line 32)

References:

Augustin-Bauditz, S., Wex, H., Kanter, S., Ebert, M., Niedermeier, D., Stolz, F., Prager, A., and Stratmann, F.: The immersion mode ice nucleation behavior of mineral dusts: A comparison of different pure and surface modified dusts, Geophys. Res. Lett., 41, 7375-7382, doi:10.1002/2014GL061317, 2014.

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