Referee report on "Ice nucleation properties of K-feldspar polymorphs and plagioclase feldspars" by André Welti et al.

The paper "Ice nucleation properties of K-feldspar polymorphs and plagioclase feldspars" by A. Welti, U. Lohmann, and Z. Kanji continues the series of experimental studies aimed at understanding the ice nucleating (IN) properties of the feldspar component of atmospheric mineral dust (MD). In particular, the role of potassium-rich feldspar and its modifications requires a thorough characterization due to its abundance in the atmosphere and the easiness it triggers ice nucleation in supercooled water or supersaturated water vapor.

Apart from reporting the results of freezing experiments, the manuscript suggests that some qualitative correlations between the feldspar genesis and its IN activity could be established. However, as many factors (pressure, temperature of crystallization, cooling rate, presence of volatile fluxes, shearing stress, variations in bulk composition of magmatic fluid, etc.) can influence the structure of the K-feldspar in igneous rocks, the authors do not attempt specifying a mechanism responsible for the strong variation of IN activity of feldspar. Even so, establishing such correlations could provide a useful tool to predict what kind of feldspar might me expected to be a better IN particle. From this point of view, the correlation between median freezing temperature and Rb/Sr ratio appears to be especially promising (more on that below). I therefore support the publication of the manuscript but would like to attract authors' attention to the following issues:

1. The manuscript reports size resolved immersion freezing experiments on 9 new types of feldspar using a single-particle continuous flow diffusion chamber (CFDC), and thus presents a large body of new data that could be used for parameterization of IN activity of feldspar-containing MD aerosols in cloud models. However, the data is not presented in terms of ice nucleating active site (INAS) density, which became standard for reporting the IN properties of aerosol particles over the past years. Although the possibility of such analysis is indicated (end of section 4.1) and obviously has been conducted for amazonite sample (Ickes et al. 2017), it was not extended to other samples and sizes in this manuscript. This is particularly unfortunate, as the experimental conditions (using mobility-selected single feldspar particles as INPs and well-defined thermodynamic conditions in the CFDC) are ideally suited for performing the INAS density-based analysis. This would substantially simplify the comparison of the results with the numerous data of recent IN experiments on feldspar. I strongly recommend including this analysis into the revised version of the manuscript. Additionally, the size distributions of aerosol particles used in the experiments have to be added to the manuscript (as a supplement) or made available for anyone who would be interested to calculate the INAS densities.

2. That the IN properties of all feldspars are size dependent, is convincingly shown by the figure 5. It is also apparent that the T50 values for the smallest particle sizes in each curve lie in the homogeneous freezing range, implying that the T50 values have been calculated for all droplets, frozen both heterogeneously and homogeneously. This doesn't make sense to me. What is the purpose of reporting the median freezing temperature for particles that did not induce freezing of supercooled droplets? Was it not possible to correct the frozen fraction for homogeneously frozen droplets? Again, this is a very strong argument for reporting the INAS densities instead of median freezing temperatures.

2. Another major (critical) comment is that the reported correlations between crystalline structure, trace element composition, and IN activity are not sufficiently supported by statistics. The authors state that IN efficiency is correlated with the degree of ordering of Si and Al atoms in the feldspar framework, implying that there must be a mechanism responsible for this correlation. This mechanism is not discussed in the manuscript, nor is the suggested correlation expressed in any quantitative manner (although such quantity can be derived, see for example, (Smith 1970, Brown and Parsons 1989). I doubt

that such correlation could be of practical use unless a mechanistic explanation is suggested or a quantitative correlation analysis is performed.

3.   With respect to the trace elements composition, the number of investigated samples is definitely too low to draw any particular conclusion. I agree that for the presented choice of samples, the correlation between the IN activity and the ratio of Rb/Sr content is striking. On the other hand, the partitioning of trace elements takes place as feldspar is cooling and forming separate phases, so that Rb replaces K and Sr replaces Ca; thus the Rb/Sr ratio is indicative for the position of feldspar on the ternary phase diagram (An-Ab-Or) and the absolute concentrations of trace elements depends on the cooling/crystallization process and abundance of trace elements in particular magmatic fluid (Parsons et al. 2008). As a consequence, the high Rb content is expected in low microcline and the observed correlation just reflects the correlation between the IN activity and microstructure of feldspar. It is still very interesting that the most IN active sample has also the highest Rb content, an order of magnitude higher than the second-best microcline. I think this fact deserves to be highlighted in the manuscript, even if no mechanistic explanation can be offered at the moment. With the amount of experimental data on IN properties of feldspars that recently became available, it would be relatively easy to improve the statistical analysis and to show if the connection of IN activity and Rb content is not just a coincidence. I would really like to see such analysis in the manuscript or in the follow-up work.

4.   I am also confused by the discussion of Pb content and its correlation with the median freezing temperature. The authors state that "*The best linear correlation between a single compound and the ice nucleation activity based on T50, was found for the Pb content in the feldspar samples (Figure 7).*", but obviously the Pb content in microcline (better IN) is lower than in orthoclase (weaker IN). The quality of the correlation as expressed by Pearson's r-coefficient is apparently influenced by the low Pb content in the plagioclase and high-temperature disordered alkali feldspar, which has been formed before any trace elements partitioning could take place. I think the plagioclase feldspars should be excluded from the correlation analysis. If you do that, the correlation between T50 and Rb/Sr content ratio would be even better than for Pb and the T50 as a function of Rb/Sr would be also monotonically rising.

On a side note, if Pb is normalized by Nd content, the correlation between T50 and Pb/Nd ratio becomes very clear, with T50 as a function of Pb / Nd staying constant for plagioclases and then monotonically rising from the level of adularia and sanidine towards amazonite. This is just to illustrate that such correlations can be constructed very easily and most of them are probably meaningless, unless a larger set of samples is analyzed or an underlying physical and chemical mechanism is suggested. I encourage the authors to do so.

5.   With respect to the potential predictability of IN activity based on the relative concentrations of trace elements, I have to point out that the measurements reported here have been conducted exclusively with the single-crystal samples. In case of real-world atmospheric mineral dust, the majority of feldspar would be coming from phenocrysts (inclusions of feldspar in e.g. granite matrix), where the trace elements content could be very different. Again, the idea of using partitioning of trace elements as a predictor for IN efficacy is very attractive and promising, but must be explored deeper and supported by extensive dataset.

Specific remarks (ordered according to page and line number, citations given in italic):

1-14. The sentence "*Ice nucleation is most efficient on the crystallographic ordered, triclinic K-feldspar species microcline, while the intermediate and disordered, monoclinic K-feldspar polymorphs orthoclase and sanidine nucleate ice at lower temperatures.*" strongly implies a causality between the degree of ordering and IN efficacy. Since such causality is not supported by the experimental data of the manuscript, I suggest that the sentence should be reformulated.

1-26 (Introduction). The introduction would greatly benefit from including a discussion of partitioning of the trace elements in feldspars. As mentioned above, the possible correlation between trace elements and IN activity can open a unique opportunity to classify the feldspars on a single-particle basis, for example in a laser ablation mass spectrometer.

2-9. The degree of order (or disorder) of Al^{3+} and Si^{4+} is not something that an average atmospheric scientist would be familiar with. This sentence requires explanation.

3-2. (Whale et al. 2017) did not conduct systematic study of crystalline structure in terms of disorder, although they report the fraction of orthoclase in their perthitic samples. A careful analysis of their samples could have reveal a correlation. Please elaborate on that issue.

3-14. (Niedermeier et al. 2015) has reported nucleation ability of size-resolved K-feldspar sample in single-particle immersion mode and according to the manuscript, the microcline data from your study has been previously published in (Ickes et al. 2017). So the statement "for the first time" must be either removed or explained, what exactly has been done in this work for the first time.

3-21 (Section 2). A more detailed description of the sample origin and the XRF analysis would be very helpful here. Was XRF analysis the only basis for identifying the samples or have you performed the powder XRD analysis, too? Could you speculate on how the chemical composition of single aerosol particles would be related to the chemical composition measured for bulk samples?

3-27. The sample that is called "orthoclase" here should be the one closest to the ideal end-member of the alkali feldspar group (Or = $KAlSi_3O_8$). On the Figure 1, however, this sample has the same composition as amazonite with almost 20% albite. Where the name "orthoclase" came from?

By the way, it is not correct to label the axes of the ternary phase diagram with fraction of K, Na, or Ca. The ternary diagram gives a sample composition in terms of weight fractions of end-members (orthoclase, albite, and anorthite), see for example (Parsons 2010). The name orthoclase is also misspelled in the legend. Please correct.

4-3. Table 3: What is the purpose of reporting compounds that could not be detected in any of the samples (FeO, NiO, H_2O, CO_2)? What is the difference between a "0" and N/D?

6-21:22. This kind of analysis has been published even before (Ickes et al. 2017) and should be mentioned here. See, for example (Wright et al. 2013, Niedermeier et al. 2015, Peckhaus et al. 2016) to name just a few.

7 (Section 4.2) This section should be expanded to include more thorough size dependence analysis, ideally complimented by the INAS density calculations. The T50 should be corrected to account for the homogeneous freezing of droplets containing the smallest particle sizes. Some specific question here: why would one expect linear dependence of T50? The median freezing temperature is a function of cooling rate and residence time, have you taken this into account when comparing T50 from your measurements and data from Atkinson et al., (2013)?

7-9. "*The minimum size triggering immersion freezing is found to be 50 nm microcline particles*". In the Sample preparation section you mention that a "*substantial fraction of larger multiple charged particles… among the 50nm particles can be expected*". How substantial is this fraction? Since the frozen fraction ends in the homogeneous freezing regime at 0.3 (Figure 3), is there a way to decide if the 50 nm microcline particles have been responsible for freezing at all or only the multiply charged larger particles are responsible? On the other hand, the freezing curve for 50 nm amazonite particles reaches value of 0.9 suggesting that all particles have been active. Could that be that even smaller particles would be IN active?

8-25 Twinning is not just symmetrical intergrowth. In alkali feldspars twinning is interrelated with phase exsolution and Na-K exchange between phases or between feldspar and external aqueous fluids (Parsons et al. 2015).

9-4. How thick was the Pt coating applied prior to SEM imaging? For the confinement effects to become important the pores should be less than 10 nm in diameter, could you reach this resolution in the SEM analysis?

9-9. "*The assumption that physical properties (e.g. hardness) are comparable among the tested feldspar species implies that the same degree of artificial surface features are introduced to all samples.*" What is the background for such assumption? Could you support it by literature data? On the page 3 line 32 I read something different: "*The different polymorphs differ in physical properties (cleavage, hardness, specific weight, melting point)…*" Could you clarify this point?

10-5. The discussion of kosmotropic vs. chaotropic cations is not very convincing. Why would the substitution of K+ for Rb+ increase the IN efficiency of K-rich feldspar if K+ is already kosmotropic? Or is there anything known about the degree of "kosmotropicity" for different kosmotropic cations? How many ions of Rb+ would one expect on the surface of an aerosol particle? Why some Na/Ca-rich feldspars exhibit a strong IN activity, having neither K+ nor Rb+ in their structure (like amelia albite in Whale et al., 2017)? This hypothesis should be either discussed in more detail or just omitted from the manuscript.

I am looking forward to the revised version of the manuscript.

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