

We thank Reviewer 2 for his/her constructive comments. We reproduce reviewer's comments in *blue* and our responses in black.

General comments

Kumar et al report on the ice nucleation activity of a range of aluminosilicate minerals and on the impact of various solute molecules on this activity. It is concluded that exchange of native cations with protons probably plays a critical role in the ice nucleating ability of aluminosilicates and that this explains why alkali salts inhibit ice nucleation by some aluminosilicates. Similarly, it is concluded that that NH₃ and NH₄⁺ adsorb to the surface of feldspars rather than exchanging with cations and from there interact with water in a way that promotes ice nucleation, and that dissolution of feldspar surfaces and formation of an amorphous surface layer inhibits ice nucleation by feldspars. The paper also summarizes the more numerous findings of the entire 3 part series of papers, concluding that relevant factors for the IN activity of silicates and aluminosilicates more generally include adsorption and ion exchange with the mineral surfaces and changes to surface structures induced by dissolution and growth of mineral surfaces exposed to water. The authors are sensibly tentative about their conclusions and suggest that molecular dynamics simulations and surface science techniques may allow them to be tested more thoroughly. The paper contains many results and reasonable interpretations. I am sure it will be of substantial interest to the audience of ACP, and possibly to those interested in heterogeneous nucleation more generally.

While I support publication, I note that the paper is long and complicated. While mostly well written, it is very hard to read and digest. It would certainly be beneficial if its bulk were reduced and the information it contains summarized more concisely. While I appreciate the difficulty in being more concise when dealing with so many different results I would strongly recommend that some effort be made to address this issue before publication. I also have some more specific scientific comments that the authors may wish to consider.

We highly appreciate the reviewer's comments. It is true that the manuscript gives a lot of information. Since we do not know what the relevant properties for ice nucleation are, we tried to collect all available information about surface properties and processes. Following the reviewer's suggestions, we rearranged the manuscript and combined results and discussion which are now ordered according to minerals.

Specific comments

I have some thoughts on the interpretation of results concerning the feldspars. Feldspar mineralogy is complex compared to that of the other minerals investigated, is clearly of substantial relevance to the topic in question but is not, to my mind, dealt with thoroughly in this manuscript. Characterization of the feldspar samples is slightly lacking. What is the chemical composition of the three samples used? That the plagioclase sample is named 'andesine' implies a composition but no precise composition is given. The sanidine and microcline samples used could have any composition between 37% K and 100% K from what has been presented. Kauffman et al. (2016) does not contain this information either, as far as I can tell and also does not have an 'andesine' sample.

The mineralogical composition of sanidine and andesine was determined by Kaufmann et al. (2016) and of microcline by Kumar et al. (2018) using X-ray diffraction (XRD). Rietveld refinement using Profex software (Döbelin and Kleeberg, 2015) was performed for a quantitative analysis. The microcline sample (Si:Al \approx 3.1; Al:K \approx 1.4) consists of 86.33% (\pm 1.71%) microcline, mixed with orthoclase (6.18% \pm 0.72%) and albite (7.49% \pm 0.48%). The sanidine sample proved to be pure sanidine with Si:Al \approx 3.1 and Al:K \approx 1.6 while andesine proved to be pure andesine with Si:Al \approx 1.7 and Ca/(Ca + Na) = 64%. Note that andesine would be

a labradorite based on Ca/(Ca + Na) ratio but crystallographically it fits best with an andesine. Also note that the andesine sample is termed as “plagioclase” in Kaufmann et al. (2016).

We have added this information in the revised manuscript in Section 2.1 (Lines 99-103).

I do not think it is reasonable to assume that the ice nucleating ability of the samples used are representative of their crystallographic structures. Harrison et al. (2016) and Whale et al. (2017) observe substantial variability in the ice nucleation effectiveness between crystallographically similar feldspars. Notably, Harrison et al. tested a sanidine sample that nucleated ice with similar effectiveness to most microclines and Whale et al. confirmed that it was sanidine using Raman spectroscopy. The argument is put forward here that the sorts of features that Whale et al. hypothesize cause ice nucleation in larger water droplets are not likely to be present in the smaller droplets used for this study. I am not sure about this. It is quite clear that different alkali feldspars have different structures across multiple scales, including the nanometer scale (Parsons et al., 2015). This is relevant because a) nanoscale features could easily be present on the ‘submicrometer’ particles used in this paper and b) nanoscale features are most probably on a scale similar to the critical ice nucleus.

Indeed, the crystallographic structure alone does not determine the ice nucleation ability of mineral dusts, rather, the crystallographic structure determines chemical and physical surface features, which influence the interaction with water and solutes. We agree that nanoscale features are of sufficient size to host a critical ice nucleus. However, even if the sites are small enough to be present on sub-micrometer particles, they might nevertheless be too rare. The type of active sites that are probed in an experimental setup depends on the mineral volume or more precisely the mineral surface present in the sample. For instance, freezing onsets of 251 K and 252 K for microcline correspond to active site densities of about $5 \cdot 10^6 \text{ cm}^{-2}$ and $5 \cdot 10^4 \text{ cm}^{-2}$ for 0.2 wt% and 20 wt% suspension concentrations, respectively (Kumar et al., 2018). These numbers are in excellent agreement with Atkinson et al. (2013) (active site density 10^6 cm^{-2} for microcline between 251 K and 252 K) who used 14 – 16 μm diameter droplets. Whale et al. (2017) explains the exceptional ice-nucleating ability of alkali feldspars by microtextures related to phase separation into Na and K-rich regions. These sites exhibit densities $< 10^3 \text{ cm}^{-2}$ and are too rare to explain the average freezing on submicrometer particles. The sites inducing ice nucleation above 260 K must be different in some respect to those becoming active only at 250 K or below. The difference might indeed be that the ones freezing at warmer temperature have in addition some suitable perthitic structure.

It is a little hard to pick out but it appears that the authors think that the plagioclase and sanidine feldspar they have tested are less active than microcline because the sites present on these feldspars are dissolved away effectively immediately on contact with water.

The dissolution rates that we collected from literature indicate that over the timescales of our emulsion freezing experiments, dissolution leads to relevant surface modifications due to the interaction of water with the feldspar surface. Moreover, we describe the dissolution process, which proceeds at near-neutral conditions via protonation of the oxygen of $\equiv\text{Al}-\text{O}-\text{Si}\equiv$ bridges with subsequent release of Al^{3+} resulting in an incongruent (deviation of ratio of released Si to Al from stoichiometric ratio) initial dissolution and leading to a $\equiv\text{Si}-\text{OH}$ rich surface. This shows that feldspar surfaces are strongly modified by water. However, it does not tell whether active sites that were initially present on sanidine or andesine are preferentially dissolved away.

Feldspar dissolution is clearly a complex topic. I do not feel I am qualified to comment on the authors' interpretation of this literature but I would note that it does not appear to be a well settled and understood subject from what I have read. It seems likely that feldspar-to-feldspar variability in dissolution rate is associated with more than just crystal structure and stoichiometry. Still it is helpful that opposing hypotheses for the differing ice nucleation abilities of feldspars now exist, as it is probably straightforward to test which is more consistent with experiments. It would, for instance, be interesting to see if the LD2 sanidine of Harrison et al. and Whale et al. nucleates ice better than a micro-texturally pristine Eifel sanidine (which is what I expect has been tested in this study) in the smaller emulsion droplets.

Feldspar dissolution is definitely a complex topic, nonetheless, a lot of work has already been done in this field. Given that it is still unclear what really makes feldspars highly IN active (or just any INP in general), it is important to approach the same question by assessing various physicochemical features of surfaces. The longer time scales of emulsion freezing experiments definitely brings surface dissolution in focus, especially when surfaces are exposed to extreme pH conditions.

It would indeed be interesting to see if the LD2 sanidine nucleates ice better than a micro-texturally pristine Eifel sanidine in emulsion freezing experiments. However, the LD2 sanidine could potentially be too coarse (sample sieved through 63 μm mesh (Whale et al., 2017)) to be accommodated by micrometer size droplets.

The citation for the dissolution rates of feldspars is wrong. I think the authors have read the numbers used from graphs in 'The mechanism of dissolution of the feldspars: Part I. Dissolution at conditions far from equilibrium' but have cited part IV.

The citation for dissolution rate for microcline and sanidine has been changed to Crundwell (2015) (The mechanism of dissolution of the feldspars: Part I. Dissolution at conditions far from equilibrium, Hydrometallurgy, 151, 151-162, doi:10.1016/j.hydromet.2014.10.006, 2015). Change in citation is made in Table 3 and Section 3.1.4.

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