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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Not all feldspar is equal: a survey of ice nucleating properties across the feldspar group of minerals” *by* A. D. Harrison et al.

Anonymous Referee #1

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The present study provides an overview of the ice nucleation activity of different feldspars varying in their chemical composition and crystal structure. In total 15 different feldspars including plagioclase and alkali feldspars were analyzed for one weight percentage using a special freezing array method called μl-NIPI (microliter Nucleation by Immersed Particle Instrument). Additionally, the samples were characterized with respect to their BET surface area and mineralogical structure at least for the dominating feldspar phase. It was found that K-feldspars generally nucleate ice more efficiently than other types of feldspar except for the two most efficient so-called “hyper-active” alkali feldspars (one of microcline and albite). One of the main statements of the study is that the observed ice nucleation efficiency of different feldspars varies. This effect was less pronounced in the case of K-feldspars. I consider this as the key information of this study. The influence of particle aging in water on the ice nucleation ability of

selected feldspars was investigated, too. Intensive change was found for albite one of the hyper-active feldspars over 16 months while other feldspars show no significant change. Ice nucleation surface site densities were derived from the data and compared to data available in literature. The paper is comprehensible and nicely written. It addresses scientific questions in the scope of ACP, but I have some major concerns about scientific quality. I recommend publication in ACP after discussing and incorporating the general and specific comments thoroughly.

General comments

(1) To analyze and characterize the chemical composition and crystallographic structure and its features more effort has to be done as realized in the present study. This fact is also explicitly stated by the authors. However, this study only present a starting point as the feldspar characterization method used in the present study is imprecise. Hence the ice nucleation ability of the different feldspars could not be related to e.g. special chemical or crystallographic features such as intracrystalline defect or any other intrinsic property. This would be of great interest. The mineralogical composition is given in Table 1 and for the dominant feldspar phase in Table 2. I am wondering if any information of the general composition (e.g. any component but feldspar) or crystal purity is available or measureable. One main result from the present study is that the ice nucleation ability varies for feldspar except for K-feldspar. What is the reason for that? Does it depend also on the source regions for the different feldspars? Would it be necessary for modellers to account for such an effect? This should be first discussed and second stated more clearly in the manuscript.

(2) The authors try to explain the observed freezing behaviour of pure feldspars and feldspars aged in water using the concept of “active sites”. It is unclear how exactly an active site is defined in the context it is used in the present study. Rather it seems that an active site is used as a construct with which almost anything can be explained if it is not related to a property of an ice nucleating particle, which should be determined from an independent measurement, see general comment (1). The concept of active sites

has to be introduced and motivated earlier in the paper and caution is required when conclusions are drawn. On page 5 line14-17, the authors distinguish between 3 different kinds of active site. Is it known for example whether the active site type (i) is similar for all feldspars? Or do they differ? This is not clear to me. The study includes many interesting indications what these special properties are or at least how they change for different types of feldspars or due to aging in water, but a clear comprehensive explanation is missing.

(3) At the moment without further tests, I am not convinced that the "hyper-activity" of one of the microcline and albite samples is real. I think the contribution from to biological ice nucleator contaminants can not be ruled out completely. The feldspar suspensions were left at room temperature (p.6 l.22). Under such conditions biological activity is not suppressed. The relatively gentle treatment in 100°C water for 15 min might destroy proteins (p.9 l.24-26) but probably not ice active polysaccharides or other organic/biological substances ice active at quite high temperature (Pummer et al., 2012; Tobo et al., 2014; O'Sullivan et al., 2014). Additional treatments with H_2O_2, H_2SO_4, etc. could be helpful as only heating is not always enough.

(4) Figure 3 and 4 has very poor quality and presents similar statements. The symbols are partly not visible. One can not distinguish between the different times of aging. The measurement uncertainties are missing, which must be known to judge if it is a real trend or just uncertainty of the experiment. This is most obvious in Fig.3 panel b) and c). I suggest to combine these figures.

Specific comments

p.1 l.16 & p.2 l.3 Specify what is meant by "soil dust". In the context of this study it seems that you mean mineral dust. Otherwise you need to clarify this statement.

p.1 l.22 Considering point 1 and 2 of my major concerns I don't agree that the feldspar samples are "well-characterized". They are only characterized with respect to their "macroscopic crystal structure" and BET surface area, but other probably decisive

properties such as intra-crystalline defects are not considered at all.

p.5 l.1-3 It might be true that the knowledge about the chemical composition of airborne mineral dust is limited. However, to be fair some studies investigating the composition of atmospheric mineral dust can be mentioned for example Glaccum and Prospero (1980), Kandler et al. (2007, 2009) to name a few.

p.5 l.24-27 and in all figures The labelling of the different feldspar samples might be precise and traceably, but totally confusing for the reader. I suggest to simplify the nomenclature in a way that it will be transparent for the reader to whom the paper is addressed. Probably a table in the Appendix could be useful for the precise description.

p.5 l.28-30, p.6 l.1-2 Please give a motivation for this treatment of the sample.

p. 6 l.10-14 In that context, Zolles et al, (2015) claimed that grinding could lead to a disclosing of active sites and even an enhancement of available active sites. This should be addressed in the manuscript as well.

p.7 l.3 Specify what is meant by "quantity". Is this quantity related to mass or mass concentration?

p.7 l.5-7 I do not understand why using a small dry nitrogen flow should prevent frozen droplets from affecting their neighbour liquid droplets?

p.7 l.7 How large are the droplets and do they vary in size? How many feldspar particles are immersed in the droplets and how does this number vary between different droplets. Statements to clarify these quantities are required. These are necessary information the reader needs to assess the reasonability of the approach of determining the uncertainty in ns.

p.8 l.2-16 As mentioned in the last section further information of the distribution of particles (hence potential active sites) over the droplet population are needed. I do not understand the procedure to derive the uncertainty in ns. Especially I could not follow how the two distributions are combined. Further, is the assumption " that each droplet contains a representative surface area distribution" justified? Maybe this is only true for rather high particle mass concentrations.

p.10 l. 5-9 I do not agree completely. I agree that flat increase in ns indicates a diversity of ice nucleation properties. However, the steeper slopes of ns or analogous quantities at higher temperature are also predicted by Classical Nucleation Theory assuming only one contact angle. In other words, even when similar ice nucleation properties (one contact angle) are assumed, the slopes become steeper at higher temperature. As a conclusion, the same effect can be explained also by a different hypothesis.

p.11 l.19-20 It seems that in Fig.3 the variation might also be explained by the measurement uncertainty? There is no trend in one direction with increasing time, or is the legend incorrectly labelled? This must be clarified.

p.11 l. 25-28 Additionally, the study of Marcolli et al. (2007) and Hartmann et al. (2016) can be mentioned.

p.13 l.26-32 Larger ns values always imply lower available particle surface area relevant for heterogeneous ice nucleation or lower number of active sites when similar ice nucleating materials are analyzed. The mass concentration and size of a droplet containing particles of different sizes (particle distribution) is not the essential quantity, but the total surface area of the particles. I feel that in both experiments (Atkinson et al., 2013 and Zolles et al., 2015) this quantity is not determined with sufficient reliability. Consequently, this is not a conclusive argument. If ns is carefully derived from the experimental data, this effect should be already considered. Error bars could clarify the uncertainty in ns derived from different experiment.

p.23 Fig.2 For the observed freezing at low temperature, it is necessary to show the limit of the measurement due to pure water freezing.

p.23 l.12 I do not agree that ns values can be simply subtracted without introducing further unnecessary uncertainty. An internal mixture of different ice nucleating particles

has to be accounted for.

Technical corrections

p.3 l.16-18 The citation list in brackets has to be sorted in the order beginning from the oldest to the recent publications. This needs to be changed in the whole manuscript.

p.16 l.2 . . . higher temperatures . . .

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