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Dear Dr. Huffman,

We have carefully addressed the reviewer comments and feel that we have now satisfied these. We have inserted our responses to both reviewer's comments below. The only significant change made to the manuscript, besides those to address the reviewers, was the change of the title to 'Not all feldspars are equal: a survey of ice nucleating properties across the feldspar group of minerals'. We have decided that this is more grammatically correct than previously. All other changes are minor improvements to language or corrections of typographical errors.

We hope that the changes made meet with your approval.

Best wishes,

Handwritten signatures of Tom Whale and Ben Murray in black ink. The signature of Tom Whale is on the left and Ben Murray is on the right, with a horizontal line underneath both.

Tom Whale and Ben Murray

# 1 Response to referee 1

2 We would like to thank the reviewer for their valuable comments. We have reworked the paper to  
3 address the relevant issues where necessary. The reviewer comments are written in italics, our  
4 response in normal type and changes to the manuscript in bold.

## 5 General comments

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

19 We think the paper is very important since it is the first survey across the feldspar group and it  
20 indicates that specific feldspars nucleate ice more efficiently than others. This means we are now in  
21 a much better position to do much more focused and detail orientated future studies where we look  
22 at specific properties of the select feldspars which nucleate ice effectively. Much of what the referee  
23 suggests in terms of trying to find what intrinsic property controls nucleation is sensible, but we view  
24 a detailed study as a next step. Nevertheless, the present results do indicate that the strongest ice  
25 nucleation is limited to the alkali feldspars and we hypothesise in the paper that the nucleating  
26 ability is related to microtexture. We are currently working on this hypothesis, but characterising  
27 microtexture and doing controlled experiments is a major study and is very much the topic of a  
28 future paper.

29 As the referee suggests, there are other properties of the feldspars which could be of interest. We  
30 have incorporated the space and point groups as well as the source locations of the minerals into  
31 tables 1 and 2 to try better display the known information for the studied minerals.

32

33

34 *(2) The authors try to explain the observed freezing behaviour of pure feldspars and feldspars*  
35 *aged in water using the concept of “active sites”. It is unclear how exactly an active site is*  
36 *defined in the context it is used in the present study. Rather it seems that an active site is*  
37 *used as a construct with which almost anything can be explained if it is not related to a*  
38 *property of an ice nucleating particle, which should be determined from an independent*  
39 *measurement, see general comment (1). The concept of active sites has to be introduced and*  
40 *motivated earlier in the paper and caution is required when conclusions are drawn. On page*

1 *5 line14-17, the authors distinguish between 3 different kinds of active site. Is it known for*  
2 *example whether the active site type (i) is similar for all feldspars? Or do they differ? This is*  
3 *not clear to me. The study includes many interesting indications what these special*  
4 *properties are or at least how they change for different types of feldspars or due to aging in*  
5 *water, but a clear comprehensive explanation is missing.*  
6

7 We have expanded our discussion of active sites in the experimental section:

8 **To allow comparison of the ability of different materials to nucleate ice, the number of active**  
9 **sites is normalised to the surface area available for nucleation. This yields the ice nucleation**  
10 **active site density,  $n_s(T)$ .  $n_s(T)$  is the number of ice nucleating sites that become active per**  
11 **surface area on cooling from 0°C to temperature  $T$  and can be calculated using (Connolly et al.,**  
12 **2009):**

$$\frac{n(T)}{N} = 1 - \exp(-n_s(T)A) \quad (1)$$

14 Where  $n(T)$  is the number of droplets frozen at temperature  $T$ ,  $N$  is the total number of droplets  
15 in the experiment and  $A$  is the surface area of nucleator per droplet.

16 Active sites may be related to imperfections in a crystal structure, such as cracks or defects, or  
17 may be related to the presence of quantities of other more active materials located in specific  
18 locations at a surface. While the fundamental nature of sites is not clear, and may be different  
19 for different materials,  $n_s$  is a pragmatic parameter which allows us to empirically define the ice  
20 nucleating efficiency of a range of materials (Vali, 2014).

21 This description is site specific and does not include time dependence. The role of time  
22 dependence in ice nucleation has recently been extensively discussed (Vali, 2014; Vali et al.,  
23 2014; Vali, 2008; Herbert et al., 2014; Wright et al., 2013). For feldspar (at least for BCS 376  
24 microcline) it is thought that the time dependence of nucleation is relatively weak and that the  
25 particle to particle, or active site to active site, variability is much more important (Herbert et  
26 al., 2014). The implication of this is that specific sites on the surface of most nucleators,  
27 including feldspars, nucleate ice more efficiently than the majority of the surface. As this study  
28 is aimed at comparing and assessing the relative ice nucleating abilities of different feldspars we  
29 have not determined the time dependence of observed ice nucleation in this work, although this  
30 would be an interesting topic for future study.

31  
32 We acknowledge the referee's comments on whether the active site type (i) is similar for all  
33 feldspars and on the absence of 'a clear comprehensive explanation' with reference to the types of

1 site. This is a problem for the entire field of ice nucleation, there is no clear, comprehensive and  
2 generally agreed upon explanation for why any substance should nucleate ice. We have made some  
3 intriguing observations which move us in the direction of a more comprehensive understanding. In  
4 the text we already discuss the different characteristics of sites on different feldspars samples. In  
5 addition we have expanded on the discussion in the conclusions section with the following lines:

6 **‘It is possible that the sites of type *i* are present on the typical K-feldspars, but we do not**  
7 **observe them because ice nucleates on more active sites. Whether these different sites are all**  
8 **related to similar features on the surfaces or if they are each related to different types of**  
9 **features is not known. Nevertheless, it appears that feldspars are characterised by a range of**  
10 **site types with varying stability and activity.’**

11

12 *(3) At the moment without further tests, I am not convinced that the “hyper-activity” of one of*  
13 *the microcline and albite samples is real. I think the contribution from to biological ice*  
14 *nucleator contaminants can not be ruled out completely. The feldspar suspensions were left*  
15 *at room temperature (p.6 l.22). Under such conditions biological activity is not suppressed.*  
16 *The relatively gentle treatment in 100°C water for 15 min might destroy proteins (p.9 l.24-26)*  
17 *but not ice active polysaccharides or other organic/biological substances ice active at quite*  
18 *high temperature (Pummer et al., 2012; Tobo et al., 2014; O’Sullivan et al., 2014). Additional*  
19 *treatments with H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, etc. could be helpful as only heating is not always enough.*

20 As the referee states the treatment of the sample at 100°C would destroy proteins but potentially  
21 not other organic substances. However the only biological substances we know to be active at the  
22 high temperatures displayed for the TUD#3 microcline and Amelia albite are proteins. This leads us  
23 to think that the activity is inherent to the feldspars. Additional treatments with H<sub>2</sub>O<sub>2</sub> or H<sub>2</sub>SO<sub>4</sub> might  
24 be helpful but may also influence ice nucleation by feldspars which would make any results difficult  
25 to interpret. We agree that we should be more cautious in our statements and have modified the  
26 text accordingly:

27 **‘Certain biological nucleators have been observed to retain their ice nucleating activity despite**  
28 **heat treatment of this type (Pummer et al., 2012;O’Sullivan et al., 2014;Tobo et al., 2014)**  
29 **however, to the best of our knowledge, no biological species has been observed to nucleate ice at**  
30 **such warm temperatures after heat treatment. Additionally, grinding of Amelia albite which**  
31 **had been stored as a powder for many years increases its ice nucleating potential, which is**  
32 **consistent with exposing fresh surfaces with features which decay away on contact with water.**  
33 **This behaviour is not consistent with biological nucleators, unless the biological entity is within**

1 **the Amelia albite particles and is somehow dispersed through the particle population during**  
2 **grinding. While we cannot exclude the possibility that some unknown biological species is**  
3 **present on microcline TUD#3 and Amelia albite it seems more likely that the minerals**  
4 **themselves are responsible for the observed ice nucleation activity.'**

5

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

11 We have combined both plots into a single figure with multiple panels. We think both panels are  
12 needed to emphasise the nature of the decay in activity over time. It is noted that the figures are  
13 difficult to see due to resizing for the discussions paper. This should improve in the final copy. In  
14 addition, we have used stronger colours for the points and error bars as well as expanding the x-axis.

15 Specific comments

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

18 The term soil dusts has been removed from the text to prevent any confusion.

19 *p.1 l.22 Considering point 1 and 2 of my major concerns I don't agree that the feldspar*  
20 *samples are “well-characterized”. They are only characterized with respect to their*  
21 *“macroscopic crystal structure” and BET surface area, but other probably decisive properties*  
22 *such as intra-crystalline defects are not considered at all.*

23 We have replaced the phrase “well characterised” with simply “characterised”.

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

28 We have now cited these papers in the relevant section and the text now reads:

1 **‘There is limited information about the composition of airborne atmospheric mineral dusts**  
2 **(Glaccum and Prospero, 1980;Kandler et al., 2007;Kandler et al., 2009); where mineralogy is**  
3 **reported the breakdown of the feldspar family has only been done in a limited way.’**

4

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

9

10 We have attempted to use naming conventions compatible with the geology literature. Our samples  
11 are named in the same fashion as they were in the studies which initially characterised them, where  
12 possible. Where we have introduced new samples we have followed the same naming conventions.  
13 We understand that the number of samples and their naming can be cumbersome but we feel that it  
14 is important to retain consistency with previous work. We would therefore prefer to use the current  
15 nomenclature.

16

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

18 We have inserted:

19 **‘As these two samples are chemically identical, differing only in that one is amorphous and the**  
20 **other crystalline, comparison of the ice nucleating efficiency of the two samples has the potential**  
21 **to reveal information about the impact of feldspar crystal structure on ice nucleating efficiency.’**

22

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

26

27 The activity increase seen by Zolles *et al*, (2015) has now been mentioned:

1 **Zolles et al. (2015) have suggested that grinding can lead to active sites being revealed, or the**  
2 **enhancement of existing active sites. It was shown in Whale et al. (2015) that differently ground**  
3 **samples of BCS 376 microcline nucleate ice similarly. In contrast Hiranuma et al. (2014) show**  
4 **that ground hematite nucleates ice more efficiently (normalised to surface area) than cubic**  
5 **hematite. The evidence suggests that the ice nucleating efficiencies of different materials**  
6 **respond differently to grinding processes.**

7

8 *p.7 1.3 Specify what is meant by “quantity”. Is this quantity related to mass or mass*  
9 *concentration?*

10 This has now been adjusted to:

11 **“Briefly, droplets of an aqueous suspension, containing a known mass concentration of feldspar**  
12 **particles are pipetted onto a hydrophobic coated glass slide.”**

13

14

15 *p.7 1.5-7 I do not understand why using a small dry nitrogen flow should prevent frozen*  
16 *droplets from affecting their neighbour liquid droplets?*

17 This has been further clarified in the text as follows:

18 **“This slide is placed on a temperature controlled stage and cooled from room temperature at a**  
19 **rate of 5 °C min<sup>-1</sup> to 0 °C and then at 1 °C min<sup>-1</sup> until all droplets are frozen. Dry nitrogen is**  
20 **flowed over the droplets at 0.2 l min<sup>-1</sup> to prevent frozen droplets from affecting neighbouring**  
21 **liquid droplets. Whale et al. (2015) demonstrated that a dry nitrogen flow prevents**  
22 **condensation and frost accumulating on the glass slide so ice from a frozen droplet cannot**  
23 **trigger freezing in neighbouring droplets.”**

24

25

26 *p.7 1.7 How large are the droplets and do they vary in size? How many feldspar particles are*  
27 *immersed in the droplets and how does this number vary between different droplets.*  
28 *Statements to clarify these quantities are required. These are necessary information the*

1 *reader needs to assess the reasonability of the approach of determining the uncertainty in*  
2 *ns.*

3 The droplets are of  $1 \pm 0.025 \mu\text{l}$  volume, we have inserted the following (the uncertainty is small  
4 because we use an electronic pipette with low uncertainty):

5

6 **‘Briefly,  $1 \pm 0.025 \mu\text{l}$  droplets of an aqueous suspension, containing a known mass concentration**  
7 **of feldspar particles are pipetted onto a hydrophobic coated glass slide.’**

8 We comment on the number of particles per droplet in the next comment

9

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

16

17 We have inserted the following to address the question of the number of particles per droplet:

18

19 **‘By assuming that the BET surface area of the feldspar powders is made up of monodisperse**  
20 **particles it can be estimated that droplets containing 1 wt% of feldspar will each contain around**  
21  **$10^6$  particles. While there will be a distribution of particle sizes we assume that there are enough**  
22 **particles per droplet that the uncertainty in surface area per droplet due to the distribution of**  
23 **particles through the droplets is negligible. In contrast, it has been suggested that ice nucleation**  
24 **data could be explained by variability of nucleator surface area through the droplet population**  
25 **(Alpert and Knopf, 2016). Our assumption that each droplet contains a representative surface**  
26 **area is supported by our previous work where we show that  $n_s$  derived from experiments with a**  
27 **range of feldspar concentrations are consistent with one another (Atkinson et al., 2013; Whale**  
28 **et al., 2015). If the particles were distributed through the droplets in such a way that some**  
29 **droplet contained a much larger surface area of feldspar than others we would expect the slope**  
30 **of  $n_s$  with temperature to be artificially shallow. The slope would be artificially shallow because**  
31 **droplets containing more than the average feldspar surface area would tend to freeze at higher**

1 temperatures and vice versa. However, the fact that  $n_s$  data for droplets made from suspensions  
2 made up with a wide range of different feldspar concentrations all line up shows that the  
3 droplet to droplet variability in feldspar surface area is minor (Atkinson et al., 2013; Whale et  
4 al., 2015). Hence, the droplet to droplet variability in feldspar surface area is neglected and the  
5 uncertainty in surface area per droplet in these experiments is estimated from the uncertainties  
6 in weighing, pipetting and specific surface area of the feldspars.'

7  
8 With regard to the description of the way the uncertainty in  $n_s$  is calculated we have changed the  
9 description of the method in an effort to make it clearer. It now reads:

10 'In order to estimate the uncertainty in  $n_s(T)$  due to the randomness of the distribution of the  
11 active sites in droplet freezing experiments, we conducted Monte Carlo simulations. Wright and  
12 Petters (2013) previously adopted a similar approach to simulate the distribution of active sites  
13 in droplet freezing experiments. In these simulations, we generate a list of possible values for  
14 the number of active sites per droplet ( $\mu$ ). The theoretical relationship between the fraction of  
15 droplets frozen and  $\lambda$  can be derived from the Poisson distribution:

$$\frac{n(T)}{N} = 1 - \exp(-\mu) \quad (2)$$

17 The simulation works in the following manner. First, we take a value of  $\mu$  and we simulate a  
18 corresponding random distribution of active sites through the droplet population for an  
19 experiment. Every droplet containing one or more active sites is then considered to be frozen. In  
20 this way, we can obtain a simulated value of the fraction frozen for a certain value of  $\mu$ .  
21 Repeating this process many times and for all the possible values of  $\mu$ , we obtain a distribution  
22 of possible values of  $\mu$  that can explain each value of the observed fraction frozen. This resulting  
23 distribution is neither Gaussian nor symmetric, so in order to propagate the uncertainty to  
24  $n_s(T)$  values, we take the following steps. First, we generate random values of  $\mu$  following the  
25 corresponding previously simulated distribution for each value of the fraction frozen. Then, we  
26 simulate random values of  $A$  following a Gaussian distribution centred on the value derived  
27 from the specific surface area per droplet with the standard deviation derived from the  
28 uncertainty in droplet volume and specific surface area. We assume that each droplet contains  
29 a representative surface area distribution as discussed above. This process results in two  
30 distributions, one for  $A$  and one for  $\mu$ , with these distributions we can calculate the resultant  
31 distribution of  $n_s(T)$  values, and from that distribution, we obtain the 95% confidence interval.'

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*p.10 l. 5-9 I do not agree completely. I agree that flat increase in  $n_s$  indicates a diversity of ice nucleation properties. However, the steeper slopes of  $n_s$  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.*

Good point, the following has been added to the paper.

**‘The smaller diversity in the sites active at warmer temperatures may explain the observed steep slopes in  $n_s$ , however it should be noted that Classical Nucleation Theory also predicts steeper slopes at higher temperatures, assuming a single contact angle.’**

*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.*

The error bars have now been shown more clearly to justify that the overall trend in of both Amelia albite and TUD#3 are not simply an artefact of experimental error. Note that there is some variability for the TUD#3, but the overall trend over 16 months is clear.

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

The papers have now been cited.

*p.13 l.26-32 Larger  $n_s$  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*

1            *quantity is not determined with sufficient reliability. Consequently, this is not a conclusive*  
2            *argument. If  $n_s$  is carefully derived from the experimental data, this effect should be already*  
3            *considered. Error bars could clarify the uncertainty in  $n_s$  derived from different experiments.*

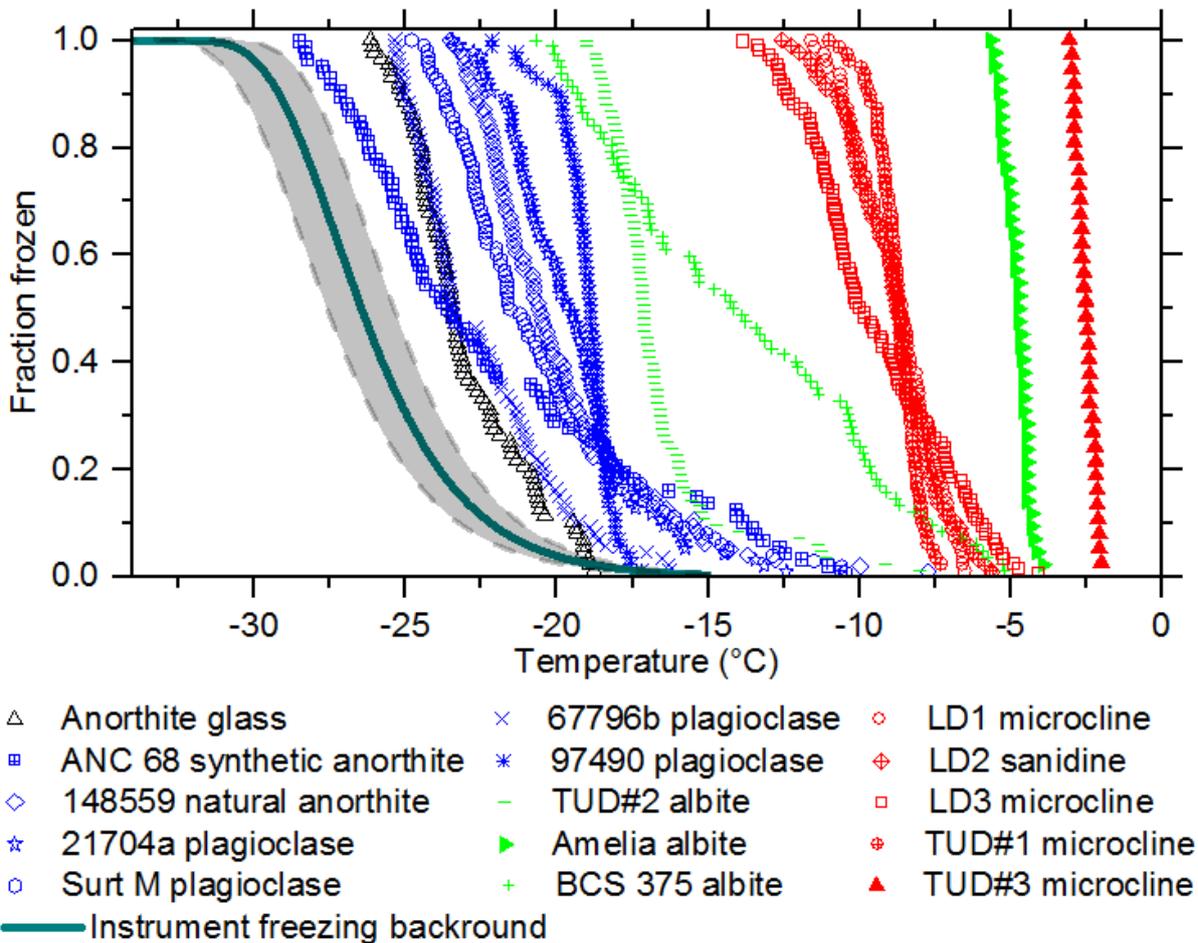
4    This is a good point, we were trying to make clear the differences between the experimental  
5    procedures used in different papers but wrote the section poorly. We agree that the total surface  
6    area of the particles in a droplet is the important quantity, but wanted to highlight the differences  
7    between the experiments. We have improved this discussion with the insertion of:

8    **“In principle,  $n_s$  should be independent of droplet volume and particle concentration, but**  
9    **differences between instruments and methods have been reported (Hiranuma et al., 2015).**  
10   **Additionally, Zolles et al. (2015) estimated the surface area of their feldspar particles using a**  
11   **combination of SEM images and the BET surface area of quartz. This leads to an unspecified**  
12   **uncertainty in their  $n_s$  values.”**

13

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

16    We have inserted a new figure showing droplet fractions frozen for all experiments, along with the  
17    freezing temperatures for pure water showing that the experiments we have conducted are not  
18    interfered with by the background freezing of the instrument, although one of the plagioclase runs  
19    gets quite close to this limit.



1

2 **Figure 1: Droplet fraction frozen as a function of temperature for 1 wt% suspensions of ground powders of various**  
 3 **feldspar samples. The K-feldspars are coloured red, the plagioclase feldspars are coloured blue, the albites are**  
 4 **coloured green and the feldspar glass is coloured black. A fit to the background freezing of pure MilliQ water in the**  
 5 **µl-NIPI instrument used by Umo et al. (2015) is also included. The shaded area around this fit shows 95% confidence**  
 6 **intervals for the fit. It can be seen that all the feldspar samples tested nucleate ice more efficiently than the**  
 7 **background freezing of the instrument.**

8

9 *p.23 l.12 I do not agree that  $n_s$  values can be simply subtracted without introducing further*  
 10 *unnecessary uncertainty. An internal mixture of different ice nucleating particles has to be*  
 11 *accounted for.*

12 We do not simply subtract  $n_s$  values and have removed the confusing statement. The process is  
 13 described in Umo et al. (2015).  $n_s$  values are not subtracted directly.  $K$  values are calculated for the  
 14 background freezing and subtracted from  $K$  values for the experiment. The resulting  $K_{\text{net}}$  values are  
 15 then converted into  $n_s$  values.

16

17 Technical corrections

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

3 This has been corrected.

4 *p.16 l.2 . . . higher temperatures . . .*

5 A correction has been made.

6

## 7 **References**

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## Response to referee 2

We thank the referee for their valuable comments. We have reworked the paper to address the relevant issues where necessary. The reviewer comments are shown in italics, our response in normal type and changes in the manuscript in bold enclosed in inverted commas.

### General comments

*(1) The information provided on the different mineralogical compositions of the feldspar minerals is good, and Figure 1 summarizes this well. I was surprised to not also see more details provided regarding the crystal lattice structure, symmetry, and space group of the different mineral phases. These properties are often referred to in the text to try to understand the observed ice nucleation properties, but without a table or figure summarizing this information it is hard to understand this important aspect. Please add as much detail regarding the other known properties of these feldspar minerals in a well organized table or similar.*

We agree that this is valuable information and the crystal lattice structure, point and space groups of the different feldspars has been added to the tables.

*(2) Introduction: It seems that the recent effort by Perlwitz et al. to incorporate better representations of the variable mineralogical composition of dust into global models should be referred to here. A major challenge regarding understanding and predicting the ice nucleation properties of atmospheric mineral particles is that we do not have a good understanding of the distribution, abundance, and transport of the different mineral types in the atmosphere.*

1 Perlwitz *et al.* has now been mentioned in the introduction in a new statement:

2

3 **‘This is an important finding as it has been demonstrated that feldspar is a common component**  
4 **of aerosolised mineral dusts (Glaccum and Prospero, 1980;Kandler et al., 2009;Kandler et al.,**  
5 **2011;Atkinson et al., 2013;Perlwitz et al., 2015)’**

6

7

8

9 *(3) On a related note, it is important to also have some discussion of the size of atmospheric*  
10 *feldspar mineral particles. What aerosol size mode are these typically found in? This is*  
11 *crucial to predict their transport, lifetime, and deposition. One of the reasons that the*  
12 *clay minerals have been focused on for so long is that they tend to be present in the*  
13 *smaller atmospheric mineral particle sizes, and thus have longer lifetimes.*

14

15 We have added the following text after the comments on the importance of feldspar for ice  
16 nucleation:

17

18 **‘Feldspar particles in the atmosphere tend to be larger than clay particles and so will have**  
19 **shorter lifetimes in the atmosphere, however aerosol modelling work has suggested that feldspar**  
20 **particles can account for many observations of INP concentrations around the world (Atkinson**  
21 **et al., 2013)’**

22

23

24

25 *(4) Although you focus on immersion freezing here – without actually stating the*  
26 *heterogeneous ice nucleation mode you measure here (please clarify this so it is clear to*  
27 *the reader), it was odd that this paper on the depositional ice nucleation properties of*  
28 *Feldspar was not cited:*

29

30 *Yakobi-Hancock, J. D.; Ladino, L. A.; Abbatt, J. P. D. Feldspar minerals as efficient*  
31 *deposition ice nuclei. Atmos. Chem. Phys. 2013, 13, 11175–11185, doi:10.5194/acp-13-*  
32 *11175-2013.*

33

34 We have now made clear in the last paragraph of the introduction and in the experimental section that  
35 we make use of heterogeneous immersion freezing:

36

37 **‘Here this technique is used to make heterogeneous immersion mode nucleation experiments.’**

38

1 Also, we have now cited the suggested work in the introduction:

2

3 **‘Work conducted below water saturation using a continuous flow diffusion chamber has also**  
4 **concluded that feldspars, particularly orthoclase feldspars, nucleate ice at low relative humidity**  
5 **in the deposition mode than other common dust minerals (Yakobi-Hancock et al., 2013).’**

6

7

8 *(5) Some discussion of the vulnerability of feldspar minerals to chemical attack by e.g.*  
9 *sulfuric acid should be included. This is quite important to understand the actual*  
10 *contribution of feldspar minerals to atmospheric ice nucleation, and also provides some*  
11 *insights into the nature of the ice active sites. Wex et al. (2014), already cited here,*  
12 *discuss some of these aspects. I believe it is well known in the mineralogy community*  
13 *that these feldspar minerals can be readily converted to amorphous clay structure*  
14 *through reaction with sulfuric acid.*

15

16 Greater detail into the weathering has been added to both the stability of active sites and the  
17 conclusions section to address this issue.

18 **‘This result is in agreement with the fact that albite weathers faster than microcline in soils as**  
19 **Na<sup>+</sup> is more readily substituted for hydrogen than K<sup>+</sup> (Busenberg and Clemency, 1976; Blum,**  
20 **1994).’**

21

22 In the conclusions:

23

24 **‘If the high energy defects along exsolution boundaries are responsible for higher ice nucleation**  
25 **activity of K-feldspars then this may offer an insight into acid passivation of ice nucleating**  
26 **ability observed in laboratory studies (Wex et al., 2014). Berner and Holdren (1979) suggest**  
27 **that the acid mediated weathering of feldspar occurs in multiple stages and suggest dissolution**  
28 **of feldspars is concentrated at high surface energy sites such as dislocations and crystal defects,**  
29 **sites which may be related to ice nucleation. More work is needed to explore the significance of**  
30 **exsolution, microtexture and the impact of weathering on feldspars with respect to ice**  
31 **nucleation activity.’**

32

33

34

35 *(6) Page 6: Why were those 3 mineral samples selected out of the 15 to perform the*  
36 *extended time in water experiments on? It would be valuable to conduct these tests*  
37 *on a larger number of the minerals, since the behavior seems quite variable between*  
38 *minerals. At the least some justification for the 3 sample chosen could be given.*

39

1 These experiments were of an opportunistic nature as a rapid decay was noticed in both the Amelia  
2 albite and TUD#3 microcline between repeat runs. The justification of these samples being chosen  
3 has been added to section 5.2 stability of active sites.

4

5 **‘TUD #3 microcline and Amelia albite were chosen for this experiment as they contained highly**  
6 **active sites, represented two different types of feldspar and were the only feldspars observed to**  
7 **exhibit this rapid decay in activity. BCS 376 microcline was also included in this activity decay**  
8 **experiment as it had provided consistent data over repeated runs and served as a standard in**  
9 **the Atkinson *et al.* (2013) paper which could therefore be tested.’**

10

11

12 *(7) Page 6, line 31: Citing 8 of the authors own publications that uses the same (and rather*  
13 *simple) experimental method seems like excessive and unnecessary self-citation,*  
14 *especially when Whale et al. (2015a) already provides a detailed discussion of the*  
15 *method. Please restrict these to the most necessary and relevant citations.*

16

17 Only the most relevant references have now been cited.

18

19 *Page 7, line 19: More of the recently published experimental work that has explored the role*  
20 *of time-dependent freezing should be cited, such as:*

21

22 *Wright, T. P.; Petters, M. D. The role of time in heterogeneous freezing nucleation. J.Geophys.*  
23 *Res. Atmos. 2013, 118, 3731–3743, doi:10.1002/jgrd.50365.*

24

25 Wright and Petters has now been cited also.

26

27

28

29 *(8) Some discussion of the similarity of the Monte Carlo approach to estimate the*  
30 *uncertainty of the ns values to other work should be presented. Is this the first time these*  
31 *authors have used this approach, or that anyone has used a similar approach? Wright &*  
32 *Petters (JGR, 2013; cited above) also used a Monte Carlo approach to analyze and*  
33 *interpret their droplet freezing data. Please discuss this. As it is presented it reads as if*  
34 *this is a completely new approach.*

35

36 We have inserted the following:

37

1 **‘Wright and Petters (2013) previously adopted a similar approach to simulate the distribution**  
2 **of active sites in droplet freezing experiments.’**

3  
4 *(9) Page 8, line 14: “We assume that each droplet contains a representative surface area*  
5 *distribution.” Please clarify what “representative” means. Is the goal to account for the*  
6 *non-uniform distribution of particle number and surface area in each droplet?*  
7

8 We have addressed this issue in response to referee 1. We added:

9  
10 **‘By assuming that the BET surface area of the feldspar powders is made up of monodisperse**  
11 **particles it can be estimated that the droplets will each contain around 106 particles. While**  
12 **there will be a distribution of particle sizes we assume that there are enough particles per**  
13 **droplet that the uncertainty in surface area per droplet due to the distribution of particles**  
14 **through the droplets is negligible. This assumption is supported by our previous work where we**  
15 **show that ns derived from experiments with a range of feldspar concentrations are consistent**  
16 **with one another (Atkinson et al., 2013). If the particles were distributed through the droplets in**  
17 **such a way that some droplet contained a much larger surface area of feldspar than others we**  
18 **would expect the slope of ns with temperature to be artificially shallow. The slope would be**  
19 **artificially shallow because droplets containing more than the average feldspar surface area**  
20 **would tend to freeze at higher temperatures and vice versa. This would mean that ns data**  
21 **derived from experiments with different feldspar concentrations would be inconsistent with one**  
22 **another. However, the fact that ns data for droplets made from suspensions made up with a**  
23 **wide range of different feldspar concentrations all line up shows that the droplet to droplet**  
24 **variability in feldspar surface area is minor (Atkinson et al. 2013). Hence, the droplet to droplet**  
25 **variability in feldspar surface area is neglected and the uncertainty in surface area per droplet**  
26 **in these experiments is estimated from the uncertainties in weighing, pipetting and specific**  
27 **surface area of the feldspars.’**

28  
29  
30 *(10) Figure 3 is hard to read at the presented size. The symbols are too small and faint.*  
31

32 We recognise that the figure is hard to read in current form. It was rescaled for the discussion paper.  
33 This should hopefully be corrected in the final paper. We have also made an effort to improve the  
34 clarity of the error bars.

35  
36  
37  
38 *(11) Figure 4 is begging for some error bars or other measurement of the uncertainties, so*  
39 *it can be determined what degree of the observed changes in median freezing*  
40 *temperature are significant and above the experimental uncertainties. It seems that only*  
41 *the Amelia albite sample displayed any significant change.*  
42

1 We have added temperature error bars to both figures and attempted to improve the clarity of both  
2 panels of what is now figure 4.

3

4 *(12) Figure 5: Some annotations/captions added directly to the figure pointing out what*  
5 *data is plotted where would improve the clarity of this paper. It is difficult to have to*  
6 *keep going back to the figure legend to decode what each dataset is from.*

7

8 We think that labelling data sets would be quite confusing and add a lot of clutter to the plot. But,  
9 we have grouped the like minerals in the key.

10

11

## 12 Technical corrections

13

14 *Page 3, line 19: "experiments"*

15

16 This has now been changed.

17

18 *Page 7, line 5: Missing a space, should be "C min-1"*

19

20 This has been corrected.

21

22 *Page 9, line 30: "(nucleation rate) vs." Versus what?*

23

24 The typo 'vs' has been removed.

25

26 *A space in-between the number and "degreeC" is often missing, such as throughout pages 12*  
27 *& 13.*

28

29 Spaces have been added in the relevant places.

30

31 *Page 14, line 18: "regimen this study". Word is missing?*

32

1 The text now reads as:

2

3 **“Within the microliter regime in this study we have observed some variability amongst the K-**  
4 **feldspars (see Figure 2), but no difference between sanidine and the 4 out of 5 microclines which**  
5 **fall around the line defined by Atkinson et al. (2013).”**

6

7 *Page 15, line 13: “sites”*

8

9 This has been changed as suggested.

10

11 *Page 15, line 15: “that are stable”*

12

13 This correction has been made in the text.

14

15

16

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18

19

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# 1 | **Not all feldspars is-are equal: a survey of ice nucleating** 2 | **properties across the feldspar group of minerals**

3  
4 | **Alexander D. Harrison<sup>1†</sup>, Thomas F. Whale<sup>1\*\*</sup>, Michael A. Carpenter<sup>2</sup>, Mark A.**  
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12  
13 | <sup>†</sup> Both authors contributed equally to the paper  
14

## 15 | **Abstract**

16 | Mineral dust particles from wind-blown soils are known to act as effective ice nucleating  
17 | particles in the atmosphere and are thought to play an important role in the glaciation of  
18 | mixed phase clouds. Recent work suggests that feldspars are the most efficient nucleators of  
19 | the minerals commonly present in atmospheric mineral dust. However, the feldspar group of  
20 | minerals is complex, encompassing a range of chemical compositions and crystal structures.  
21 | To further investigate the ice-nucleating properties of the feldspar group we measured the ice  
22 | nucleation activities of 15 characterised feldspar samples. We show that alkali feldspars, in  
23 | particular the potassium feldspars, generally nucleate ice more efficiently than feldspars [in](#)  
24 | [the plagioclase series which](#) containing significant amounts of calcium ~~in the plagioclase~~  
25 | [series](#). We also find that there is variability in ice nucleating ability within these groups.  
26 | While five out of six potassium-rich feldspars have a similar ice nucleating ability, one  
27 | potassium rich feldspar sample and one sodium-rich feldspar sample were significantly more  
28 | active. The hyper-active Na-feldspar was found to lose activity with time suspended in water  
29 | with a decrease in mean freezing temperature of about 16°C over 16 months; the mean  
30 | freezing temperature of the hyper-active K-feldspar decreased by 2°C over 16 months,

1 whereas the ‘standard’ K-feldspar did not change activity within the uncertainty of the  
2 experiment. These results, in combination with a review of the available literature data, are  
3 consistent with the previous findings that potassium feldspars are important components of  
4 [arid or fertile](#) soil dusts for ice nucleation. However, we also show that there is the  
5 possibility that some alkali feldspars can have enhanced ice nucleating abilities, which could  
6 have implications for prediction of ice nucleating particle concentrations in the atmosphere.

## 8 **1 Introduction**

9 Clouds containing supercooled liquid water play an important role in our planet’s climate and  
10 hydrological cycle, but the formation of ice in these clouds remains poorly understood  
11 (Hoose and Möhler, 2012). Cloud droplets can supercool to below -35°C in the absence of  
12 particles capable of nucleating ice (Riechers et al., 2013; Herbert et al., 2015), hence clouds  
13 are sensitive to the presence of ice nucleating particles (INPs). A variety of aerosol types  
14 have been identified as INPs (Murray et al., 2012; Hoose and Möhler, 2012), but mineral  
15 dusts from deserts are thought to be important INPs over much of the globe and in a variety  
16 of cloud types (DeMott et al., 2003; Hoose et al., 2008; Hoose et al., 2010; Niemand et al.,  
17 2012; Atkinson et al., 2013).

18 Atmospheric mineral dusts are composed of weathered mineral particles from rocks and soils,  
19 and are predominantly emitted to the atmosphere in arid regions such as the Sahara (Ginoux  
20 et al., 2012). The composition and relative concentrations of dust varies spatially and  
21 temporally but it is generally made up of only a handful of dominant minerals. The most  
22 common components of dust reflect the composition of the continental crust and soil cover,  
23 with clay minerals, feldspars and quartz being major constituents. [Perlwitz, et al. \(2015\) have](#)  
24 [recently tried to to better improve understanding of the mineral variable composition of](#)  
25 [airborne mineral dusts to incorporate into models but there is still much significant uncertainty](#)  
26 [in this area.](#) Until recently, major emphasis for research has been placed on the most  
27 common minerals in transported atmospheric dusts, the clays. It has now been shown that,  
28 when immersed in water, the feldspar component nucleates ice much more efficiently than  
29 the other main minerals that make up typical desert dust (Atkinson et al., 2013; Augustin-  
30 Bauditz et al., 2014; O’Sullivan et al., 2014; Niedermeier et al., 2015; Zolles et al., 2015). [This](#)  
31 [is an important finding as it has been demonstrated that feldspar is a common component of](#)  
32 [aerosolised mineral \*\*limited information about\*\* dusts \(Atkinson et al., 2013\) \(Perlwitz, 2015;](#)

1 ~~Glaccum and Prospero, 1980; Kandler, 200x~~. (Glaccum and Prospero, 1980;Kandler et al.,  
2 2009;Kandler et al., 2011;Atkinson et al., 2013;Perlwitz et al., 2015). Feldspar particles in the  
3 atmosphere tend to be larger than clay particles and so will have shorter lifetimes in the  
4 atmosphere, however aerosol modelling work has suggested that feldspar particles can  
5 account for many observations of INP concentrations around the world (Atkinson et al.,  
6 2013)<sup>2</sup>. Work conducted below water saturation using a continuous flow diffusion chamber  
7 has also concluded that feldspars-, particularly orthoclase feldspars, nucleate ice at warmer at  
8 lower relative humidity in the deposition mode temperatures than other common dust  
9 minerals (Yakobi-Hancock et al., 2013). While all available evidence indicates that feldspars  
10 are very effective INPs, it must also be recognised that feldspars are a group of minerals with  
11 differing compositions and crystal structures. Therefore, in this study we examine immersion  
12 mode ice nucleation by a range of feldspar samples under conditions pertinent to mixed phase  
13 clouds.

14 An additional motivation is that determining the nature of nucleation sites is of significant  
15 fundamental mechanistic interest and is likely to help with further understanding of ice  
16 nucleation in the atmosphere (Vali, 2014;Freedman, 2015;Slater et al., 2015). By  
17 characterising a range of feldspars and associating them with differences in ice nucleation  
18 activity it might be possible to build understanding of the ice nucleation sites on feldspars.  
19 Some work has been conducted in this area already. Augustin-Bauditz et al. (2014) concluded  
20 that microcline nucleates ice more efficiently than orthoclase on the basis of ice nucleation  
21 results looking at a microcline feldspar and several mixed dusts. Zolles et al. (2015) recently  
22 found that a plagioclase and an albite feldspar nucleated ice less well than a potassium  
23 feldspar and suggested that the difference in the ice nucleation activity of these feldspars is  
24 related to the difference in ionic radii of the cations and the local chemical configuration at  
25 the surface. They suggested that only potassium feldspar will nucleate ice efficiently because  
26 the  $K^+$  is kosmotropic (structure making) in the water hydration shell while  $Ca^{2+}$  and  $Na^+$  are  
27 chaotropic (structure breaking).

28 There has been much interest in the study of ice nucleation using molecular dynamics  
29 simulations (e.g. Hu and Michaelides, 2007;Cox et al., 2012;Reinhardt and Doye, 2014;Lupi  
30 and Molinero, 2014;Lupi et al., 2014;Zielke et al., 2015;Cox et al., 2015b, a;Fitzner et al.,  
31 2015). To date there has been little overlap between work of this nature and laboratory  
32 experiments. This has been due to difficulties in conducting experiments on similar  
33 timescales and spatial extents between real-world and computational systems. While these

1 obstacles are likely to remain in place for some time, the feldspars may offer the opportunity  
2 to address this deficit by providing qualitative corroboration between computational and  
3 laboratory results. For instance, it may be possible to study ice nucleation on different types  
4 of feldspar computationally. If differences in nucleation rate observed also occur in the  
5 laboratory greater weight may be placed on mechanisms determined by such studies and so a  
6 mechanistic understanding of ice nucleation may be built up.

7 In this paper we have surveyed 15 feldspar samples with varying composition for their ice  
8 nucleating ability in the immersion mode. It will be shown that feldspars rich in alkali metal  
9 cations tend to be much better at nucleating ice than those rich in calcium. First, we  
10 introduce the feldspar group of minerals.

11

12

## 13 **2 The feldspar group of minerals**

14 The feldspars are tectosilicates (also called framework silicates) with a general formula of  
15  $XAl(Si,Al)Si_2O_8$ , where X is usually potassium, sodium or calcium (Deer et al., 1992).

16 Unlike clays, which are phyllosilicates (or sheet silicates), tectosilicates are made up of three  
17 dimensional frameworks of silica tetrahedra. Substitution of Si with Al in the structure is  
18 charge balanced by cation addition or replacement within the cavities in the framework. This  
19 leads to a large variability of composition in the feldspars and means that most feldspars in  
20 rocks have compositions between end-members of sodium-, calcium- or potassium-feldspars  
21 (Deer et al., 1992; Wenk and Bulakh, 2004). A ternary representation of feldspar  
22 compositions is shown in Figure 1. All feldspars have very similar crystal structures, but the  
23 presence of different ions and degrees of disorder related to the conditions under which they  
24 crystallised from the melt (lava or magma) yields subtle differences which can result in  
25 differing symmetry.

26 There are three polymorphs (minerals with the same composition, but different crystal  
27 structure) of the potassium end-member, which are microcline, orthoclase and sanidine. The  
28 polymorphs become more disordered in terms of Al placement in the tetrahedra from  
29 microcline to sanidine, respectively. The structures of feldspars which form from a melt vary  
30 according to their cooling rate. If cooling is fast (volcanic), sanidine is preserved. If cooling is  
31 slow, in some granites for example, microcline may be formed. Feldspars formed in

1 metamorphic rocks have high degrees of Al/Si order. The sodium end-member of the  
2 feldspars is albite and the calcium end-member is anorthite. Feldspars with compositions  
3 between sodium and calcium form a solid solution and are collectively termed the plagioclase  
4 feldspars with specific names for different composition ranges. Feldspars between sodium  
5 and potassium end-members are collectively termed the alkali feldspars and can be  
6 structurally complex. A solid solution series exists between high albite and sanidine ('high'  
7 refers to high temperature character which is preserved on fast cooling), but not between low  
8 albite and microcline ('low' refers to low temperature character which is indicative of slow  
9 cooling rates). In contrast to the series between sodium and calcium, and sodium and  
10 potassium, there are no feldspars between calcium and potassium end-members because  
11 calcium and potassium ions do not actively substitute for one another within the framework  
12 lattice due their difference in size and ionic charge (Deer et al., 1992;Wenk and Bulakh,  
13 2004).

14 There is limited information about the composition of airborne atmospheric mineral dusts  
15 (Glaccum and Prospero, 1980;Kandler et al., 2007;Kandler et al., 2009); where mineralogy is  
16 reported the breakdown of the feldspar family has only been done in a limited way. Atkinson  
17 et al. (2013) compiled the available measurements and grouped them into K-feldspars and  
18 plagioclase feldspars (see the Supplementary Table 1 in Atkinson et al. (2013)). This  
19 compilation indicates that the feldspar type is highly variable in atmospheric dusts, with K-  
20 feldspars ranging from 1 to 25% by mass (with a mean of 5%) and plagioclase feldspars  
21 ranging from 1 to 14% (with a mean of 7%). The feldspar component of airborne -dusts is  
22 highly variable and the nucleating ability of the various components needs to be investigated.

23 In order to aid the discussion and representation of the data we have grouped the feldspars  
24 into three groups: the plagioclase feldspars (not including albite), albite (the sodium rich  
25 corner of the ternary diagram) and potassium (K-) feldspars (microcline, sanidine and  
26 orthoclase). The K-feldspars contain varying amounts of sodium, but their naming is  
27 determined by their crystal structure. We also collectively refer to albite and potassium  
28 feldspars as alkali feldspars.

29

### 30 **3 Samples and sample preparation**

1 A total of 15 feldspars were sourced for this study. Details of the plagioclase feldspars tested  
2 are in Table 1 and details of the alkali feldspars are in Table 2. We have made use of a series  
3 of characterised plagioclase feldspars which were assembled for previous studies (Carpenter  
4 et al., 1985;Carpenter, 1986;Carpenter, 1991). The other samples were sourced from a range  
5 of repositories, detailed in Tables 1 and 2. The naming convention we have used in this paper  
6 is to state the identifier of the specific sample followed by the mineral name. For example,  
7 BCS 376 microcline is a microcline sample from the Bureau of Analysed Samples with  
8 sample code 376. In other cases, such as Amelia Albite, the sample is from a traceable  
9 source and is commonly referred to with this name and when a code is used, such as 97490  
10 plagioclase, the code links to the cited publications.

11 ~~A~~The anorthite glass and ~~tested~~synthetic anorthite ANC 68 were tested for ice nucleating  
12 efficiency to investigate the ~~relevance~~impact of crystal structure in feldspar. The anorthite  
13 glass was produced by Carpenter (1991) by melting natural calcite with reagent grade SiO<sub>2</sub>  
14 and Al<sub>2</sub>O<sub>3</sub> at 1680°C for 3 hours. The melt was then stirred before air cooling. The resulting  
15 glass was then annealed at 800°C to relieve internal stresses. The composition of the resulting  
16 glass was shown to be stoichiometric CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>. Synthetic anorthite ANC 68 was produced  
17 by heating a sample of this glass to 1400°C for 170 hours. As these two samples are  
18 chemically identical, differing only in that one is amorphous and the other crystalline,  
19 comparison of the ice nucleating efficiency of the two samples has the potential to reveal  
20 information about the impact of feldspar crystal structure on ice nucleating efficiency.---

21 Feldspars 148559, 21704a, 67796b and 97490 plagioclase and Amelia albite are natural  
22 samples that form a solid solution series covering the plagioclase series from nearly pure  
23 anorthite to nearly pure albite as seen in Table 1.

24 The alkali feldspars used here have not previously been characterised. Rietveld refinement of  
25 powder XRD patterns was carried out using TOtal Pattern Analysis Solutions (TOPAS) to  
26 determine the phase of the feldspar present. The results of this process are presented in Table  
27 2. The surface areas of all the feldspars were measured by Brunauer-Emmett-Teller (BET)  
28 nitrogen gas adsorption (see Sect. 4). All samples, unless otherwise stated, were ground to  
29 reduce the particle size and increase the specific surface area using a mortar and pestle which  
30 were scrubbed with pure quartz then cleaned with deionised water and methanol before use.  
31 Grinding of most samples was necessary in order to make the particles small enough for our  
32 experiments. Amelia albite was the only material tested both in an unground state (or at least

1 | not a freshly ground state) and a freshly ground state. ~~Zolles et al. (2015) (2015) suggested~~  
2 | ~~that grinding may increase the availability of active sites, however as this study is a survey of~~  
3 | ~~feldspars relative to one another and all samples were treated in the same way this effect is of~~  
4 | ~~little concern for these experiments.~~ Suspensions of known concentration were made up  
5 | gravimetrically using Milli-Q water (18.2 MΩ.cm). Except where stated otherwise the  
6 | suspensions were then mixed for a few minutes using magnetic stirrers prior to use in ice  
7 | nucleation experiments.

8 | ~~The activity of Amelia albite and TUD #3 microcline displayed activity decrease during~~  
9 | ~~repeat experimentss runs (on the order of 30 minutes) conducted approximately 30 minutes~~  
10 | ~~after initial experiments. Based on this observation~~ Three samples, the BCS 376 microcline,  
11 | ground Amelia albite and TUD #3 microcline, were tested for changes in ice nucleating  
12 | efficiency with time, when left in suspension at room temperature. ~~BCS 376 microcline was~~  
13 | ~~chosen as it has been the previously studied and the activity decrease was not seen on the~~  
14 | ~~time scale of ~ 30 minutes previously.~~ Ice nucleation efficiency was quantified at intervals  
15 | over 11 days. Between experiments the suspensions were left at room temperature without  
16 | stirring and then stirred to re-suspend the particulates for the ice nucleation experiments.  
17 | Suspensions of the three dusts were also tested 16 months after initial experiments were  
18 | performed to determine the long term impact of contact with water on ice nucleation  
19 | efficiency.

#### 21 | 4 Experimental method and data analysis

22 | In order to quantify the efficiency with which a range of feldspar dusts nucleate ice we made  
23 | use of the microliter Nucleation by Immersed Particle Instrument (μl-NIPI). This system has  
24 | been used to make numerous ice nucleation measurements in the past (~~O' Sullivan et al.,~~  
25 | ~~2015;Hiranuma et al., 2015;Whale et al., 2015b;Herbert et al., 2014;O'Sullivan et al.,~~  
26 | ~~2014;Atkinson et al., 2013;Umo et al., 2015;Wilson et al., 2015)~~ and has been described in  
27 | detail by Whale et al. (2015). ~~Here this technique is exploited to make heterogeneous~~  
28 | ~~immersion mode nucleation experiments.~~ Briefly,  $1 \pm 0.025 \mu\text{l}$  droplets of an aqueous  
29 | suspension, containing a known ~~mass concentration~~ quantity of feldspar particles are pipetted  
30 | onto a hydrophobic coated glass slide. This slide is placed on a temperature controlled stage  
31 | and cooled from room temperature at a rate of  $5 \text{ }^\circ\text{C}_{\text{min}}^{-1}$  to  $0 \text{ }^\circ\text{C}$  and then at  $1 \text{ }^\circ\text{C}_{\text{min}}^{-1}$  until

1 all droplets are frozen. Dry nitrogen is flowed over the droplets at  $0.2 \text{ l min}^{-1}$  to prevent  
2 frozen droplets from affecting neighbouring liquid droplets. Whale et al. (2015) demonstrated  
3 that a dry nitrogen flow prevents condensation and frost accumulating on the glass slide so  
4 ice from a frozen droplet cannot trigger freezing in neighbouring droplets. The dry nitrogen  
5 flow acts to prevent condensation accumulating on the glass slide so a freezing event cannot  
6 initiate across droplets cause freezing of other droplets. Freezing is observed with a digital  
7 camera, allowing determination of the fraction of droplets frozen as a function of  
8 temperature. Multiple experiments have been combined to produce single sets of data for  
9 each mineral. Suspensions of the feldspars were made up gravimetrically and specific surface  
10 areas of the samples were measured using the Brunauer–Emmett–Teller (BET)  $\text{N}_2$  adsorption  
11 method using a Micromeritics TriStar 3000. Here this  $\mu\text{l-NIPI}$  technique is used to make do  
12 heterogeneous immersion mode nucleation experiments.

13 To allow comparison of the ability of different materials to nucleate ice, the number of active  
14 sites is normalised to the surface area available for nucleation. This yields the ice nucleation  
15 active site density,  $n_s(T)$ .  $n_s(T)$  is the number of ice nucleating sites that become active per  
16 surface area on cooling from  $0^\circ\text{C}$  to temperature  $T$  and can be calculated using (Connolly et  
17 al., 2009):

$$\frac{n(T)}{N} = 1 - \exp(-n_s(T)A) \quad (1)$$

19 Where  $n(T)$  is the number of droplets frozen at temperature  $T$ ,  $N$  is the total number of  
20 droplets in the experiment and  $A$  is the surface area of nucleator per droplet.

21 Active sites may be related to imperfections in a crystal structure, such as cracks or defects,  
22 or may be related to the presence of quantities of other more active materials located in  
23 specific locations at a surface. While the fundamental nature of sites is not clear, and may be  
24 different for different materials,  $n_s$  is a pragmatic parameter which allows us to empirically  
25 define the ice nucleating efficiency of a range of materials (Vali, 2014).

26 This description is site specific and does not include time dependence. The role of time  
27 dependence in ice nucleation has recently been extensively discussed (Vali, 2014; Vali et al.,  
28 2014; Vali, 2008; Herbert et al., 2014; Wright et al., 2013). For feldspar (at least for BCS 376  
29 microcline) it is thought that the time dependence of nucleation is relatively weak and that the  
30 particle to particle, or active site to active site, variability is much more important (Herbert et  
31 al., 2014). The implication of this is that specific sites on the surface of most nucleators,

1 including feldspars, nucleate ice more efficiently than the majority of the surface. As this  
 2 study is aimed at comparing and assessing the relative ice nucleating abilities of different  
 3 feldspars we have not determined the time dependence of observed ice nucleation in this  
 4 work, although this would be an interesting topic for future study. To allow comparison of  
 5 the ability of different materials to nucleate ice, the number of active sites is normalised to  
 6 the surface area available for nucleation. This yields the ice nucleation active site density,  
 7  $n_s(T)$ .  $n_s(T)$  is the number of ice nucleating sites that become active per surface area on  
 8 cooling from  $0^\circ\text{C}$  to temperature  $T$  and can be calculated using  
 9 and allow comparison of different nucleators  $n_s(T)$  values are calculated.  $n_s(T)$  is the  
 10 number of ice nucleating sites that become active per surface area on cooling from  $0^\circ\text{C}$  to  
 11 temperature  $T$ .  $n_s(T)$  can be calculated using (Connolly et al., 2009):

$$\frac{n(T)}{N} = 1 - \exp(-n_s(T)A) \quad (1)$$

13 Where  $n(T)$  is the number of droplets frozen at temperature  $T$ ,  $N$  is the total number of  
 14 droplets in the experiment and  $A$  is the surface area of nucleator per droplet. This description  
 15 is site specific and does not include time dependence. The role of time dependence in ice  
 16 nucleation has recently been extensively discussed (Wright and Petters, 2013; Herbert et al.,  
 17 2014; Vali, 2014). For feldspar (at least for BCS 376 microcline) it is thought that the time  
 18 dependence of nucleation is relatively weak (at least for BCS 376 microcline) and that the  
 19 particle to particle, or active site to active site, variability is much more important (Herbert et  
 20 al., 2014). specific sites on it has been argued that there is no physical basis for active sites and  
 21 that ice nucleation data could be explained by variability of nucleant surface area through the  
 22 droplet population (Alpert and Knopf, 2016) there is significant evidence that that nucleation  
 23 occurs on specific sites which have variable nucleating properties (e.g. Herbert et al., 2014;  
 24 Vali, 2014; Vali, 2008; Vali, 2015; Wright and Petters, 2014). it is our opinion that the  
 25 available evidence strongly suggests that they do exist. We have conducted our analysis  
 26 through this paper under this paradigm.

27 By assuming that the BET surface area of the feldspar powders is made up of monodisperse  
 28 particles it can be estimated that droplets containing 1 wt% of feldspar will each contain  
 29 around  $10^6$  particles. While there will be a distribution of particle sizes we assume that there  
 30 are enough particles per droplet that the uncertainty in surface area per droplet due to the  
 31 distribution of particles through the droplets is negligible. In contrast, it has been suggested  
 32 that ice nucleation data could be explained by variability of nucleator surface area through the

1 droplet population (Alpert and Knopf, 2016). Our assumption that each droplet contains a  
2 representative surface area is supported by our previous work where we show that  $n_s$  derived  
3 from experiments with a range of feldspar concentrations are consistent with one another  
4 (Whale et al., 2015;Atkinson et al., 2013). If the particles were distributed through the  
5 droplets in such a way that some droplet contained a much larger surface area of feldspar than  
6 others we would expect the slope of  $n_s$  with temperature to be artificially shallow. The slope  
7 would be artificially shallow because droplets containing more than the average feldspar  
8 surface area would tend to freeze at higher temperatures and vice versa. However, the fact  
9 that  $n_s$  data for droplets made from suspensions made up with a wide range of different  
10 feldspar concentrations all line up shows that the droplet to droplet variability in feldspar  
11 surface area is minor (Atkinson et al., 2013;Whale et al., 2015). Hence, the droplet to droplet  
12 variability in feldspar surface area is neglected and the uncertainty in surface area per droplet  
13 in these experiments is estimated from the uncertainties in weighing, pipetting and specific  
14 surface area of the feldspars.

15 ~~By assuming that the BET surface area of the feldspar powders is made up of monodisperse~~  
16 ~~particles it can be estimated that the droplets will each contain around  $10^6$  particles. While~~  
17 ~~there will be a distribution of particle sizes we assume that there are enough particles per~~  
18 ~~droplet that the uncertainty in surface area per droplet due to the distribution of particles~~  
19 ~~through the droplets is negligible. This assumption is supported by our previous work where~~  
20 ~~we show that  $n_s$  derived from experiments with a range of feldspar concentrations are~~  
21 ~~consistent with one another (Atkinson et al., 2013). If the particles were distributed through~~  
22 ~~the droplets in such a way that some droplet contained a much larger surface area of feldspar~~  
23 ~~than others we would expect the slope of  $n_s$  with temperature to be artificially shallow. The~~  
24 ~~slope would be artificially shallow because droplets containing more than the average~~  
25 ~~feldspar surface area would tend to freeze at higher temperatures and vice versa. This would~~  
26 ~~mean that  $n_s$  data derived from experiments with different feldspar concentrations would be~~  
27 ~~inconsistent with one another. However, the fact that  $n_s$  data for droplets made from~~  
28 ~~suspensions made up with a wide range of different feldspar concentrations all line up shows~~  
29 ~~that the droplet to droplet variability in feldspar surface area is minor (Atkinson et al. 2013).~~  
30 ~~Hence, the droplet to droplet variability in feldspar surface area is neglected and the~~  
31 ~~uncertainty in surface area per droplet in these experiments is estimated from the~~  
32 ~~uncertainties in weighing, pipetting and specific surface area of the feldspars.Indeed, Murray~~  
33 ~~et al (2011) found that even with picolitre droplets containing 10's of particles per droplet~~

1 median nucleation temperatures scaled well with surface area per droplet calculated in the  
2 way used in this work.

3 “In order to estimate the uncertainty in  $n_s(T)$  due to the randomness of the distribution of the  
4 active sites in droplet freezing experiments, we conducted Monte Carlo simulations. Wright  
5 and Petters (2013) previously adopted a similar approach to simulate the distribution of active  
6 sites in droplet freezing experiments. In these simulations, we generate a list of possible  
7 values for the number of active sites per droplet ( $\mu$ ). The theoretical relationship between the  
8 fraction of droplets frozen and  $\mu$  can be derived from the Poisson distribution:

$$\frac{n(T)}{N} = 1 - \exp(-\mu) \quad (2)$$

10 The simulation works in the following manner. First, we take a value of  $\mu$  and we simulate a  
11 corresponding random distribution of active sites through the droplet population for an  
12 experiment. Every droplet containing one or more active sites is then considered to be frozen.  
13 In this way, we can obtain a simulated value of the fraction frozen for a certain value of  $\mu$ .  
14 Repeating this process many times and for all the possible values of  $\mu$ , we obtain a  
15 distribution of possible values of  $\mu$  that can explain each value of the observed fraction  
16 frozen. This resulting distribution is neither Gaussian nor symmetric, so in order to propagate  
17 the uncertainty to  $n_s(T)$  values, we take the following steps. First, we generate random  
18 values of  $\mu$  following the corresponding previously simulated distribution for each value of  
19 the fraction frozen. Then, we simulate random values of  $A$  following a Gaussian distribution  
20 centred on the value derived from the specific surface area per droplet with the standard  
21 deviation derived from the uncertainty in droplet volume and specific surface area. We  
22 assume that each droplet contains a representative surface area distribution as discussed  
23 above. This process results in two distributions, one for  $A$  and one for  $\mu$ , with these  
24 distributions we can calculate the resultant distribution of  $n_s(T)$  values, and from that  
25 distribution we obtain the 95% confidence interval.

26 In order to estimate the uncertainty in  $n_s(T)$  due to the randomness of the distribution of the  
27 active sites in droplet freezing experiments, we conducted Monte Carlo simulations. In these  
28 simulations, we generate a list of possible values for the number of active sites per droplet  
29 ( $k$ ). The theoretical relationship between the fraction of droplets frozen and  $k$  can be derived  
30 from the Poisson distribution:

$$\frac{n(T)}{N} = 1 - \exp(-k) \quad (2)$$

and we can calculate  $n_s(T)$  using the following:

$$n_s = \frac{k}{A} \quad (3)$$

The simulation works in the following manner. First, we take a value of  $k$  and we simulate a corresponding random distribution of active sites through the droplet population for an experiment. Every droplet containing one or more active sites is then considered to be frozen. In this way, we can obtain a simulated value of the fraction frozen for a certain value of  $k$ . Repeating this process many times and for all the possible values of  $k$ , we obtain a distribution of possible values of  $n_k$  that can explain every value of the observed fraction frozen. This resulting distribution is neither Gaussian nor symmetric, so in order to propagate the uncertainty in Equation 3, we take the following steps. First, we generate random values of  $k$  following the corresponding previously simulated distribution for every value of the fraction frozen. Then, we simulate random values of  $A$  following a Gaussian distribution centred on the value derived from the specific surface area per droplet with the standard deviation derived from the uncertainty in droplet volume and specific surface area. We assume that each droplet contains a representative surface area distribution as discussed above. By combining these two distributions of simulated values, we calculate the distribution of  $n_s(T)$  values, and from that distribution, we obtain the 95% confidence interval.

## 5 Results and discussion

### 5.1 Ice nucleation efficiencies of plagioclase and alkali feldspars

Droplet fraction frozen from  $\mu\text{l}$ -NIPI for the 15 feldspar samples are shown in Figure 2. The values of  $n_s(T)$  derived from these the freezing experiments of the 15 feldspar samples are experiments are shown in Figure 3 ~~Figure 2~~ along with the  $n_s(T)$  parameterisation from Atkinson et al. (2013) for BCS 376 microcline. The various groups of feldspars are indicated by colour which corresponds to the regions of the phase diagram in Figure 1. We define potassium (K-) feldspars (red) as those rich in K including microcline, orthoclase and

1 sanidine; the Na end-member is albite (green); and plagioclase series feldspars (blue) are a  
2 solid solution between albite and the calcium end-member, anorthite.

3 Out of the six K-feldspars studied, five fall on or near the line defined by Atkinson et al.  
4 (2013). These include three microcline samples and one sanidine sample, which have  
5 different crystal structures. Sanidine has disordered Al atoms, microcline has ordered Al  
6 atoms and orthoclase has intermediate order; these differences result in differences in  
7 symmetry and hence space group (see Tables 1 and 2). The freezing results indicate that Al  
8 disordering does not play an important role in nucleation. However, one K-feldspar sample,  
9 TUD#3 microcline, was substantially more active. This indicates that crystal structure and  
10 composition are not the only factors dictating the ice nucleating ability of K-feldspars.

11 All plagioclase feldspars tested were less active ice nucleators than the K-feldspars which  
12 were tested. There was relatively little variation in the ice nucleation activities of the  
13 plagioclase solid solution series characterised by Carpenter (1986) and Carpenter et al.  
14 (1985). For instance, of those feldspars that possess the plagioclase structure, greater sodium  
15 content does not systematically increase effectiveness of ice nucleation. Overall, the results  
16 for plagioclase feldspars indicate that they have an ice nucleating ability much smaller than  
17 that of the K-feldspars.

18 It is also interesting to note that the ANC 68 synthetic anorthite had different nucleating  
19 properties to the anorthite glass from which it was crystallised (and had the same  
20 composition). The ANC 68 synthetic anorthite sample has a much more shallow  $n_s(T)$  curve  
21 than the glass. This is noteworthy, because the composition of these two materials is  
22 identical, but the phase of the material is different. It demonstrates that crystallinity is not  
23 required to cause nucleation, but the presence of crystallinity can provide rare sites which can  
24 trigger nucleation at much warmer temperatures. In a future study it would be interesting to  
25 attempt to probe the nature of these sites.

26 We tested three predominantly Na-feldspars (albites). Amelia albite was found to be highly  
27 active, approaching that of TUD#3 microcline. The others, BCS 375 albite, and TUD#2 albite  
28 were less active, intermediate between the K-feldspars and plagioclase feldspars.

29 To ensure that the high activity of Amelia albite and microcline TUD#3 was not caused by  
30 contamination from biological INPs the samples were heated to 100°C in Milli-Q water for  
31 15 minutes. This treatment will disrupt any protein based nucleators present (O'Sullivan et

1 al., 2015). No significant reduction in freezing temperatures (beyond what would be expected  
2 from the activity decay described in Sect. 5.2) was observed suggesting that the highly active  
3 INPs present are associated with the feldspars rather than biological biological protein  
4 contamination. Certain biological nucleators have been observed to retain their ice nucleating  
5 activity despite heat treatment of this type (Pummer et al., 2012; O'Sullivan et al., 2014; Tobo  
6 et al., 2014) however, to the best of our knowledge, no biological species has been observed  
7 to nucleate ice at such warm temperatures after heat treatment. This behaviour does not seem  
8 consistent with biological nucleators, unless the biological entity is within the Amelia albite  
9 particles and is somehow dispersed through the particle population during  
10 grinding. Additionally, the behaviour of Amelia albite when ground and left in water  
11 (described in Sect. 5.2) is not consistent with biological ice nucleation and use of chemical  
12 agents to destroy possible biological contamination may cause changes in ice nucleation  
13 activity of feldspars also, which would not be distinguishable from the elimination of  
14 biological contamination. While we cannot exclude the possibility that some heretofore  
15 unknown biological species is present on microcline TUD#3 and Amelia albite it seems more  
16 likely that the minerals themselves are responsible for the observed ice nucleation activity.

17  
18 It has been noted by Vali (2014) that there is an indication that nucleators which are more  
19 active at higher temperatures tend to have steeper slopes of  $\ln J$  (nucleation rate) vs. We have  
20 observed this trend here in the data shown in Figure 2-3 ( $n_s(T)$  is proportional to  $J$  for a  
21 single component). The slopes of experiments where freezing occurred at colder temperatures  
22 (plagioclases) generally being flatter than those where freezing took place at warmer  
23 temperatures (alkali feldspars). Vali (2014) suggests that this maybe the result of different  
24 observational methods. In this study we have used a single method for all experiments so the  
25 trend is unlikely to be due to an instrument artefact. The implication is that sites with lower  
26 activity tend to be more diverse in nature. This may indicate that there are fewer possible  
27 ways to compose a site that is efficient at nucleating ice and that there will be less variation in  
28 these sites as a result. The active sites of lower activity may take a greater range of forms and  
29 so encompass a greater diversity of activation temperatures. The lower diversity in the sites  
30 active at warmer temperatures may explain the steep slopes in  $n_s$  seen, however it should be  
31 noted that Classical Nucleation Theory also predicts steeper slopes at higher temperatures  
32 assuming a single contact angle.

1 To summarise, plagioclase feldspars tend to have relatively poor ice nucleating abilities, all  
2 K-feldspars we tested are relatively good at nucleating ice and the albites are variable in their  
3 nucleating activity. Out of the six K-feldspars tested, five have very similar activities and are  
4 well approximated by the parameterisation of Atkinson et al. (2013) in the temperature- $n_s$   
5 regime we investigated here. However, we have identified two alkali feldspar samples, one  
6 K-feldspar and one albite, which are much more active than the others indicating that a factor  
7 or factors other than the polymorph or composition determines the efficiency of alkali  
8 feldspars as ice nucleators.

## 9 **5.2 The stability of active sites**

10 It was observed that the ice nucleation activity of ground Amelia albite and ground TUD #3  
11 microcline declined over the course of ~30 minutes, the time between successive runs. Only  
12 the initial run is shown in Figure [2-3](#) where the feldspar had spent only about 10 minutes in  
13 suspension. This decay in activity over the course of ~30 mins was not seen in the other  
14 feldspars. To investigate this effect samples of BCS 376 microcline, Amelia albite and TUD  
15 #3 microcline were left in water within a sealed vial and tested at intervals over the course of  
16 16 months, with a focus on the first 11 days. TUD #3 microcline and Amelia albite were  
17 chosen for this experiment as they contained highly active sites, represented two different  
18 types of feldspar and were the only feldspars observed to exhibit this rapid decay in activity.  
19 BCS 376 microcline was also included in this activity decay experiment as it had provided  
20 consistent data over repeated runs and served as a standard in the Atkinson et al. (2013) paper  
21 which could therefore be tested TUD #3 microcline and Amelia albite were chosen for this  
22 experiment as they contained highly active sites, represented two different types of feldspar  
23 and were the only feldspars observed to exhibit this rapid decay in activity. BCS 376  
24 microcline was also included in this potassium. The results of these experiments are shown  
25 in Figure [4s-3 and 4](#). The median freezing temperature of the Amelia albite sample was most  
26 sensitive to time spent in water, decreasing by 8 °C in 11 days and by 16 °C in 16 months.  
27 The TUD#3 microcline sample decreased by about 2 °C in 16 months, but the freezing  
28 temperatures of the BCS 376 did not change significantly over 16 months (within the  
29 temperature uncertainty of  $\pm 0.4^\circ\text{C}$ ). Clearly, the stability of the active sites responsible for ice  
30 nucleation in these samples is highly variable.

31 Amelia albite is a particularly interesting case, where the highly active sites are also highly  
32 unstable. For Amelia albite we observed that the ice nucleation ability of the powder directly

1 as supplied (the sample had been ground many years prior to experiments) was much lower  
2 than the freshly ground sample. The  $n_s$  values for the ‘as-supplied’ Amelia albite are shown in  
3 Figure 34. This suggests that the sites on Amelia albite are unstable and in general are  
4 sensitive to the history of the sample. We note that from previous work that BCS 376 feldspar  
5 ground to varied extents nucleates ice similarly (Whale et al., 2015) and we have not  
6 observed a decay of active sites of the BCS 376 microcline sample when stored in a dry vial  
7 over the course of two years. It is also worth noting that freshly ground BCS 376 microcline  
8 did not nucleate ice as efficiently as Amelia albite or TUD#3 microcline. These results  
9 indicate that BCS 376 microcline contains very active sites, but that these sites are much  
10 more stable than those found in Amelia albite. This result is in agreement with the common  
11 knowledge well known result/observation that albite weathers roughly ten times faster  
12 than microcline in common soils as  $\text{Na}^+$  is more actively/readily substituted for hydrogen than  
13  $\text{K}^+$  (Busenberg and Clemency, 1976; Blum, 1994).  
14 (2015)(2015)-Zolles et al. (2015) have suggested that grinding can lead to active sites being  
15 revealed, -or the enhancement of existing active sites. It was shown in Whale et al. (2015)  
16 that differently ground samples of BCS 376 microcline nucleate ice similarly. In contrast  
17 Hiranuma et al. (2014) show that ground hematite nucleates ice more efficiently (normalised  
18 to surface area) than cubic hematite. The evidence suggests that the ice nucleating  
19 efficiencies of different materials respond differently to grinding processes.  
20 Indeed, ~~It~~ is evident from this study that highly active sites in Amelia albite are generated  
21 by grinding but lose activity when exposed to liquid water, and probably lose activity during  
22 exposure to (presumably wet) air, returning to an activity level comparable to that of the  
23 plagioclase feldspars. TUD#3 microcline also possesses a highly active site type sensitive to  
24 water exposure but falls back to a level of activity higher than the other K-feldspars we have  
25 tested. This second, less active site type is shown to be stable in water over the course of 16  
26 months. TUD#3 must possess populations of both more active, unstable sites and less active  
27 (although still relatively active compared to the sites on other K-feldspars) stable sites.  
28 Amelia albite possesses only unstable sites and much less active sites similar to those found  
29 on the plagioclase feldspars we have tested.

30 These results indicate something of the nature of the active sites on feldspars. Throughout  
31 this paper we refer to nucleation occurring on active sites, or specific sites, on the surface of  
32 feldspar. It is thought that nucleation by most ice active minerals is consistent with nucleation

1 on active sites with a broad spectrum of activities (Marcolli et al., 2007;Lüönd et al.,  
2 2010;Niedermeier et al., 2010;Augustin-Bauditz et al., 2014;Herbert et al., 2014;Vali,  
3 2014;Wex et al., 2014;Wheeler et al., 2015;Hiranuma et al., 2015;Niedermeier et al.,  
4 2015;Hartmann et al., 2016). However, the nature of these sites is not known. It is postulated  
5 that active sites are related to defects in the structure and therefore that each site has a  
6 characteristic nucleation ability, producing a spectrum of sites. Defects are inherently less  
7 stable than the bulk of the crystal and we might expect these sites to be affected by  
8 dissolution processes, or otherwise altered, in preference to the bulk of the crystal (Parsons et  
9 | al., 2015). The fact that we observe ice nucleation by populations of active sites with  
10 different stabilities in water implies that these sites have different physical or chemical  
11 characteristics. Furthermore, the fact that some populations of active sites are sensitive to  
12 exposure to water suggests that the history of particles can be critical in determining the ice  
13 nucleating ability of mineral dusts. This raises the question of whether differences in ice  
14 nucleation efficiency observed by different instruments (Emersic et al., 2015;Hiranuma et al.,  
15 2015), could be related to the different conditions particles experience prior to nucleation.

### 16 **5.3 Comparison to literature data**

17 We have compared the  $n_s(T)$  values for various feldspars from a range of literature sources  
18 | with data from this study in Figure 65. Inspection of this plot confirms that K-feldspars  
19 nucleate ice more efficiently than the plagioclase feldspars. Also, with the exception of the  
20 hyper-active Amelia albite sample, the K-feldspars are more active than the albites.

21 Results for BCS 376 microcline have been reported in several papers (Atkinson et al.,  
22 2013;O'Sullivan et al., 2014;Whale et al., 2015;Emersic et al., 2015). There is a discrepancy  
23 between the cloud chamber data from Emersic et al. (2015) and the picolitre droplet cold  
24 stage experiments at around  $-18^{\circ}\text{C}$ , whereas the data at about  $-25^{\circ}\text{C}$  are in agreement.  
25 Emersic et al. (2015) attribute this discrepancy to aggregation of feldspar particles in  
26 microlitre scale droplet freezing experiments reducing the surface area of feldspar exposed to  
27 water leading to a lower  $n_s(T)$  value. It is unlikely that this effect can account for the  
28 discrepancy because in the temperature range of the Emersic et al. (2015) data the  
29 comparison is being made to results from picolitre droplet freezing experiments which  
30 Emersic et al. (2015) argue should not be affected by aggregation because there are not  
31 enough particles present in each droplet to result in significant aggregation. Atkinson et al.  
32 (2013) estimated that on average even the largest droplets only contained a few 10s of

1 particles. We also note that our microscope images of droplets show many individual  
2 particles moving independently around in the picolitre droplets in those experiments,  
3 indicating that the feldspar grains do not aggregate substantially. Hence, the discrepancy  
4 between the data of Emersic et al. (2015) and Atkinson et al. (2013) at around  $-18^{\circ}\text{C}$  cannot  
5 be accounted for by aggregation. Furthermore, Atkinson et al. (2013) report that the surface  
6 area determined from the laser diffraction size distribution of BCS 376 microcline in  
7 suspension is 3.5 times smaller than that derived by the gas adsorption measurements (see  
8 supplementary Figure 5 in Atkinson et al. (2013) and the corresponding discussion). This  
9 difference in surface area can be accounted for by the fact that feldspar grains are not smooth  
10 spheres, as assumed in the analysis of the laser diffraction data. Feldspar grains are well-  
11 known to be rough and aspherical (Hodson et al., 1997). Atkinson et al. (2013) also note that  
12 the laser diffraction technique lacks sensitivity to the smallest particles in the distribution  
13 which will also lead to an underestimate in surface area. Nevertheless, the data presented by  
14 Atkinson et al. (2013) suggests that aggregation of feldspar particles leading to reduced  
15 surface area is at most a minor effect. As such the discrepancy between different instruments  
16 remains unexplained and more work is needed on this topic.

17 Ice nucleation by single size-selected particles of TUD#1 microcline has been investigated by  
18 Niedermeier et al. (2015) at temperatures below  $-23^{\circ}\text{C}$ . We found that TUD#1 microcline  
19 was in good agreement with [the](#) K-feldspar parameterisation from Atkinson et al. (2013)  
20 between about  $-6$  and  $-11^{\circ}\text{C}$ . Between  $-23$  and  $-25^{\circ}\text{C}$ , the  $n_s(T)$  values produced by  
21 Niedermeier et al. (2015) are similar (lower by a factor of roughly 4) to that of the Atkinson  
22 et al. (2013) parameterisation, despite the different sample types. Niedermeier et al. (2015)  
23 used the Leipzig Aerosol Cloud Interaction Simulator (LACIS), in which they size selected  
24 particles, activated them to cloud droplets and then quantified the probability of freezing at a  
25 particular temperature. It is interesting that the Niedermeier et al. (2015)  $n_s(T)$  values curve  
26 off at lower temperatures to a limiting value which they term  $n_s^*$ , indicating that nucleation  
27 by K-feldspars may hit a maximum value and emphasises why we need to be cautious in  
28 extrapolating  $n_s(T)$  parameterisations beyond the range of experimental data.

29 The data for a microcline, a plagioclase (andesine) and albite from Zolles et al. (2015) is  
30 consistent with our finding that plagioclase feldspars are less effective nucleators than K-  
31 feldspars. It is also consistent with Atkinson et al. (2013) who found that albite is less  
32 efficient at nucleating ice than microcline. However, the data for K-feldspar from Zolles et al.  
33 (2015) sits below the line from Atkinson et al. (2013) for BCS 376 microcline and are lower

1 than the points from Niedermeier et al. (2015) for TUD#1 microcline. Their measurements  
2 involved making up ~~concentrated~~-suspensions (~~19.62-4.8-5~~wt%) ~~suspensions~~ and then  
3 creating a water-in-oil emulsion where droplets were between 10-40  $\mu\text{m}$ . They quote their  
4 particle sizes as being between 1-10  $\mu\text{m}$  for the feldspars. Atkinson et al. (2013) worked with  
5 0.8 wt% suspensions, with droplets of 9 to 19  $\mu\text{m}$  where the mode particle size was  $\sim 700$  nm.  
6 Hence, Zolles et al. (2015) worked with ~~a significantly~~ more concentrated suspensions and  
7 larger particles than used by Atkinson et al. (2013). In principle,  $n_s$  should be independent of  
8 droplet volume and particle concentration, but differences between instruments and methods  
9 have been reported (Hiranuma et al., 2015). ~~(Hiranuma et al., 2015). Both the mass~~  
10 ~~concentration and droplet size are used to calculate the total surface area of particles per~~  
11 ~~droplet and furthermore  $n_s$ . It is not inconceivable that the higher mass concentrations,~~  
12 ~~differences in particle size and differences in droplet volumes could lead to different  $n_s$~~   
13 ~~results. Additionally, Zolles et al. (2015) estimated the surface area of their feldspar particles~~  
14 ~~using a combination of SEM images and the BET surface area of quartz (Zolles et al., 2015).~~  
15 ~~This also leads to an unspecified uncertainty in their  $n_s$  values. This may also lead to a~~  
16 ~~difference in  $n_s$  values.~~ However, it is not possible to determine whether the observed  
17 difference in  $n_s$  is due to differences in the sample or the techniques used, but may mean that  
18 certain K-feldspars nucleate ice less well than those defined by the Atkinson et al. (2013) line  
19 in this temperature regime. This would be a very interesting result as it may provide a point  
20 of difference that could provide insight into why K-feldspars nucleate ice efficiently. There  
21 has been relatively little work on what makes feldspar a good nucleator of ice. Zolles et al.  
22 (2015) suggest that only K-feldspars will nucleate ice well on the basis that  $\text{Ca}^{2+}$  and  $\text{Na}^+$  are  
23 chaotropic (structure breaking in water) while  $\text{K}^+$  is kosmotropic (structure making in water).  
24 We have only observed one feldspar that contains little  $\text{K}^+$  but nucleates ice relatively  
25 efficiently, Amelia albite. This feldspar loses its activity quickly in water and eventually  
26 becomes more comparable to the plagioclase feldspars. It may be that the strong nucleation  
27 observed is associated with the small amount of  $\text{K}^+$  it contains and that once this dissolves  
28 away the feldspar behaves like a plagioclase.

29 Augustin-Bauditz et al. (2014) tentatively concluded that microcline may nucleate ice more  
30 efficiently than orthoclase at  $n_s(T)$  values above about  $10^6 \text{ cm}^{-2}$  and at temperatures below -  
31  $23^\circ\text{C}$ , the conditions where they performed their measurements. They arrived at this  
32 conclusion by noting that NX-illite and Arizona test dust both contain orthoclase (8 and 20%,

1 respectively), but the  $n_s(T)$  values they report for these materials are more than one order less  
2 than microcline.

3 ~~Within the microliter regimen in this study we have observed some variability amongst the~~  
4 ~~K-feldspars (see Figure 2), but no difference between sanidine and the 4 out of 5 microclines~~  
5 ~~which fall around the line defined by Atkinson et al. (2013)~~  
6 ~~Within the microliter regime in~~  
7 ~~this study we have observed some variability amongst the K-feldspars (see Figure 2), but no~~  
8 ~~difference between sanidine and the 4 four out of 5 five microclines which fall around the line~~  
9 ~~defined by Atkinson et al. (2013).~~ As discussed above, the Al in sanidine is the least ordered,  
10 with microcline the most ordered and orthoclase at an intermediate order, hence we observe  
11 no clear dependency on the ordering of Al in K-feldspars. Further investigations of the ice  
12 nucleating ability of the various K-feldspar phases at low temperature would be valuable. We  
13 could not do this in the present study with the samples used here because we did not have  
14 sufficient quantities of the samples.

## 15 6 Conclusions

16 In this study we have analysed the ice nucleating ability of 15 well-characterised feldspar  
17 samples. These minerals include plagioclase feldspars (in the solid solution series between Ca  
18 and Na end-members), the K-feldspars (sanidine, ~~orthoclase~~ and microcline) and albite (the  
19 Na end-member). The results indicate that the alkali feldspars, including albite and K-  
20 feldspars, tend to nucleate ice more efficiently than plagioclase feldspars. The plagioclase  
21 feldspars nucleate ice at the lowest temperatures with no obvious dependence on the Ca-Na  
22 ratio. The albites have a wide variety of nucleating abilities, with one sample nucleating ice  
23 much more efficiently than the microcline sample Atkinson et al. (2013) studied. This hyper-  
24 active albite lost its activity over time while suspended in water. Five out of six of the K-  
25 feldspar samples we studied nucleated ice with a similar efficiency to the ‘generic’  
26 microcline studied by Atkinson et al. (2013). A single K-feldspar we studied had a very high  
27 activity, nucleating ice as warm as  $-2^{\circ}\text{C}$  in our microliter droplet assay. The striking activity  
28 of this hyperactive microcline decayed with time spent in water, but not to the same extent as  
29 the hyper-active albite sample. While the hyperactive sites are sensitive, to varying degrees,  
30 to time spent in water, the activity of the ‘generic’ microcline sample used by Atkinson et al.  
31 (Atkinson et al., 2013) did not change significantly.

1 In light of these findings, we suggest that there are at least three classes of site present in the  
2 feldspars studied here: *i*) relatively inactive sites associated with plagioclase feldspars; *ii*)  
3 more active sites associated with K-feldspars that are stable in water over the course of  
4 many months; *iii*) hyper-active sites associated with one albite and one K-feldspar that we  
5 studied that loses activity when exposed to water. It is possible that the sites of type *i* are  
6 present on the typical K-feldspars, but we do not observe them because ice nucleates on more  
7 active sites. Whether these different sites are all related to similar features on the surfaces or  
8 if they are each related to different types of features is not known. Nevertheless, it appears  
9 that feldspars are characterised by a range of site types with varying stability and activity.

10 The specific details of these active sites continue to elude us, although it appears that they are  
11 only present in alkali feldspars and in particular, the K-feldspars. Unlike the plagioclase  
12 feldspars which form a solid solution, the Na and K feldspars in alkali feldspars are often  
13 exsolved, possessing intergrowths of the Na and K feldspars referred to as microtexture  
14 (Parsons et al., 2015). It is possible that the boundaries between the two phases in the  
15 intergrowth provide sites for nucleation that are not present in plagioclase feldspars. If the  
16 high energy defects along exsolution boundaries are responsible for higher ice nucleation  
17 activity of K-feldspars then this may offer an insight into acid passivation of ice nucleating  
18 ability observed in laboratory studies (~~Wex et al., 201x; others~~) (Wex et al., 2014; Augustin-  
19 Bauditz et al., 2014). Berner and Holdren (1979) suggest that the acid mediated weathering  
20 of feldspar occurs in multiple stages and suggest dissolution of feldspars is concentrated at  
21 high surface energy sites such as dislocations and crystal defects, sites which may be related  
22 to ice nucleation. More work is needed to explore the significance of exsolution, microtexture  
23 and the impact of weathering on feldspars with respect to ice nucleation activity. If these  
24 defects along exsolution boundaries are responsible for higher ice nucleation activity then it  
25 stands to reason that these zones would be susceptible to alteration with time spent in water.  
26 This leads to the importance of weathering of aerosols in the atmosphere and the effects of  
27 acid aging. Berner and Holdren (1979) postulated that the weathering of feldspar occurs in  
28 two stages. First is the dissolution of ultrafine (< 1µm diameter) particles which attach  
29 themselves to larger grains. A second process, and possibly more relevant to the hyper active  
30 feldspars observed here, is dissolution concentrated at high surface energy areas such as  
31 dislocations and crystal defects. This is thought to be the most dominant weathering  
32 procedure of the feldspars in nature. More work is needed to explore the influence of

1 microtexture and the impact of weathering on feldspars inwith respect to ice nucleation  
2 activity.

3 In a previous study Atkinson et al. (2013) used an  $n_s(T)$  parameterisation of a single K-  
4 feldspar (BCS 376 microcline) to approximate the ice nucleating properties of desert dust in a  
5 global aerosol model. Given that ~~five~~four out of ~~six~~five of the K-feldspars we studied here  
6 have very similar ice nucleating abilities, this approximation seems reasonable. However, we  
7 have identified two hyper-active feldspars and do not know how representative these samples  
8 are of natural feldspars in dust emission regions. We also note that the active sites on these  
9 feldspars are less stable than those of BCS 376 microcline. Nevertheless, there is the  
10 possibility that the parameterisation used by Atkinson et al. (2013) underestimates the  
11 contribution of feldspars at warmer temperatures above about  $-15^{\circ}\text{C}$ .

12 In the longer term it may be possible to identify what it is that leads to the variation in ice  
13 nucleation activity between the different feldspar classes. In particular, the nature of the  
14 active sites in the hyper-active feldspars and the reason plagioclase is so much poorer at  
15 nucleating ice are subjects of interest. The instability of the sites in the hyperactive feldspars  
16 may be related to dissolution of feldspar in water and investigation of this process may allow  
17 progress towards understanding of nucleation by feldspars. The results presented here are  
18 empirical in nature and do not provide a thorough underpinning understanding of the nature  
19 of the active sites. Nevertheless, the fact that the feldspar group of minerals have vastly  
20 different ice nucleating properties despite possessing very similar crystal structures may  
21 provide us with a means of gaining a fundamental insight to heterogeneous ice nucleation.

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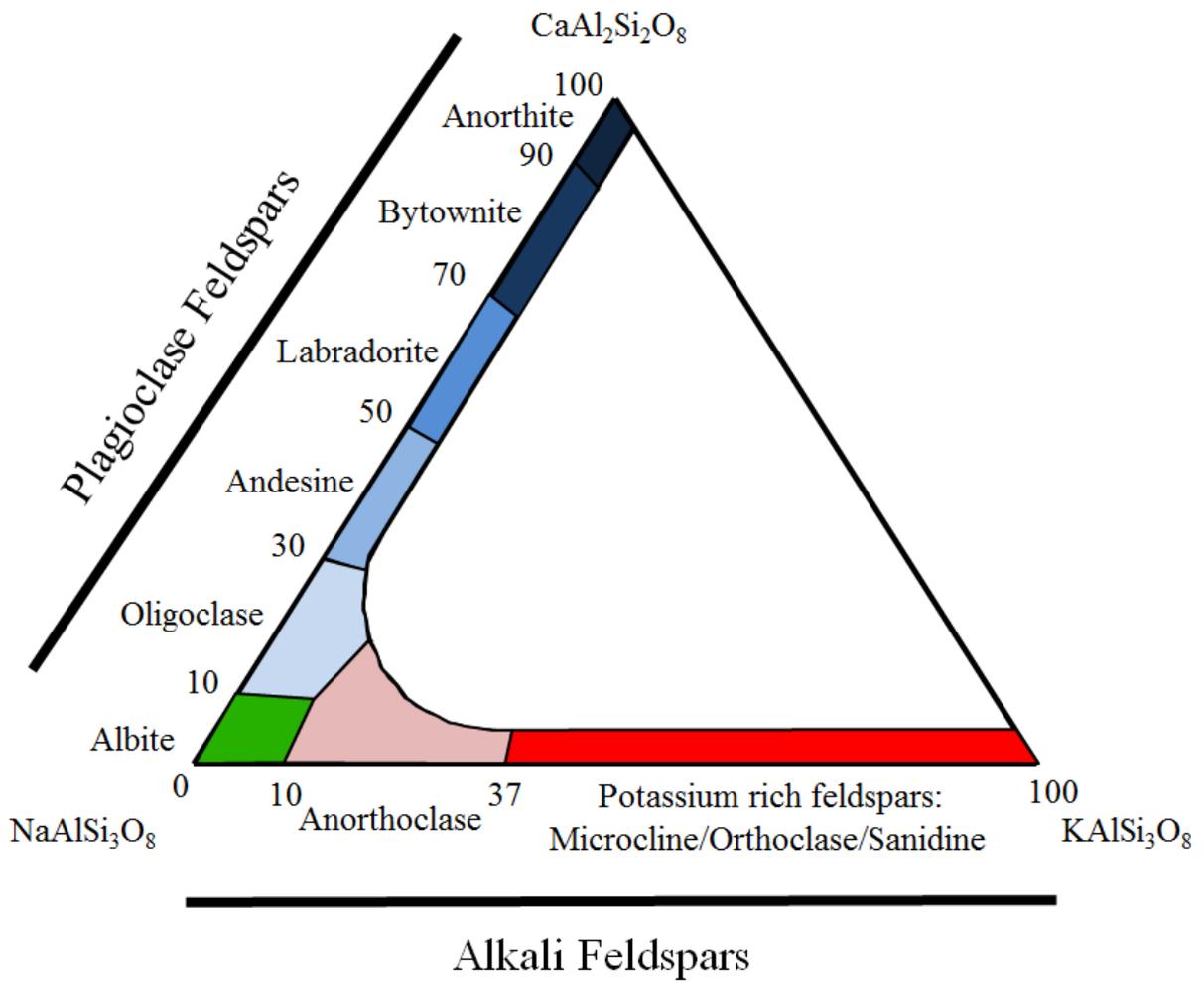
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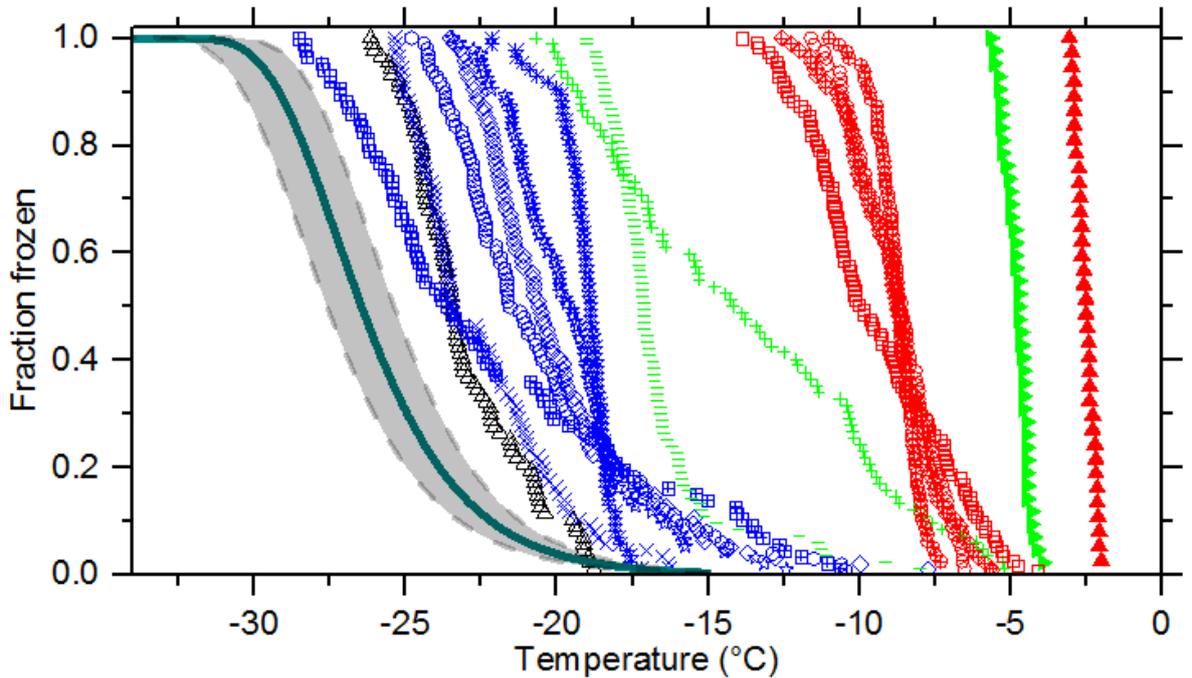


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3 Figure 2: The ternary composition diagram for the feldspars group based on similar figures in  
4 the literature (Wittke and Sykes, 1990; Deer et al., 1992).

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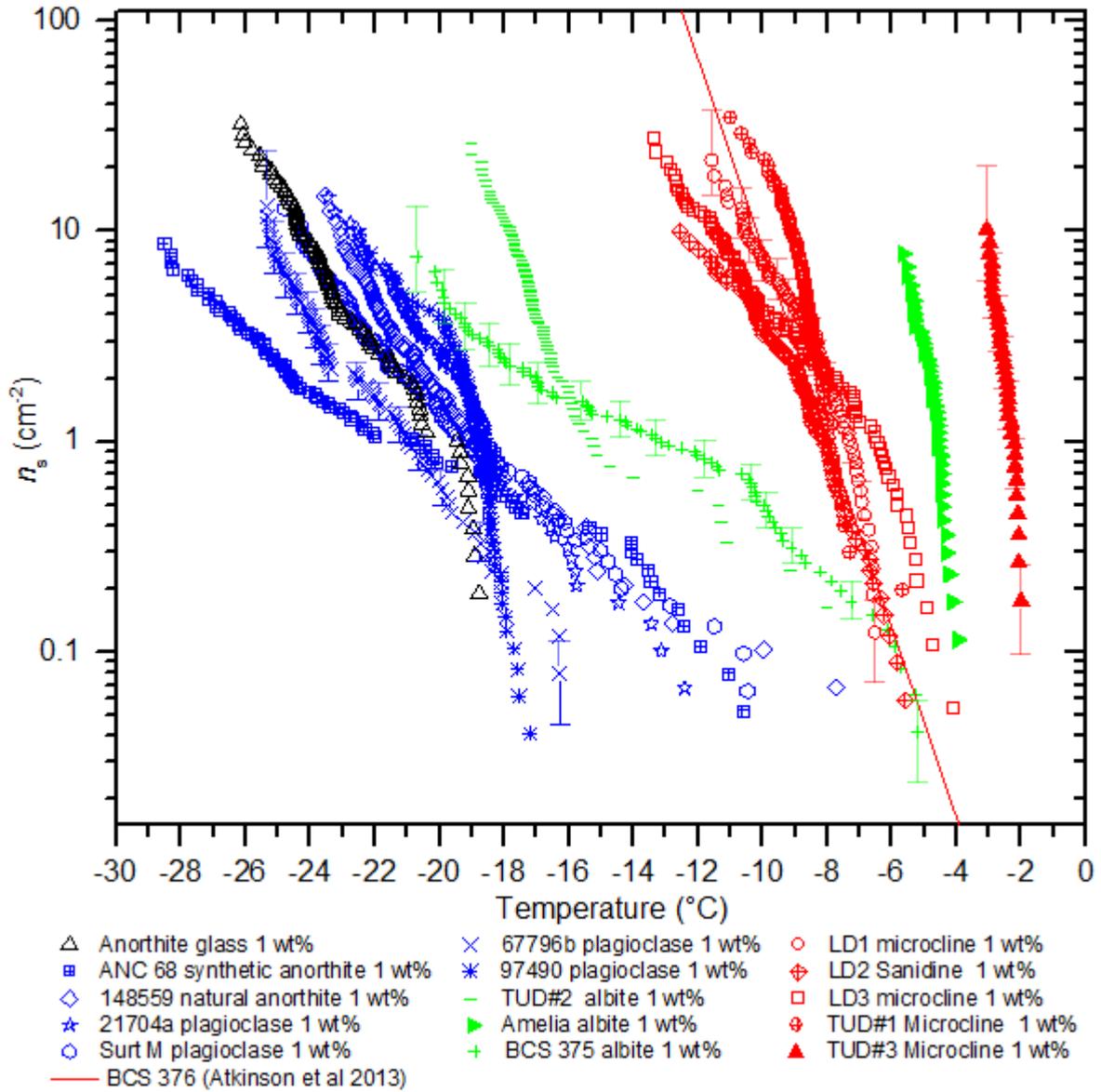


- △ Anorthite glass
- ANC 68 synthetic anorthite
- ◇ 148559 natural anorthite
- ☆ 21704a plagioclase
- Surt M plagioclase
- × 67796b plagioclase
- \* 97490 plagioclase
- TUD#2 albite
- ▶ Amelia albite
- + BCS 375 albite
- ◇ LD1 microcline
- ◊ LD2 sanidine
- LD3 microcline
- ⊕ TUD#1 microcline
- ▲ TUD#3 microcline
- Instrument freezing background

2

**Figure 3:** Droplet fraction frozen as a function of temperature for 1 wt% suspensions of ground powders of various feldspar samples. The K-feldspars are coloured red, the plagioclase feldspars are coloured blue, the albites are coloured green and the feldspar glass is coloured black. A fit to the background freezing of pure MilliQ water in the  $\mu$ l-NIPI instrument used by Umo et al. (2015) is also included. The shaded area around this fit shows 95% confidence intervals for the fit. It can be seen that all the feldspar samples tested nucleate ice more efficiently than the background freezing of the instrument. (2015)

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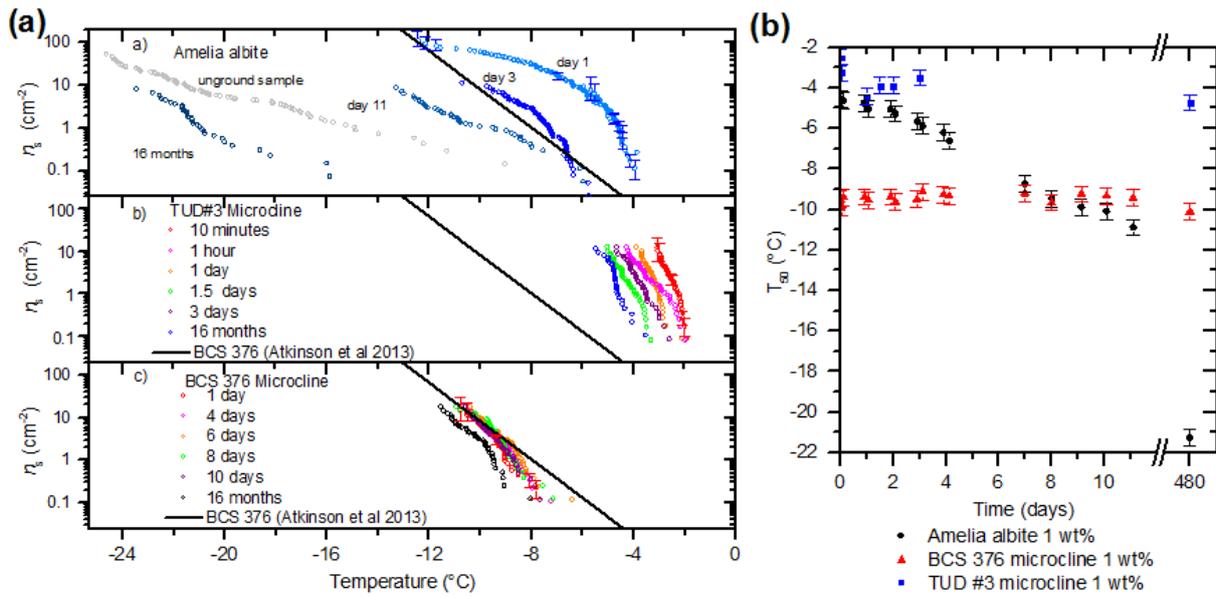


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2 Figure 4: Ice nucleation efficiency expressed as  $n_s(T)$  for the various feldspars tested in this  
 3 study. The K-feldspars are coloured red, the plagioclase feldspars are coloured blue, the  
 4 albites are coloured green and the feldspar glass is coloured black. Except for Amelia albite  
 5 and TUD#1 microcline all samples were tested twice and the data from the two runs  
 6 combined. Sample information can be found in tables 1 and 2. Temperature uncertainty is  
 7  $\pm 0.4^{\circ}\text{C}$ . Y-Error bars calculated using the Poisson Monte Carlo procedure described in Sect.  
 8 4. Data points with large uncertainties greater than an order of magnitude have been removed,  
 9 these are invariably the first one or two freezing events of a given experiment. For clarity  
 10 error bars have only been included on a selection of datasets (TUD#3 microcline, LD1  
 11 microcline, BCS 375 albite and 67796b plagioclase). The error bars shown are typical.

12 ~~Background subtraction of the type conducted by O'Sullivan et al. (2015) made insignificant~~  
 13 ~~difference to the reported  $n_s(T)$  values.~~

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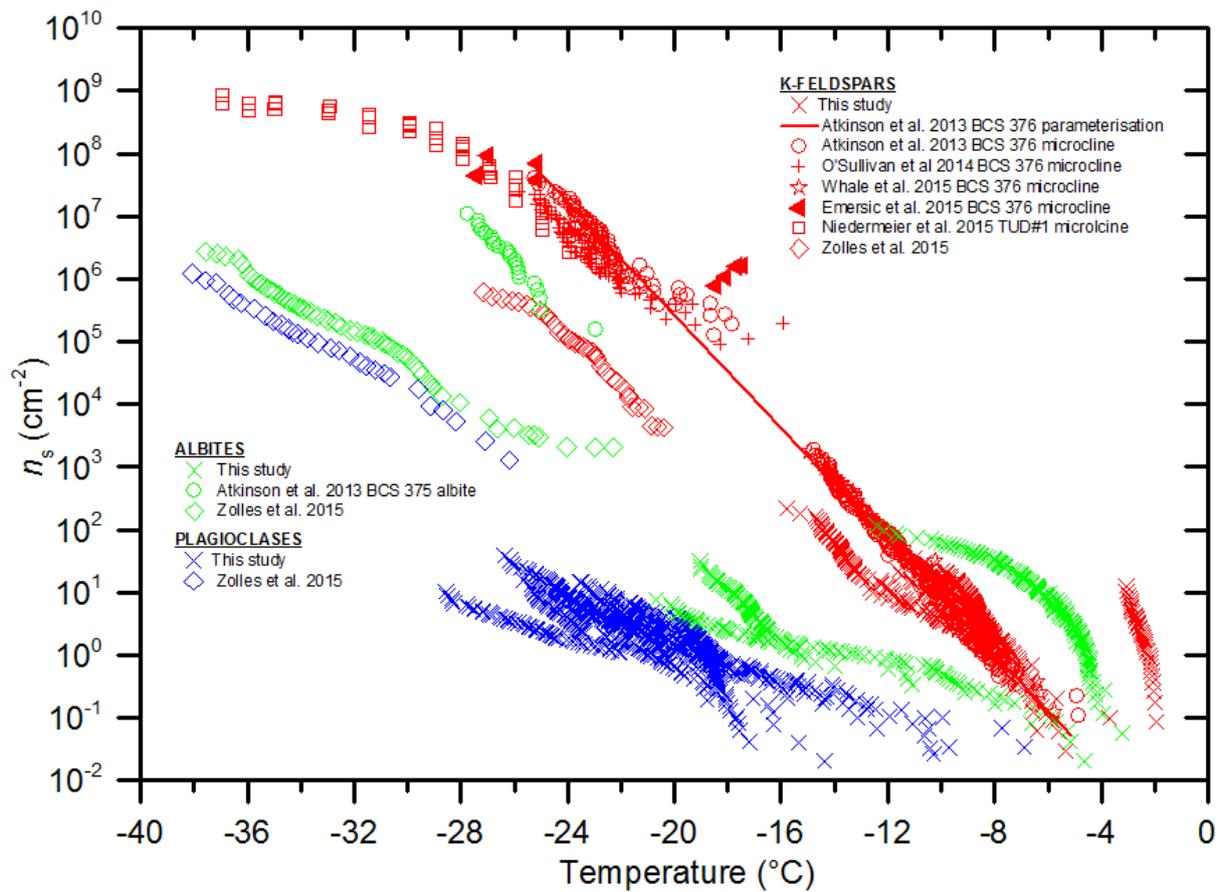


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2 **Figure 3: Figure 5 (a)** The dependence of  $n_s$  on time spent in water for three feldspar samples.  
 3 The time periods indicate how long samples were left in contact with water. Fresh samples  
 4 were tested minutes after preparation of suspensions. Note that ice nucleation temperatures of  
 5 BCS 376 are almost the same after 16 months in water while those of Amelia albite decreases  
 6 by around 16°C. TUD #3 microcline loses activity quickly in the first couple of days of  
 7 exposure to water but total decrease in nucleation temperatures after 16 months is only  
 8 around 2°C. **(b) Median freezing temperature against time left in suspension for BCS 376**  
 9 **microcline, TUD#3 microcline and Amelia albite.**

10

11



1  
 2  
 3 **Figure 6:** Comparison of literature data from Atkinson et al. (2013), Emersic et al.
 4 (2015), Niedermeier et al. (2015) and Zolles et al. (2015) with data from this study. Feldspars
 5 are coloured according to their composition, as in Figure 23. 0.1 wt% data for Amelia albite
 6 and LD1 microcline, which is not shown in figure 23, has been included. Where samples are
 7 known to lose activity with time the most active runs have been shown. Note that data from
 8 Niedermeier et al. (2015) includes some data from Augustin-Bauditz et al. (2014).

1

2 Table 1. Plagioclase feldspars used in this study.

3

<u>Sample</u>	<u>Composition*</u>	<u>Source location</u>	<u>Source of composition/phase data</u>	<u>Space group</u>	<u>Point group</u>	<u>Crystal system</u>
<u>Anorthite glass</u>	<u>An<sub>100</sub></u>	<u>Synthetic sample</u>	<u>(Carpenter, 1991)</u>	<u>=</u>	<u>=</u>	<u>=</u>
<u>ANC 68</u>	<u>An<sub>100</sub></u>	<u>Synthetic sample</u>	<u>(Carpenter, 1991) describes similar feldspars</u>	<u>P<math>\bar{1}</math></u>	<u><math>\bar{1}</math></u>	<u>triclinic</u>
<u>148559</u>	<u>An<sub>99.5</sub>Ab<sub>0.5</sub></u>	<u>University of Cambridge mineral collection</u>	<u>-----</u>	<u>P<math>\bar{1}</math></u>	<u><math>\bar{1}</math></u>	<u>triclinic</u>
<u>21704a</u>	<u>An<sub>86</sub>Ab<sub>14</sub></u>	<u>Viakfontein, Bushveld complex, Transvaal (Harker collection no. 21704)</u>	<u>(Carpenter et al., 1985)</u>	<u>P<math>\bar{1}</math>-<math>\bar{1}</math></u>	<u><math>\bar{1}</math></u>	<u>triclinic</u>
<u>Surt M</u>	<u>An<sub>64</sub>Ab<sub>36</sub></u>	<u>Surtsey (no. 7517, Iceland Natural History Museum) Phenocrysts from volcanic ejecta</u>	<u>(Carpenter, 1986)</u>	<u>C<math>\bar{1}</math></u>	<u><math>\bar{1}</math></u>	<u>triclinic</u>
<u>67796b</u>	<u>An<sub>60</sub>Or<sub>1</sub>Ab<sub>39</sub></u>	<u>Gulela Hills, Tanzania (Harker collection no. 67796)</u>	<u>(Carpenter et al., 1985)</u>	<u>Incommensurate order</u>	<u>=</u>	<u>triclinic</u>
<u>97490</u>	<u>An<sub>27</sub>Or<sub>1</sub>Ab<sub>71</sub></u>	<u>Head of Little Rock Creek, Mitchell co., N. Carolina (P. Gay, U.S.N.M. no. 97490)</u>	<u>(Carpenter et al., 1985)</u>	<u>Incommensurate order</u>	<u>=</u>	<u>triclinic</u>

4

5 \*This refers to the chemical makeup of the feldspars. An stands for anorthite, the calcium end-  
6 member, Ab stands for albite, the sodium end-member and Or stands for orthoclase, the potassium  
7 end-member.

1

2 Table 2. Alkali feldspars used in this study.

<u>Sample</u>	<u>Dominant feldspar phase</u>	<u>Source location</u>	<u>Source of composition/phase data</u>	<u>Space group</u>	<u>Point group</u>	<u>Crystal system</u>
<u>LD1 microcline</u>	<u>microcline</u>	<u>University of Leeds rock collection</u>	<u>XRD</u>	<u><math>C\bar{1}</math></u>	<u><math>\bar{1}</math></u>	<u>triclinic</u>
<u>LD2 sanidine</u>	<u>sanidine</u>	<u>University of Leeds rock collection</u>	<u>XRD</u>	<u><math>C2/m</math></u>	<u><math>2/m</math></u>	<u>monoclinic</u>
<u>LD3 microcline</u>	<u>microcline</u>	<u>University of Leeds rock collection</u>	<u>XRD</u>	<u><math>C\bar{1}</math></u>	<u><math>\bar{1}</math></u>	<u>triclinic</u>
<u>BCS 376 microcline</u>	<u>microcline</u>	<u>Bureau of Analysed Samples Ltd</u>	<u>Reference sample/XRD (Atkinson et al., 2013)</u>	<u><math>C\bar{1}</math></u>	<u><math>\bar{1}</math></u>	<u>triclinic</u>
<u>Amelia Albite (un-ground)</u>	<u>albite</u>	<u>Amelia Courthouse, Amelia Co., Virginia (Harker mineral collection)</u>	<u>(Carpenter et al., 1985)</u>	<u><math>C\bar{1}</math></u>	<u><math>\bar{1}</math></u>	<u>triclinic</u>
<u>Amelia Albite ground</u>	<u>albite</u>	<u>Amelia Courthouse, Amelia Co., Virginia (Harker mineral collection)</u>	<u>(Carpenter et al., 1985)</u>	<u><math>C\bar{1}</math></u>	<u><math>\bar{1}</math></u>	<u>triclinic</u>
<u>TUD#1 microcline</u>	<u>microcline</u>	<u>Minas Gerais, Brazil</u>	<u>XRD</u>	<u><math>C\bar{1}</math></u>	<u><math>\bar{1}</math></u>	<u>triclinic</u>
<u>TUD#2 albite</u>	<u>albite*</u>	<u>Norway</u>	<u>XRD</u>	<u><math>C\bar{1}</math></u>	<u><math>\bar{1}</math></u>	<u>triclinic</u>
<u>TUD#3 microcline</u>	<u>microcline</u>	<u>Mt. Maloso, Malawi</u>	<u>XRD</u>	<u><math>C\bar{1}</math></u>	<u><math>\bar{1}</math></u>	<u>triclinic</u>
<u>BCS 375 albite</u>	<u>albite</u>	<u>Bureau of Analysed Samples Ltd</u>	<u>Reference sample/XRD (Atkinson et al., 2013)</u>	<u><math>C\bar{1}</math></u>	<u><math>\bar{1}</math></u>	<u>triclinic</u>

3

4 \* We note that the XRD pattern was also consistent with oligoclase, which is close to albite in  
5 composition. The identification of albite is consistent with that of Alexei Kiselev (Personal  
6 communication).

