Atmospheric mineral dust and its role in ice formation

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Abstract

Water can supercool below -35°C without the presence of Ice Nucleating Particles (INP's) which makes INPs important for the development of mixed phase clouds. Mineral dust is known to be a substantial source of active INPs in the atmosphere. At present our ability to accurately predict the global distribution of atmospheric mineral dust INP is limited by both a fundamental understanding of which specific components nucleate ice, how efficiently they do so and how they are processed or altered while in the atmosphere, as well as the lack of instrumentation to reliably and routinely quantify INP concentrations in the atmosphere. In my PhD project I have already begun to address questions around which feldspars are most important at nucleating ice and in the longer term I propose to build a new instrument to make direct field measurements to increase datasets for global distributions of INP. A major topic of this essay is my investigation of the role of feldspar composition and structure on its ice nucleating efficiency. We find that alkali feldspars are the most active group of feldspars, with plagioclases being the least active. There is also a wide range of activities within each group and the stability of active sites on each feldspar can vary. I also briefly discuss the concept for the new field instrument and where I hope to measure INP concentrations.

1.0 Introduction

Ice formation in clouds is poorly understood yet it is important for determining the planet's climate and hydrological cycle (Hoose and Möhler, 2012). Murray et al (2012) have shown the significance of INP presence for the formation of clouds, as water is known to supercool below -35°C in the absence of particles which have ice nucleating capabilities (Riechers et al., 2013). Desert dust has been identified as a crucial source of INPs around much of the globe (Atkinson et al., 2013,DeMott et al., 2003,Hoose et al., 2010, Hoose, 2008, Niemand et al., 2012).

At present our ability to predict global distributions of atmospherically relevant INPs is limited. We need an increase in the fundamental understanding of ice nucleation from lab based studies as well as new instrumentation to take INP measurements in the field. Field studies are essential to further understand naturally occurring INP such as mineral dust.

These dusts are composed of minerals entrained from the top soil layer with the three major components being the clays, quartz and feldspars. Many studies have been conducted on the efficiency of the most common dust mineral group, the clays, but only recently has the importance of feldspar been identified (Augustin-Bauditz et al., 2014;O'Sullivan et al., 2014;Atkinson et al., 2013, Niedermeier et al., 2015, Zolles, 2015).

In order to understand the role of mineral dust in ice nucleation processes within clouds we need to 1) develop our fundamental understanding of the feldspar mineral group and 2) increase the amount of direct atmospheric measurements of INP.

2.0 Aims of the project

2.1 Development of an instrument for detecting low concentrations of INPs

The first objective of this study is to adapt our lab based technique into an automated instrument capable of taking field measurements by making use of available cryopreservation technology. The ice nucleation field is still within its infancy and one of the major limitations in research is the lack of relevant instrumentation. At present there is only one commercial INP counter on the market: Spectrometer for Ice Nuclei (SPIN) (Droplet Measurement Technologies, Boulder, Co). However, this instrument is not ideal for field campaigns due to its size, weight and complex nature. The absence of a suitable machine for the field has led to a dearth of INP measurements globally (Fig. 1). These measurements are crucial for global climate models and at present potentially important INP rich regions, such as Asia and Africa, are under populated. The instrument proposed to be designed here should tackle these issues and allow for a commercial machine to be built which may be used by the scientific

community. We aim for the instrument to be able to sample and detect low concentrations of INP in the field which will help increase our understanding of global INP concentrations .

One problem for field measurements is that INP concentrations are often low and their detection is difficult in drop freezing assay experiments or other techniques. To counter this we plan to build an instrument capable of using large volumes of suspension to improve the detection limits. Current multiwell systems used for cryopreservation technology may be suitable for such assays and may be adapted for this purpose. We also need to reduce the occurrence of background freezing events in the pure water, which limits our detection of low concentrations of INP at present. I intend to investigate variables such as the purification of water and substrates for freezing. To achieve this we have set a goal to try reach homogenous freezing within microliter droplet experiments. In reducing the baseline we hope to be able to conduct experiments in n_s regimes which are currently not accessible, where n_s is the measure used to quantify the number of nucleating sites per unit surface area that become active at certain temperature.

### 2.2 Investigate the role of dust INP in the atmosphere

Once developed the instrument is to be deployed on a number of field campaigns which will be used as 1) a testing exercise for the machine, 2) a means to quantify the concentration of dust (and other) INP in the atmosphere. We aim to target dust rich regions with possible expeditions exploring areas such as the Tropical Atlantic in the Saharan outflow and contrast this will dust poor regions such as the southern ocean. Aircraft based measurements are also to be conducted using the FAAM aircraft which will provide INP concentrations closer to the altitudes where ice formation in clouds occurs. Contrasting sites may also be explored to determine the overall impact of dust INP in the atmosphere. Agricultural locations in the UK will allow an insight to a different source of mineral dust along with biological influences. The ACE campaign to the southern ocean has also been outlined as a point of interest as it is a dust poor region.

2.3. Which components of desert dust are most important for ice nucleation?

Recent work by Atkinson et al., (2013) has shown that feldspars are the most active of the mineral phases present in mineral dusts yet little study has previously been implemented based around the group. Therefore an emphasis of study will be placed on the fundamental understanding of feldspar nucleation. Not only will this improve our understanding of the relevance of feldspar in cloud formation processes but we hope that a greater understanding of ice nucleation sites can be developed.

In the next sections we investigate the role of feldspar composition on its ice nucleating efficiency by examining a range of well categorised samples under conditions similar to those in mixed phase clouds. There is limited understanding of these sites and it is likely any developments will enhance the knowledge of ice nucleation in the atmosphere (Vali, 2014;Freedman, 2015). Work by Augustin-Bauditz et al (2014) has proposed that microcline feldspar nucleates ice more efficiently than orthoclase feldspar and Zolles et al (2015) saw

that potassium feldspar acted as a more effective INP than two plagioclases. The work here gives a wider survey of feldspars to help better understand the ice nucleating efficiency of the group as well as the characteristics of the active sites for nucleation.
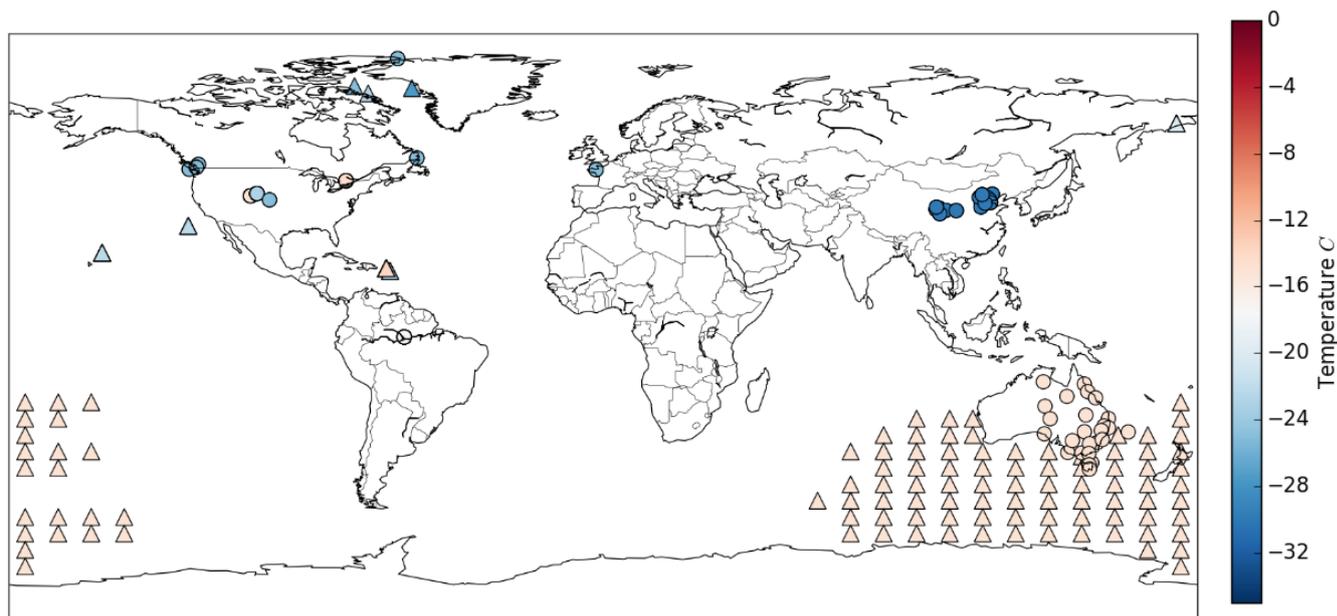

Figure 1. Map showing the global distribution of INP field measurements. Triangles correspond to locations considered to be marine INP influenced locations and circles to terrestrial INP dominated locations. The freezing temperatures of water in the presence of the INP's is indicated by the symbol colour

3.0 A survey of ice nucleation across the feldspar family of minerals

In this section I expand upon my recent work in which I have surveyed the ice nucleating ability of a range of feldspars with varying composition and crystal structure.

Feldspar is a group of aluminium silicate minerals, within the framework silicate group, with the general formula of $XAl(Si,Al)Si_2O_8$. X is predominantly K^+, Na^+ or Ca^{2+} and Al content varies depending on the cations present (Deer et al., 1992). The framework silicate group is defined by the mineral structure being composed of three dimensional frameworks of silica tetrahedral. Si and Al within the tetrahedra can substitute for one another and the charge can be balanced by the addition or replacement of a cation within the interstitial sites in the cavities of the framework lattice. The ability to replace cations leads to a large variability in the composition of the feldspars, with most feldspars being compositions between end members of sodium-, calcium- or potassium-feldspars (Wenk and Bulakh, 2004). See figure 2 for a ternary plot of feldspar compositions. It should be noted that there is no solid solution series between the calcium end member (anorthite) and the potassium endmember (orthoclase) as the difference in ionic charge and radius of the cations does not allow for active substitution. The sodium endmember is referred to as albite. There are three

polymorphs (minerals with the same composition but different crystal structure) of the end member for the potassium feldspar. These polymorphs are microcline, orthoclase and sanidine and they become more disordered in terms of the placement of Al in the tetrahedrons, respectively from microcline to sanidine. Which polymorph forms from a melt (lava or magma) depends on the temperature of formation for the mineral. Sanidine forms at the highest temperature and microcline at the lowest.
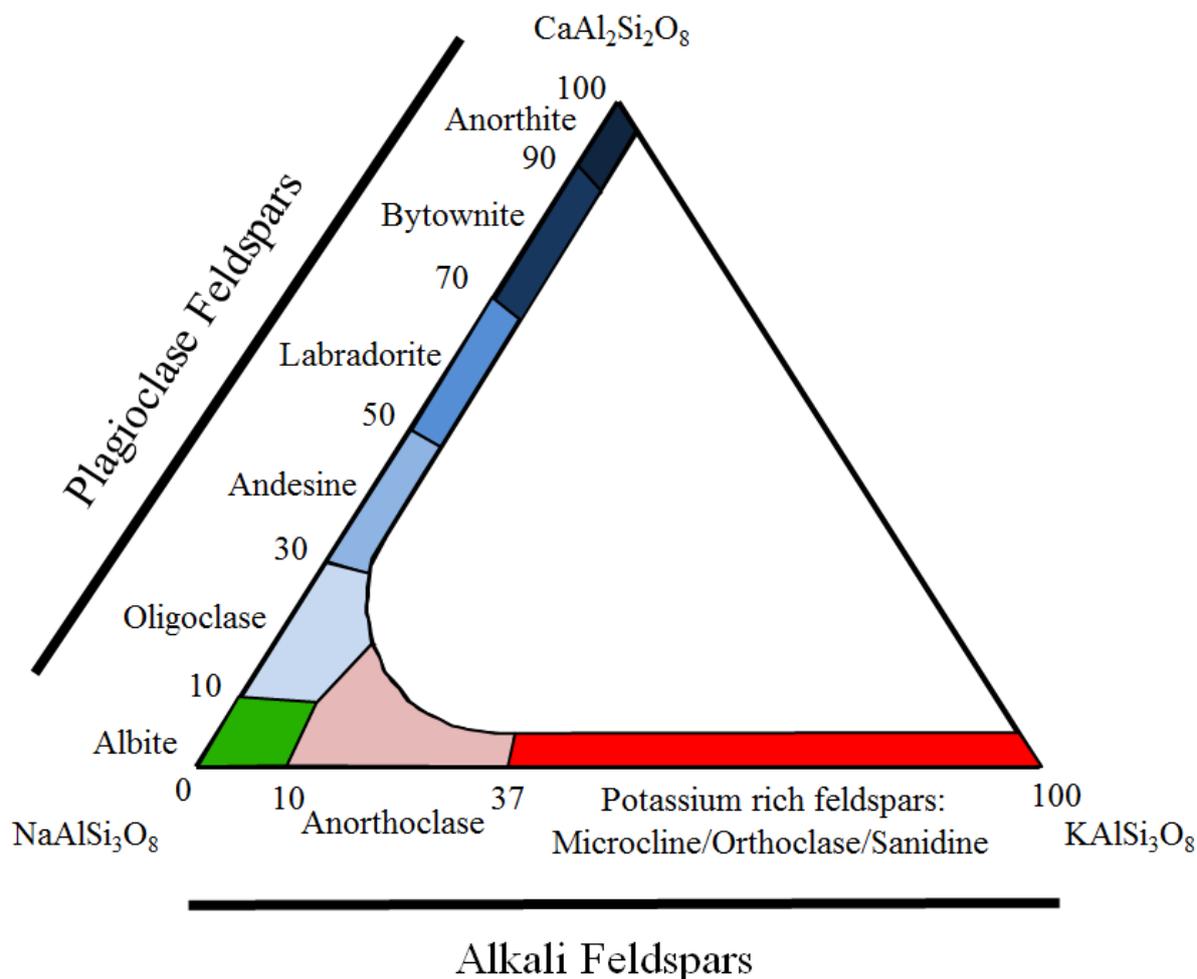
Figure 2. Ternary diagram representing the compositional range of feldspars based on similar figures in literature (Wittke, 2009; Deer et al. 1992).

3.1 The feldspar samples

For this study we have collected 15 samples of feldspar with varying compositions. For ease of understanding we collectively name feldspars with compositions between the Ca and Na endmembers the plagioclases (excluding albite from this group). The range of compositions between the Na and K endmembers are termed the alkali feldspars (including albite), although we often refer to albite as a separate entity. Details for the plagioclase samples can be found in table 1 and those for the alkali feldspars in table 2. Amelia albite can be classed as both an alkali and a plagioclase feldspar so appears in both tables. Samples have been sourced from previous studies (Carpenter, 1991;Carpenter, 1986;Carpenter et al., 1985;Zhu et

al., 1994) and from multiple repositories, details can be found in tables 1 and 2. Samples are referred to by their identifier followed by their mineral classification e.g. BCS 376 microcline. For samples that have not been previously defined, rietveld refinement of powder XRD patterns was carried out using TOtal Pattern Analysis Solutions (TOPAS) to determine the phase of the feldspar present. Samples were ground (unless otherwise stated) and Brunauer-Emmett-Teller (BET) nitrogen gas adsorption was used to measure dust surface areas using a Micromeritics TriStar 3000.

Table 1. Plagioclase feldspars used in this study.

Sample	BET Surface area (m²/g)	Composition *	Source of composition/phase data
Anorthite glass	1.18 ± 0.0148 m²/g	An_{100}	(Carpenter, 1991)
ANC 68	4.25 ± 0.0192 m²/g	An_{100}	(Carpenter, 1991)
148559	3.07 ± 0.0151 m²/g	$An_{99.5}Ab_{0.5}$	(Zhu et al., 1994)
21704a	3.07	$An_{86}Ab_{14}$	(Carpenter et al., 1985
Surt M	3.00 ± 0.0475 m²/g	$An_{64}Ab_{36}$	(Carpenter, 1986)
67796b	2.80	$An_{60}Or_1Ab_{39}$	(Carpenter et al., 1985)
97490	5.63	$An_{27}Or_1Ab_{71}$	(Carpenter et al., 1985)

*This refers to the chemical makeup of the feldspars. An stands for anorthite, the calcium endmember, Ab stands for albite, the sodium endmember and Or stands for orthoclase, the potassium endmember.

Table 2. Alkali feldspars used in this study.

Sample	BET Surface area (m²/g)	Dominant feldspar phase	Source of composition/phase data
LD1 microcline	1.99 ± 0.0517 m²/g	microcline	XRD
LD2 Sanidine	3.77	sanidine	XRD
BCS 376 microcline	2.03 ± 0.0091 m²/g	microcline	Reference sample/XRD (Atkinson et al., 2013)
Amelia Albite (un-ground)	0.73 ± 0.0196 m²/g	albite	(Carpenter et al., 1985)
Amelia Albite ground	3.94	albite	(Carpenter et al., 1985)
TUD#1 microcline	1.23	microcline	XRD
TUD#3 microcline	2.84	microcline	XRD
BCS 375 albite	5.8	albite	Reference sample/XRD (Atkinson et al., 2013)
TUD#2 albite	1.39	albite*	XRD

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

3.2 Experimental procedure

To establish the efficiency of ice nucleation by a variety of feldspar dusts we first made the dusts into suspensions gravimetrically using a known amount of sample and Milli-Q water (18.2 MΩ cm). The suspensions were then stirred with magnetic stirrer bars before making

use of the microliter Nucleation by Immersed Particle Instrument (µl-NIPI). The technique involves pipetting microliter droplets, of dust suspensions with known particle concentrations, on to a hydrophobic glass slide which is placed on top of a cold stage plate (Asymptote EF600). This plate is then cooled at a rate of 5°C min^{-1} to 0°C and then at 1°C min^{-1} until all droplets are frozen. The whole process is monitored with a digital camera and freezing events are recorded along with the temperature. The full technique is described in detail by Whale et al. (2015a). At present the pipetting and analysis stage of this experiment are labour intensive and it is these elements which we wish to automate with future work as well as introducing an automatic dust sampling technique, to collect INP's to make up the aqueous suspensions.

Some suspensions were left over a period of time and re-stirred before carrying out the droplet freezing experiment. This allowed us to build up a time series for certain samples left in suspension and investigate the role of chemistry on INP's. The samples investigated for the role of time left in suspension were Amelia albite, BCS 376 microcline and TUD #3 microcline. Droplet freezing experiments were carried out over 12 days and then a further run was carried out 16 months after initial suspension creation.

$n_s(T)$ for each sample can be calculated where n_s is the amount of nucleation sites active at a given temperature and can be calculated using (Connolly et al., 2009):

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

$n(T)$ is the number of droplets frozen at temperature (T), N is the total number of droplets and A is the specific surface area of the nucleator per droplet. This method does not take into account the role of time dependence as it is site specific (Herbert et al. 2014, Vali, 2014). In the case of feldspar the nature of the active sites is thought to be the most important factor effecting ice nucleation.

3.3 Results and Discussion

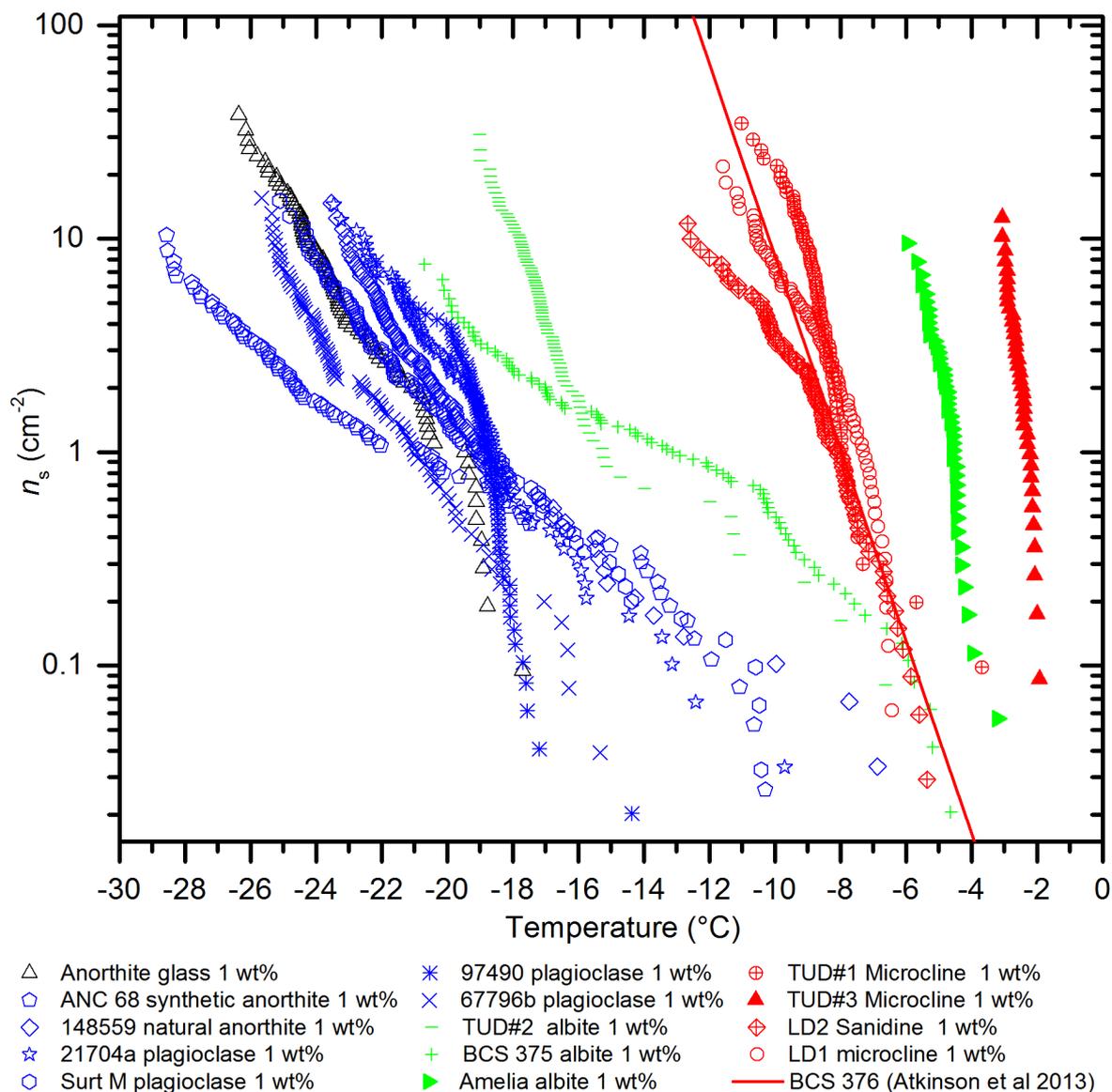### 3.3.1 Plagioclase and alkali feldspar activity

Figure 3 displays the n_s values calculated for various samples along with the Atkinson et al (2013) parameterisation for BCS 376 microcline. The plot is colour co-ordinated to match the colours in figure 2 with plagioclase feldspars highlighted in blue, alkali feldspars in red and albites coloured in green.

It was found that four out of five K-feldspar samples lie near the Atkinson parameterisation. These four samples included three microclines and a sanidine, which has a different crystal structure. One K-feldspar, TUD #3 microcline, proved to be substantially more active. This suggests that crystal structure and composition are not the only factors effecting ice nucleating activity.

When examining the plagioclase solid solution series, characterised by Carpenter (1986) and Carpenter et al (1985), there is little variation in the ice nucleation activities. No clear correlation between Ca-Na content was seen, i.e. as Na content increased ice nucleation activity was not seen to increase. However, TUD #2 albite, BCS 375 albite and Amelia albite were all more active than the rest of the plagioclases showing that this albite sample has something unique which makes it an effective ice nucleator compared to other plagioclases.

Albite proved to be a more effective ice nucleator than the plagioclases and it could span a range of ice nucleating temperatures between those seen for K-feldspars to those for plagioclases. This range in activity seen by albite may be due to the nature of its active sites and whether they are more comparable to those found in plagioclases or K-feldspar. It is interesting that Amelia albite gave a higher activity than four out of the five K-feldspars. This high activity was ruled out as a biological effect by heating of the suspension at 100°C for 15 minutes, the same was done for TUD #3 microcline. Both samples showed no major change in activity which would have been expected if biological ice nucleating proteins were present and denatured (O′Sullivan et al., 2015), meaning the highly active nature of the dusts were owed to the nature of the sites on the feldspar grains.

Overall a general trend can be seen in the n_s plots (Fig.3). There are two clear regimes for ice nucleation efficiency in feldspar. Alkali feldspars are seen to nucleate ice at higher temperatures than plagioclases and this is seen by the two clusters of data (red and blue). Albite however seems to be able to span between these two regimes. The results here are in accordance with other research (Zolles et al., 2015, Augustin-Bauditz et al., 2014) with microcline feldspars nucleating more efficiently than plagioclase. One possible suggested explanation is the differences in cation ionic radius and a localised chemical configuration (Zolles et al., 2015). We have however found that albite can be more effective than K-feldspars. The large degree of variability within each group of feldspars and the hyper active Amelia albite suggests that composition and structure is not the only factor affecting the ice nucleating capabilities of the minerals. One suggestion is that the microstructure may be of importance. Microstructure can vary dependent on the degree of exsolution in the mineral and the formation processes it has undergone. Exsolution lamella (seen as bands of Na and K rich zones) is a common feature of alkali feldspars so perhaps planes of weakness and defects associated with these structures are important for ice nucleation.

Figure 3. Plot showing the ice nucleation efficiency of 15 feldspars plotted as an expression of n_s(T). Alkali feldspars are displayed in red, plagioclases in blue and albite in green. A synthetic feldspar glass has been coloured in black as it is not naturally occurring. Corresponding sample information can be found in tables 1 and 2. Temperature uncertainty is ±0.4°C with the uncertainty in n_s calculated by propagation of uncertainties from weighing, pipetting and background subtraction (O'Sullivan et al., 2015).

3.3.2 Stability of active sites

Repeat experiments (~30 minutes between runs) of each sample were taken to improve the reliability of data. It was however noticed that for the most active feldspars, TUD #3 microcline and Amelia albite, that a decrease in activity occurred that was not seen in other samples. Only the first experiment (~10 minutes time left in suspension) is shown in figure 3 for these two samples. To investigate this decrease in activity TUD #3 microcline, Amelia albite and BCS 376 microcline were created into suspensions and were tested over a period of 16 months with major emphasis being placed on the first 11 days. The results of this experiment can be seen in figure 4. The median freezing temperature of the Amelia albite sample was most sensitive to time spent in water, decreasing by 8°C in 11 days and by 16°C in 16 months. After 16 months in suspension Amelia albite moved back to sit within the plagioclase regime. The TUD #3 microcline sample decreased by about 2°C in 16 months, but the freezing temperatures of the BCS 376 did not change significantly in 11 days and only changed by about 1°C in 16 months. Clearly, the stability of the active sites responsible for ice nucleation in these samples is highly variable.
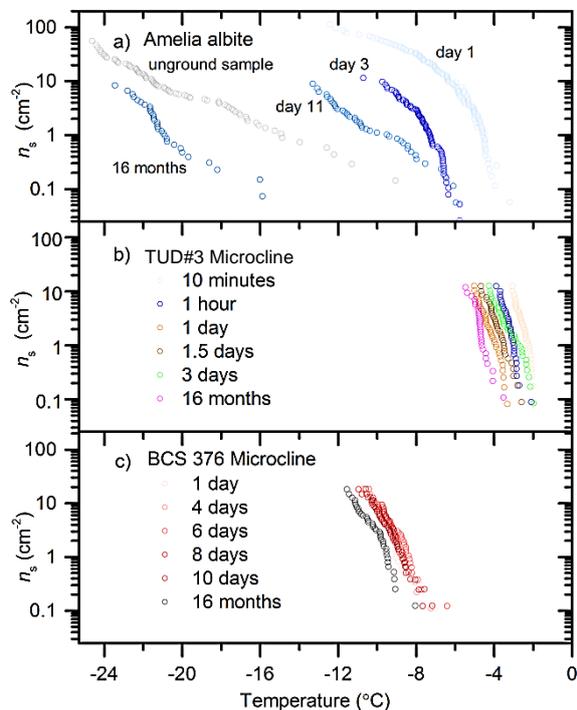
Figure 4. Ice nucleating efficiency of three samples over time displayed as a function of $n_s(T)$

6.0 Conclusions and Summary

Overall there is much variability in ice nucleating capabilities within the feldspar group, which cannot be fully resolved by composition and crystal structure alone. It is likely that some other factor, such as microstructure, effects the nature of the active sites. Alkali feldspars are universally the most efficient ice nucleators of the feldspar mineral group. Ca rich feldspars prove to be poorer nucleators but still more active than common minerals previously examined, such as clays and quartz (Atkinson et al., 2013). We can suggest that there are at least three major types of sites recorded here. A hyper active site noticed within the Amelia albite and TUD #3 microcline, a relatively active site within the K-feldspars and a less active plagioclase site. The most active sites appear to be the most susceptible to time left in suspension and therefore are most likely to be impacted by processes such as weathering.

The importance of feldspar as an INP in the atmosphere is now apparent but the global distribution of INP in general, including mineral dust INP, is poorly constrained (Fig. 1). Future work aims to improve our knowledge of these active sites in feldspar and to build on the laboratory based technique to make field measurements of INP concentrations. Key areas to target should be dust rich regions (e.g. the tropical Atlantic) and contrasting dust poor regions (e.g. the Southern Ocean).

7.0 References

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