## **Response to referee comments**

We would like to thank both referees for their insightful comments. Below we have addressed the referee comments (in red) with our responses in black and changes made to the manuscript in blue.

## Response to referee #1

## General comment

This study investigated the ice-nucleating abilities of 10 different  $\alpha$ -quartz samples and compare the obtained results with feldspar literature data. The authors found a large variability in the ice nucleation behaviour of the 10 samples with some being very efficient (e.g., Bombay chalcedony and Atkinson quartz). It was also found that the ice-nucleating abilities of some of the studied quartz samples were affected by ageing and milling. With the current and literature data the authors produced a new set of parametrizations for quartz and different feldspar. The authors found that the new K-feldspar parameterisation provides a good representation of the icenucleating activity of dust from field and laboratory studies. Finally, their analysis show that quartz is of second order importance for desert dust's ice-nucleating ability.

This is a well written and sound manuscript with interesting results for the ice nucleation community. The experiments were well designed and were properly executed. The paper nicely fits with the ACP scope and it can be accepted for its publication after the following points are properly addressed.

## **Major Comment**

Although I really like the manuscript, I am having a hard time to find the atmospheric relevance of the obtained results. Given that milling is a process that does not takes place in nature the way it was conducted in the laboratory, I am not fully convinced that the obtained parametrisations can really be used in climate models as the representation of true atmospheric mineral dust particles.

We note that this comment on the relevance of milling is similar to referee 2, who asks us to motivate the use of milled samples.

In nature, the path from rock through to a fine dust powder which can be aerosolised is complex and the referee is correct to question the relevance of simply taking a rock sample and milling it. The assumption in this study (and others from groups around the world) is the ice-nucleating ability of the mineral samples is inherent to the material and that milling is representative of the mechanical processes which produce fine airborne dust in nature. We argue this on the basis that the processes which produce atmospheric dusts are mechanical and energetic. Rocks are broken down into soil particles through mechanical and chemical weathering processes and also dust is aerosolised through the saltation process which involves impactions of particles which are aggressive enough to round grains and cause fragmentation of

aggregates. With mechanical processes occurring in nature we think that milling of macroscopic rock samples to fine grain sizes is relevant. This approach has the advantage that we can obtain relatively pure minerals in the form of rocks or large crystals; whereas soils are mixtures of many minerals.

There are of course processes which will occur in nature that are likely to change the activity of natural dusts since they are exposed to air and water for many years prior to aerosolisation. In general, ageing processes are thought to reduce the icenucleating activity of freshly ground powders, hence we make the assumption that milled samples are likely to exhibit a maximum activity and this may decrease with ageing. We have found that water and air exposure does not substantially decrease the activity of K-feldspar (Harrison et al., 2016; Whale et al., 2017) (although acid may be another story (Kumar et al. (2018)). However, quartz shows a strong sensitivity to time spent in water and so we stress in the paper that the quartz parameterisation is likely an upper limit representation of the ice-nucleating ability of quartz. On the other hand, the saltation aerosolisation process is mechanically vigorous and may expose fresh surfaces, hence taking this upper limit is reasonable. When taking this upper limit for quartz it is still seen to be only of second order importance in terms of its contribution to the atmospheric INP population relative to K-feldspars. Hence we think our conclusion regarding the atmospheric importance of quartz relative to K-feldspar is justified.

We then went on to compare the predicted INP concentrations based on our K-feldspar and quartz parameterisations to atmospheric measurements in this paper and find that we get a reasonable prediction of the INP concentration based the on K-feldspar parameterisation. This is consistent with the milled K-feldspar samples from the literature being of relevance to the atmosphere.

The other point we would like to make is that it is not clear how else these studies could be done. One approach might be to take desert dust samples and examine their ice-nucleating ability (as we and other groups have done). While this approach has value (and should be used) it has a number of caveats associated with it too:

- 1. Without knowledge of which components of desert dust are causing it to nucleate ice, predictive capacity of the ice-nucleating activity of desert soils from different regions with different compositions is limited.
- 2. Without knowledge of which components nucleate ice we cannot predict how desert dust's activity will evolve as the largest particles are removed on transport (mineralogy is size dependent with K-feldspars and quartz being preferentially in the larger size range).
- 3. Sampling and re-suspension of desert dusts may influence its ice-nucleating ability. Mechanical aerosolisation processes, such as rotating brushes, used to resuspend dust may well change the surface properties of desert dust particles in a manner different to the way dust is altered in the saltation process.

Hence, we think that in order to gain a predictive and accurate quantitative description of ice nucleation by atmospheric mineral dusts it is necessary to do experiments with both desert dusts and also the individual minerals in a relatively pure state as well as conduct experiments examining the sensitivity of these dusts to ageing processes.

To address this issue in the paper we have added a new paragraph in the introduction and a new schematic diagram, as well as a brief statement in the methods section stating: 'These samples were reground to ensure all samples initially had freshly exposed surfaces for ice nucleation experiments. The milling process was used to break down mineral crystals/powders to a sufficient size so that they may be suspended in water. We argue that these freshly milled samples are relevant in that they represent the fresh surfaces which are likely produced by mechanical processes in nature as rocks are broken down and particles aerosolised through the saltation process (see Figure 1 and discussion in the introduction). We suggest that these freshly ground samples of quartz represent an upper limit to the ice-nucleating ability of quartz in atmospheric mineral dust since ageing processes may reduce this activity.'

## Similarly, I also found that the very long ageing times (i.e., > several months) are not atmospherically relevant.

We think that these times are relevant for dust in the atmosphere, because the dust on the ground is exposed to water and air for very long periods of time. Hence, exposure to air and water for many months was a pragmatic semi-quantitative way of assessing the sensitivity of these active sites to ageing processes. We think the new figure and the new paragraph in the introduction help to clarify this.

### **Minor comments**

1. The title states: "The ice-nucleating ability of quartz immersed in water and its atmospheric importance compared to K-feldspar". Can the laboratory experiments be assumed to be relevant to the atmosphere? Does milling takes place in the atmosphere and soil the way it was done in the laboratory?

We have addressed this in the above response to the major comment.

2. The abstract is very descriptive without quantitative data. I suggest to add the most important quantitative results here.

The abstract has been amended with some pertinent numbers to illustrate the key points.

3. The authors indicate that the base line was obtained from Umo et al. (2015). Does it mean that you did not run these type of experiments prior to the heterogeneous ice

## nucleation ones? How confident are the authors that this did not change since 2015? I suggest to add your own data and to remove the Umo et al. (2015).

The Umo et al. (2015) baseline fit was developed from a large compilation of baseline measurements to incorporate the variability within the  $\mu$ L-NIPI technique. This fit provides a convenient yet robust expression of the variability within this experimental procedure. Baseline experiments were conducted prior to the start of each experimental day with the fraction frozen curves typically being represented by the lower range of freezing values presented by Umo et al. (2015). With this being said we have used the Umo et al. (2015) parameterisation to show the variability of the experiment with greater statistics and to show a conservative estimate of the background (in general our baseline has improved since 2015). As can be seen from figure 2 it is observable that all experiments provided freezing events that are well above the baseline even with the more conservative representation by Umo et al. (2015). The text in the methodology has been amended to read:

"Prior to the start of each experimental day purified water droplets were used to determine the background freezing signal. Umo et al. (2015) compiled a large collection of background freezing results to create a fit which represents the variability of the background in the  $\mu$ L-NIPI instrument. The background signal measured in this study was in line with the lower bound set by Umo et al. (2015)."

## 4. Section 4.2: Is milling atmospherically relevant at all? Can this happen in nature to this extent? Please motivate this deeply.

Please see response to major comments above.

## 5. Conclusions: Although the authors provide potential explanations for their observations, several sentences/conclusions seems to be speculative.

We have improved the conclusions section by adding additional references and making it clearer what new work needs to be done in the future.

### We have amended the paragraph on ageing to read:

"Related to this, we also note that solutes can alter the ice-nucleating ability of mineral samples (Whale et al., 2018;Kumar et al., 2018;Kumar et al., 2019a, b). Sensitivity to these ageing processes and solutes could be very important in determining the dominant INP types globally (Boose et al. 2019). Hence, we suggest further studies aim to build a better understanding of the relationship between the experimental observations and field collected samples to determine the role of ageing in the atmosphere."

## We have added:

"Sparse data sets available for the albite and plagioclase mineral groups lead to lower confidence when creating parameterisations for these mineral groups. It is suggested that future studies expand on the current datasets of the ice-nucleating behaviour of minerals to improve these parameterisations."

### And clarified that the quartz parameterisation should be thought of as an upper limit:

"Also note that the parameterisation for quartz is for freshly milled quartz and the ageing results presented here and elsewhere (Zolles et al., 2015;Kumar et al., 2019a) suggest that the active sites on quartz are removed on exposure to air and water. Therefore the parameterisation for milled quartz should be regarded as an upper limit. Even with this upper limit, quartz is of secondary importance relative to K-feldspars which appear to be less sensitive to ageing processes."

## 6. References: Add the Doi to all references. The journal names must be abbreviated. I find exaggerated to have 20 citations from the same research group.

We have amended the reference list as suggested.

We have removed James et al. But, we think that the other references are all necessary and justified. Our research group has contributed significantly to this area of research, hence the number of citations.

### **Technical comments**

Line 25-26: for ice nucleation. Now corrected.

Line 27: "less active". By how much? "...generally less active than K-feldspars by roughly 7 °C"

Line 29: "more active". By how much? "...the quartz samples are generally more active by roughly 5 °C"

Line 51: Add a reference after "incomplete". Amended to "However, our understanding of which type of aerosol particles serve as effective INPs is incomplete (Vergara-Temprado et al., 2017;Kanji et al., 2017)."

Line 54: "Observations of aerosol at the centre of ice crystals have shown that mineral dust". Is it really at the centre? "Observations of aerosol within ice crystals"

Lines 54-56: Either state that this sentence focuses on MPC only or add other studies such as Cziczo et al. (2013). "...act as INPs within mixed phase clouds"

Lines 61-62: I suggest to add the review of Hoose and Mohler (2012) given that this list is too short to reflect the huge amount of work done with clays. Now added.

Line 117: Add a reference after "dust aerosol". Added "(Deer et al., 1992)".

Lines 185-186: "and a study of nitric acid hydrate nucleation on meteoric material (James et al., 2018)." It does not fit here. The sentence has been amended to read "This technique has been used in several previous ice nucleation studies e.g. (Atkinson et al., 2013;O'Sullivan et al., 2014;Harrison et al., 2016)."

Line 188: "was vigorously shaken". Manually? Thank you, this has been amended to "...the suspension was vigorously shaken manually"

Lines 119-121: "An almost identical method was described by Harrison et al. (2016), which was similar to the work of Wright and Petters (2013)." Unnecessary selfcitation. Changed to: "This methodology was based on the work of Wright and Petters (2013)."

Line 243: Delete "approximately 1 h later" It is redundant. This has been deleted.

Lines 245-246: "There is also consistency for some quartz samples between run to run from this study". This was already mentioned seven lines above: "In the cases of Bombay chalcedony, Brazil amethyst and Smokey quartz, the first and second runs where identical within the uncertainties". The sentence has been removed

Line 295: "sealed glass vial for". Under dark conditions? "...sealed glass vial under dark conditions for..."

Line 309: "a dark cupboard in sealed glass vials". Why under dark conditions? What atmospheric process does it represent? The aim of this time series investigation was not to simulate the atmosphere – see comments above. We have simply described what we did.

Line 316: "by about 3 °C". Do the authors consider this a significant change? Text has been amended to read "its activity decreased by about 3 °C after four months in water which is well outside the uncertainties of the experiment."

Line 321: "by 2 °C". Do the authors consider this a significant change? This is addressed in the previous sentence in the text "In contrast, the activity of Atkinson quartz decreased dramatically"

Line 321: "after 16 months in water". Is this atmospherically relevant?

We have addressed this above.

Line 326: "for 20 months". Is this atmospherically relevant?

We have addressed this above.

Line 329: "for ~5 years in a glass vial". Is this atmospherically relevant?

We have addressed this above. It is certainly a relevant time period for dust sitting on the surface. In this case, 5 years was simply the time the sample had been in the lab which we opportunistically made use of.

Line 544-545: "quartz, but the parameterisation we present here probably represents an upper limit to its activity." I am wondering if the ice-nucleating abilities of the quartz samples are unintentionally overestimated by milling. This issue is very much related to the 1<sup>st</sup> major comment on milling, which we have now addressed much more thoroughly. The short answer, is yes, the quartz parameterisation based on freshly milled material may be an overestimate. This is why we refer to it as an upper limit. We have made this clearer throughout the paper, including in the conclusions.

## Response to referee #2

## **General Comment**

The manuscript I was asked to evaluate is dedicated to the experimental study of immersion freezing behaviour of several  $\alpha$ -quartz samples in pure water droplets. The authors highlight the variability of the ice nucleation activity over different freshly milled quartz samples and investigate the short term as well as long term aging effects due to exposure to air and water. They further propose active site density parameterizations for several minerals and discuss the dominance of K-feldspar in the ice nucleation particle population in desert dusts. While I support the publication, I do have few remarks that the authors should address while preparing the final version of the manuscript.

## **Major Comments**

Line 387 It should rather be "....parameterisation is representative of freshly milled quartz dust". Airborne dust is eroded and gets exposed to air and even water. The authors should add a discussion about how representative is this for airborne dust. Proposing such parameterization - especially for 'freshly milled' quartz – is a bit of a stretch for now, given that we barely understand the surface due to limited work done and the high variability in its ice nucleation efficiency reported so far (including this work).

This issue has been also been raised by referee 1 and we have now included a new paragraph in the introduction and methods to justify our use of milled samples and how these samples relate to the complex processes dust experiences in nature. Please see the response to the major comment by reviewer 1.

We have changed Line 387 as recommended.

It should be clearly stated in the abstract that the study is on "freshly milled quartz" particles (also throughout the text) and should include a comment on the atmospheric relevance of such fresh surfaces when drawing comparisons with atmospheric dusts.

## Done

There are instances in Discussion section about cautiously using plagioclase and albite parameterization, yet this feature does not translate in the figures. In general, the devised parameterizations are a result of over-simplification and multiple assumptions which, though wellfitting, might not give a comprehensive view.

The parameterisations are created based on the current available data. Although crude, these parameterisations provide evidence that K-feldspar is the dominant mineral within mineral dusts which is supported by the good agreement between

field observations and model predictions using lab based K-feldspar predictions. We have now added to the conclusions section to outline the importance of advancing our current datasets for mineral ice-nucleating abilities:

"Sparse data sets available for the albite and plagioclase mineral groups lead to lower confidence when creating parameterisations for these mineral groups. It is suggested that future studies expand on the current datasets of the ice-nucleating behaviour of minerals to improve these parameterisations"

Given that members of K-feldspars show huge variations in their ice nucleation ability, with only microcline as a standout for most part (Harrison et al., 2016; Kaufmann et al., 2016; Welti et al., 2019), would the authors say that the K-feldspar parameterization proposed here is actually more representative for just microcline?

We think it is very important that we provide a parameterisation for K-feldspar in general. We base this on the finding that microtexture is important, not the subtle differences in crystal structure which give rise to the three K-feldspars (microcline, sanidine and orthoclase). Microcline has an ordered AI position, whereas sanidine is disordered with orthoclase having some intermediate disorder. The distinction between these polymorphs is therefore somewhat arbitrary with X-ray diffraction and Raman techniques since there is a continuum in ordering of AI.

The work by Harrison et al. (2016), Whale et al. (2017) and Welti et al. (2019) show that orthoclase nucleates ice in the same regime as microcline (in most instances). How the nucleating ability of sanidine compares to microcline and orthoclase is more complicated. There are examples of sanidine that are less active than microcline/orthoclase as an ice-nucleator (whale et al. 2017, Welti et al. 2019) and those that nucleate ice in the same regime (Harrison et al. 2016). This is interesting and maybe a function of the formation processes. Sanidine is a high temperature K-feldspar and so can cool much faster than other K-feldspar polymorphs and so could exhibit phase separation to a lesser extent.

With this said, sanidine is rarely observable in atmospheric mineral dusts (Boose et al. 2016) and so the parametrisation is a fair representation of the K-feldspars for the atmosphere and is supported by the agreement with field observations of atmospheric dusts (Atkinson et al., 2013;Price et al., 2018;O'Sullivan et al., 2018).

The 4<sup>th</sup> paragraph in section 5.2 has been modified to clarify these points:

"The data included in these plots includes all three polymorphs of K-feldspar (microcline, orthoclase and sanidine), although most of the data is for microcline. The strongly hyperactive TUD #3, examined by Harrison et al. (2016) and Peckhaus et al. (2016), was excluded as it exhibited extremely high activity and appears to be an exceptional case which is generally unrepresentative of the K-feldspar group of minerals. With this in mind we have developed a parameterisation which represents K-feldspars that possess exsolution microtexture." In addition, following the information given in line 419-420, surprisingly recent data on natural dust mineralogy (Boose et al., 2016; Kaufmann et al., 2016) was not considered which may have painted a different picture.

The values quoted in Boose et al. (2016) for transported dust mineralogy are consistent with those in Atkinson et al. (2013). Kaufmann et al. (2016) looked at surface scooped samples only, whereas we have taken values for airborne dust subject to transport. A reference to Boose et al. (2016) has been added in section 5.2.

Figure 2 & Methodology: It is unclear in the methodology whether the suspensions were tested just once or multiple times and why no uncertainties are shown in Fraction Frozen curves. This has been made clearer in section 3.2 "A second run for each sample suspension, with a fresh array of droplets, was performed immediately after the first experiment with approximately 1 hour between the two runs." The temperature uncertainty for the fraction frozen plots is quoted in the text as 0.4 K, but not shown in the figures for clarity.

Figure 3: There are no error bars for freezing data of quartz samples undergone long-term aging in either water or exposed to air. Are these single suspension measurements? This should be made clear in the methodology section.

The errors are only shown for one experiment in order to present the data more clearly. The errors do not significantly change from run to run as there is the same surface area of nucleator per droplet (as we use the same suspension) and the number of droplets is similar in each run. This has been made clearer in figure caption 3. "Error bars for the first run of each time series are shown, but omitted for the other datasets for clarity."

## **Minor Comments**

Line 129 Stone sample milling: average particle size range information of the samples could be helpful. I assume from the methodology that the stones were "hand-milled". Given that quartz is such a hard mineral, one might still end up with powders consisting of large particles which contribute more to the mass fraction when preparing suspensions. I would highly encourage the authors to consider adding a discussion on size of mineral particles typically found at/near source regions versus the size range of particles probed in the experiments and its atmospheric relevance.

We make the assumption that ice nucleation scales with surface area, and report the ice active sites per unit surface area. We also make this assumption when considering the atmosphere. Whether the density of sites varies with particle size is an interesting question, but beyond the scope of this project. The BET surface areas are all within a factor of ~5, hence the mean particle size of the different samples is similar. Based on the BET surface area and a density of 2.65 g cm<sup>-3</sup> we expect a spherical equivalent average size of ~ 0.5  $\mu$ m to 2.5  $\mu$ m. Table 1 has been amended

to show these sizes and the new figure (figure 1) includes information on grain sizes in nature.

Lines 139-141 Glass vials as suspension storage containers: Glass is a source of Si and other ionic contamination. If the suspension reaches supersaturation in Siconcentration with respect to quartz surface, it is likely that the quartz surface will start to grow over longer time scales and affect the ice nucleation ability of quartz (Kumar et al., 2019a). This process is governed by several factors eg. Si concentration, particle surface exposed, growth rate, etc. (Baughman, 1991), which does not seem to lead to similar deteriorating IN efficiency in quartz samples tested here in this study. It would be good if the authors could comment on this or add a discussion.

We discuss Kumar's results in the second paragraph of section 4.3.

Line 248-286 Could it be that the indifferent IN ability in cases of Bombay Chalcedony and Smoky quartz during aging in water compared to Atkinson quartz be due to lower particle surface area exposed (low BET hence slower aging effect) for former 2 samples? Would have been interesting to see the long-term aging of the other chalcedony (Grape) which has similar BET value as Atkinson quartz.

This is an interesting concept and one we cannot definitively answer given our data. Grape chalcedony did show one of the largest sensitivities in the initial experiments (an hour left in water until the repeat run of the suspension). However, we do see that Bombay chalcedony does show less sensitivity to time left in water opposed to Smoky quartz (which has a similar surface area). We also see in the initial experiments that some quartz samples that had similar or lower surface areas than Bombay Chalcedony showed sensitivity (to time left in water) on the hourly time scale. This would indicate that the amount of surface area exposed cannot entirely explain the sensitivity of the samples and likely the nature of the sites also dictates the effect of ageing.

Line 293 what exactly is meant by "dangling OH groups"? Highly hydroxylated quartz surfaces are dominated by vicinal and germinal silanols (Muster et al. (2001) and references therein) which then tend to create network of H-bonds with each other (Musso et al., 2011; 2012), therefore, not really free and "dangling" per se.

We have changed this to refer to surface OH groups.

## **Technical comments**

Since the manuscript exclusively talks about ice nucleating ability of various minerals, I would suggest the term "material/materials" be replaced by "mineral/minerals" throughout the manuscript (eg. line 19, 171, 207 etc.) The text has been altered accordingly.

Line 24-28 This is a long sentence. This can be split into 2 to better convey the meaning, eg. 2nd sentence could be "the ice nucleation particle population in desert

dust aerosol is dominated by Kfeldspars rather than quartz (or other minerals)." Thank you. The abstract has been edited accordingly.

Line 41 "type of aerosol particles" instead of "aerosol types" Now corrected Line 43 "Field observations of ice crystal residuals" instead of "Observations of aerosol at the centre of ice crystals" We acknowledge this suggestion but have edited the text as follows. We wanted to avoid the term residual, since those unfamiliar with the field won't know what it is. The other referee also had a suggestion for this sentence. "Observations of aerosol within ice crystals have shown that mineral dust is often present…"

Line 44 Cite the accepted ACP version of Eriksen Hammer et al. (2018) Now updated.

Line 46-49 May consider splitting this into "Atmospheric mineral dusts are composed of several components. Clay is the major component of airborne mineral dust and is sufficiently small that its atmospheric lifetime is relatively long. Hence recent ice nucleation studies have focused on the clay group of minerals." Thank you, this has now been reworded as follows "Atmospheric mineral dusts are composed of several components. Clay is the major component of airborne mineral dust and is sufficiently small that its atmospheric lifetime is relatively long. Hence, historically ice nucleation studies have focused on the clay group of minerals (Broadley et al., 2012;Murray et al., 2011;Wex et al., 2014;Mason and Maybank, 1958;Pinti et al., 2012;Roberts and Hallett, 1968)."

Should be 'INPs' in place of 'ice nucleants' (line 51) and 'ice nucleating material' (line 71) corrected

Line 67 'repeated' instead of 'repeat' Corrected

Line 70 remove 'quite' Amended

Line 74 "over time when suspended in water or exposed to air" would be better in place of 'to time spent in water or air'. Thank you for this suggestion. However, the particles were not suspended in water during the time series experiments. They were left in water over time and so would settle to the base of the vial. They would only be suspended prior to the start of a new experiment. We have amended the text as follows "We also explore the stability of a subset of these samples to time spent in water or exposed to air"

## Line 104 TiO2 is mentioned twice. Remove one of them Corrected

Line 139 this line gives the impression that the samples undergoing BET tests were used to make suspensions, which I believe is not the case. Consider removing "After BET analysis" In some instances we had small amounts of sample so that we did have to use the same sample as what was used in the BET tests. We have added the following section of text as clarification "In some instances we had small amounts of sample so the sample used for BET analysis was subsequently used for the succeeding ice-nucleation experiments."

Line 176-177 delete 'specific' from line 176 and add it before "surface area" in line

177 Thank you, this is now amended

Line 293-295 give references after 'configuration'

This is our own inference based on our understanding of the system.

Line 332 "It may be these microtextural differences that lead to the observed variability in icenucleating ability" Amended

Line 377-379 Consider re-phrasing the lines to "However, we constrained the polynomial fits because the unconstrained fits poorly represented the data at the warmest and coldest ends." for easy understanding. We have reworded the text as follows "These fits were constrained at the warmest and coldest temperatures due to a poor representation of the data at these regimes when left unconstrained."

Line 415 "its exceptionally high ice nucleation ability" in place of 'it exhibiting exceptional behaviour' This has been rephrased as follows "Amelia albite from the Harrison et al. (2016) study was excluded due to its exceptional ice-nucleating ability making it unrepresentative of the other five albite samples."

Line 447 can also add Kumar et al. (2018); Kumar et al. (2019b) in the references in regards to aging of K-feldspar microcline Thank you. The references have been added.

Line 471-472 Fig 8b shows parameterisation for desert dust by Niemand et al. (2012) in blue dashed lines and the K-feldspar parameterisation proposed in this study by solid red lines Amended as follows "K-feldspar parameterisation developed by Atkinson et al. (2013) (in black dashed lines), the parameterisation for desert dust by Niemand et al. (2012) (blue dashed lines) and the K-feldspar parameterisation proposed here (red solid lines)."

Lines 506-510 Weathering in solutes has already been addressed by Whale et al. (2018) and 3 Parts series from Kumar et al. and should be addressed as part of this paper rather than referring to future work We have now added the following section of text "Related to this, we also note that solutes can alter the ice-nucleating ability of mineral samples (Whale et al., 2018;Kumar et al., 2018;Kumar et al., 2019a, b). Sensitivity to these ageing processes and solutes could be very important in determining the dominant INP types globally (Boose et al., 2019). Hence, we suggest further studies aim to build a better understanding of the relationship between the experimental observations and field collected samples to determine the role of ageing in the atmosphere."

Line 642, 666 and 673 - cite the accepted ACP version of these papers: Kumar et al. (2019a), Peckhaus et al. (2016), Pinti et al. (2012) Amended

Figure 2 add suspension concentration in caption Done

Figure 5 Niedermeier et al. (2015) - correct author name in figure legend. Also, the curves are difficult to read, especially with orange-red tones, maybe use other dark colors. Size of symbols in legend needs to be increased for better readability Done

Figure 8 Check references to Boose et al 2016 (for 'a' and/or 'b') for data used in the figure. Symbol size in legend should be increased. Corrected

In line 826 "....the natural mineral variability of freshly milled quartz highlighted...." Line 795-796 equation formatting needs improvement Corrected

We would also like to bring to the attention of the reviewers that an erratum has been issued for Zolles et al. (2015). As a result the quartz parameterisation from this study has been amended. We have also added quartz data from a volcanic ash study to increase the data density for quartz (Losey et al., 2018). This has resulted in a slightly modified milled quartz parameterisation which is then used in the proceeding plots and discussions. The amended parameterisation did not significantly change and it has had no impact on the discussion and conclusions of the paper.

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## The ice-nucleating ability of quartz immersed in water and its atmospheric importance compared to K-feldspar

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Alexander D. Harrison<sup>1</sup>, Katherine Lever<sup>1</sup>, Alberto Sanchez-Marroquin<sup>1</sup>, Mark A. Holden<sup>1,2\*</sup>,
Thomas F. Whale<sup>1,2</sup>, Mark D. Tarn<sup>1,3</sup>, James B. McQuaid<sup>1</sup> and Benjamin J. Murray<sup>1</sup>

6 <sup>1</sup>School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK

<sup>7</sup> <sup>2</sup>School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK

8 <sup>3</sup>School of Physics, University of Leeds, Leeds, LS2 9JT, UK

9 \* Now at School of Physical Sciences and Computing, University of Central Lancashire, Preston PR1 2HE, UK

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11 Abstract. Mineral dust particles are thought to be an important type of ice-nucleating particle (INP) in the mixed-12 phase cloud regime around the globe. While K-feldspar has been identified as being a particularly important component of mineral dust for ice nucleation, it has been shown that quartz is also relatively ice nucleation active. 13 14 Given quartz typically makes up a substantial proportion of atmospheric desert dust it could potentially be 15 important for cloud glaciation. Here, we survey the ice-nucleating ability of 10 a-quartz samples (the most common quartz polymorph) when immersed in microlitre supercooled water droplets. Despite all samples being 16 17  $\alpha$ -quartz, the temperature at which they induce freezing varies by around 12 °C for a constant active site density. 18 We find that some quartz samples are very sensitive to ageing in both aqueous suspension and air, resulting in a 19 loss of ice-nucleating activity, while other samples are insensitive to exposure to air and water over many months. 20 For example, the ice nucleation temperatures for one quartz sample shifted down by ~2°C in 1 hour and 12°C 21 after 16 months in water. The sensitivity to water and air is perhaps surprising as quartz is thought of as a 22 chemically resistant mineral, but this observation suggests that the active sites responsible for nucleation are less 23 stable than the bulk of the mineral. We find that the quartz group of minerals are generally less active than K-24 feldspars by roughly 7 °C, although the most active quartz samples are of a similar activity to some K-feldspars 25 with an active site density,  $n_s(T)$ , of 1 cm<sup>-2</sup> at -9 °C. We also find that the freshly milled quartz samples are 26 generally more active by roughly 5 °C than the plagioclase feldspar group of minerals and the albite end-member 27 has an intermediate activity. Using both the new and literature data, active site density parameterisations have been proposed for freshly milled quartz, K-feldspar, plagioclase and albite. Combining these parameterisations 28 29 with the typical atmospheric abundance of each mineral supports previous work that suggests that K-feldspar is 30 the most important ice-nucleating mineral in airborne mineral dust

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Deleted: and comparing the results with measured atmospheric ice-nucleating particle concentrations, supports previous work that suggests that K-feldspar dominates, rather than quartz (or other minerals), the ice nucleation particle population in desert dust aerosol. This provides further evidence for the ice nucleation particle population in desert dust aerosol being dominated by K-feldspars rather than quartz (or other minerals).

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#### 51 1 Introduction

52 The formation of ice in supercooled clouds strongly affects hydrometeor size which in turn impacts cloud lifetime, 53 precipitation and radiative properties (Kanji et al., 2017). There are a number of primary and secondary 54 mechanisms through which ice can form in clouds. Homogeneous freezing of cloud droplets becomes increasingly 55 important below -33 °C (Herbert et al., 2015), but clouds commonly glaciate at much warmer temperatures (Kanitz 56 et al., 2011;Ansmann et al., 2009). Freezing at these warmer temperatures can occur through secondary ice 57 production (Field et al., 2017) or heterogeneous freezing on ice-nucleating particles (INPs) (Murray et al., 58 2012; Hoose and Möhler, 2012). The presence of INPs, which tend to comprise only a small fraction of cloud 59 condensation nuclei, can dramatically reduce the lifetime of shallow clouds (Vergara-Temprado et al., 2018), and 60 alter the development of deep convective clouds through, for example, the release of latent heat which invigorates 61 the updraft thus altering cloud structure (Lohmann, 2017;Rosenfeld et al., 2011). It is also recognised that an 62 accurate representation of cloud phase is important for assessments of climate sensitivity (Tan et al., 2016:Ceppi 63 et al., 2017). However, our understanding of which type of aerosol particles serve as effective INPs is incomplete 64 (Vergara-Temprado et al., 2017;Kanji et al., 2017).

65 Mineral dust has been inferred to be an effective INP in the atmosphere from field, model and laboratory studies 66 (Hoose and Möhler, 2012; Vergara-Temprado et al., 2017). Observations of aerosol within ice crystals have shown 67 that mineral dust is often present, suggesting they act as INPs within mixed phase clouds (Iwata and Matsuki, 2018; Eriksen Hammer et al., 2018; Pratt et al., 2009). Laboratory studies also demonstrate mineral dusts are 68 69 relatively effective at nucleating ice (Hoose and Möhler, 2012; Murray et al., 2012; DeMott et al., 2015). 70 Atmospheric mineral dusts are composed of several components, <u>Clay</u> is a major component of airborne mineral 71 dust and is sufficiently small that its atmospheric lifetime is relatively long. Hence, historically ice nucleation 72 studies have focused on the clay group of minerals (e.g. Broadley et al., 2012; Murray et al., 2011; Wex et al., 73 2014; Mason and Maybank, 1958; Pinti et al., 2012; Roberts and Hallett, 1968; Hoose and Möhler, 2012). However, more recent work shows that K-rich feldspars (K-feldspars) are very effective INPs when immersed in 74 75 supercooled water (Whale et al., 2017;Zolles et al., 2015;Tarn et al., 2018;Peckhaus et al., 2016;DeMott et al., 76 2018; Reicher et al., 2018; Harrison et al., 2016; Niedermeier et al., 2015; Atkinson et al., 2013). However, there are 77 other minerals present in the atmosphere, many of which are relatively poorly characterised in terms of their ice-78 nucleating activity.

79 Quartz is a major component of aerosolised atmospheric mineral dust (Perlwitz et al., 2015;Glaccum and Prospero, 80 1980) and studies have shown that it can be active as an INP (Zolles et al., 2015; Atkinson et al., 2013; Isono and 81 Ikebe, 1960;Holden et al., 2019;Kumar et al., 2019a;Losey et al., 2018). Boose et al. (2016) showed a correlation 82 between the INP activity of nine desert dusts and the concentration of K-feldspar at temperatures of -20°C. However, at lower temperatures (-35 to -28 °C) the ice-nucleating activity of the dusts correlated with the 83 84 combined concentration of quartz and K-feldspar. Boose et al. (2016) thus emphasised the importance of 85 understanding quartz and feldspars present in the atmosphere for the modelling of INPs. Recently, Kumar et al. 86 (2018) investigated five milled quartz samples (two synthetic, three naturally occurring) for their ice-nucleating 87 activity, demonstrating the activity of milled quartz. Very recently, Holden et al. (2019) demonstrated that 88 nucleation on quartz is indeed site specific, through repeated freezing experiments with high-speed 89 cryomicroscopy, and found that micron sized defects tended to be collocated with the nucleation sites. While our 90 understanding of ice nucleation by quartz has improved recently, it is still unclear how variable quartz samples 91 are in their ice-nucleating ability, which prevents an assessment of its atmospheric importance as an ice-nucleating 92 particle relative to other minerals.

93 When designing experiments focused on understanding the ice-nucleating activity of atmospheric mineral dusts, 94 we must consider the processes that lead to the production of dust in the atmosphere (these processes are illustrated 95 in Figure 1). It is common practice to mill relatively pure samples to fine powders which can be studied in the 96 laboratory (Atkinson et al., 2013;Harrison et al., 2016;Peckhaus et al., 2016;Zolles et al., 2015;DeMott et al., 97 2018;Kumar et al., 2018;Niedermeier et al., 2015) for the purposes of characterising the ice-nucleating ability of 98 individual minerals, but the relevance of this mechanical milling process to natural airborne mineral dusts needs 99 some discussion. Ultimately, atmospheric mineral dust is derived from bulk rocks which are mechanically broken 100 down to finer particles through erosion processes (Blatt et al., 1980). The finer material that results can be 101 transported by rivers or wind and forms soils in deserts or fertile regions. The particles in these soils undergo 102 complex ageing chemistry (and biology), which converts certain minerals into clay minerals (Wilson, 2004), 103 Minerals such as pyroxenes and amphiboles are relatively readily converted to clays over geological timescales,

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117 but quartz and to a lesser extent feldspars are relatively inert and therefore persist in soils (Goldich, 1938; Wilson, 118 2004), However, the ageing state of the surfaces of these minerals is unclear. While ageing processes may modify 119 120 the surfaces relative to the original fresh surfaces, these aged materials are continually exposed to aeolian processes that involve grains mechanically abrading against one another, resulting in rounding of grains and the 121 break-up of aggregates (Bagnold, 1941; Pye, 1994). These vigorous aeolian processes result in the generation of 122 123 small airborne dust particles which most likely have fresh surfaces. Hence, the commonly applied practice of mechanically milling rock samples for laboratory characterisation has some justification, but it would be wise to 124 test how sensitive the active sites on these surfaces are to exposure to air and water. Previous studies indicate that 125 K-feldspars tend to be relatively insensitive to exposure to water and air (Harrison 2016; Whale 2017), although 126 acids can deactivate K-feldspars (Kumar et al., 2018). Hence, in the absence of strong acids, freshly milled K-127 feldspar is thought to be relevant for atmospheric mineral dust. Quartz on the other hand has been shown to be 128 129 very sensitive to exposure to water and re-milling these samples appears to readily expose or create new active sites (Zolles et al., 2015;Kumar et al., 2019a).

In this study we present a survey of the ice-nucleating ability of 10 naturally occurring quartz samples and demonstrate the variability in ice-nucleating ability within natural quartz. We also explore the stability of a subset of these samples to time spent in water or exposed to air confirming that the activity of some quartz samples are very sensitive to ageing, in contrast to K-feldspars. Then, in order to compare the potential contribution of quartz to the atmospheric INP population to that of other minerals we have generated a parameterisation for freshly milled quartz based on the experimental work in this study. In addition we present new parameterisations for Kfeldspar, plagioclase feldspar, and albite feldspar based on datasets available in the literature. This allows us to compare the potential contribution of quartz, albite, plagioclase and K-feldspar to the atmospheric INP population.

#### 138 2 Quartz, the mineral

139 Quartz is the second most abundant mineral in the Earth's crust after the feldspar group of minerals. Its hardness 140 (Moh's scale 7) and chemical nature along with its lack of cleavage planes mean it is also a common constituent 141 of sands and soils as it is resistant to weathering processes. Although quartz does not have cleavage planes it does 142 exhibit conchoidal fracturing meaning particles tend to have smoothly curving surfaces as a result of fracturing 143 (Deer et al., 1966), rather than planes with steps that might be expected on a cleavage plane. As it is a common 144 constituent to soils, including desert soils, it can be lofted into the atmosphere and is found within transported 145 mineral dusts (Caquineau et al., 1998;Avila et al., 1997;Kandler et al., 2011;Kandler et al., 2009).

146 The silica minerals are composed of SiO2 tetrahedra with each silicon being bonded to four oxygen atoms and 147 these tetrahedra form a 3D framework which can be in six or eight membered loops (Deer et al., 1992). There are 148 three principle crystalline types of SiO2: quartz, cristobalite and tridymite, with stishovite and coesite being other 149 high pressure polymorphs. The polymorph that is present depends on the temperature and pressure during 150 formation (Koike et al., 2013;Swamy et al., 1994). All three crystalline silica types (quartz, cristobalite and 151 tridymite) can exist in two polymorphs, both a high temperature ( $\beta$ ) and low temperature ( $\alpha$ ) state.  $\alpha$ -quartz is most commonly found at or near the Earth's surface due to it being the most stable at atmospheric conditions and 152 153 thus is the dominant polymorph of quartz found in soils and in atmospheric desert dust aerosol\_(Deer et al., 1992).

154 In fact,  $\alpha$ -quartz is so common that by convention it is referred to simply as quartz.

155 Generally, quartz samples tend to be close to 100 % SiO<sub>2</sub> although it is common to find small amounts of oxides 156 as inclusions or liquid infillings within cavities (Deer et al., 1966). The substitution of  $Al^{3+}$  for  $Si^{4+}$  allows for the 157 introduction of alkali ions such as Li<sup>+</sup> and Na<sup>+</sup>. These subtle impurities can lead to a variety of colours. If quartz 158 with impurities (for example Al) is exposed to low levels of naturally occurring radiation then one pair of electrons 159 from an oxygen adjacent to Al can be emitted leaving unpaired electrons otherwise known as "hole defects" 160 (Nassau, 1978). This forms the basis for colour centres, which cause the colouration of amethyst. Amethyst is 161 typically violet in colour and differs from standard  $\alpha$ -quartz in that it has a larger proportion of Fe<sub>2</sub>O<sub>3</sub> inclusions 162 and marginally more TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in its structure (Deer et al., 1966). Rose quartz generally contains higher 163 amounts of alkali oxides, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and MnO<sub>2</sub> (Deer et al., 1966). It has a pinkish colour which is thought to be 164 attributed to the presence of a fibrous mineral which was first suggested to be dumortierite (Kibar et al., 165 2007; Applin and Hicks, 1987) but has been suggested to be a different, unclassified type of mineral (Goreva et 166 al., 2001). Smoky quartz has a black colour which is caused by colour centres created by the irradiation of iron 167 (Nassau, 1978). Chalcedony is a form of cryptocrystalline or microcrystalline  $\alpha$ -quartz (Deer et al., 1966). It has 168 been suggested that it is also commonly intergrown with another polymorph of quartz known as moganite (Heaney 169 and Post, 1992;Götze et al., 1998). Moganite has a monoclinic crystal structure opposed to the trigonal crystal

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system of quartz. Chalcedony often includes micropores within its structure due to its microcrystalline nature(Deer et al., 1966).

#### 179

#### 180 3 Materials and Methods

#### 181 3.1 Samples and preparation

182 10  $\alpha$ -quartz samples were tested for their ice-nucleating ability. These included four typical  $\alpha$ -quartzes, two 183 amethysts, two microcrystalline quartzes (chalcedony), one rose quartz and one smoky quartz, as summarised in 184 Table 1. Photographs of the samples are presented in Figure 2. These samples were selected to investigate the 185 natural variability of the ice-nucleating ability of  $\alpha$ -quartz.

These samples were sourced from various gem sellers. The minerals were visually inspected, using their colour, crystal habit, lustre and cleavage to confirm whether the mineral was quartz and, if so, what type of quartz Rietveld refinement of powder X-ray diffraction (XRD) patterns was then used to verify the silica polymorph and identify any significant crystalline impurities. The results of this process are presented in Table 1. Raman spectroscopy was used in conjunction with XRD to test for the presence of moganite within the two chalcedony samples based on the work of Götze et al. (1998). However, both methods indicated that no moganite was present above the limit of detection (~1 wt%).

193 Eight of the samples were prepared from bulk rock or crystal samples by first rinsing the rock surface with 194 isopropanol and pure water and placing in a clean sealed plastic bag before chipping off fragments and then 195 grinding them into a powder with an agate mortar and pestle. The mortar and pestle were cleaned before use by 196 scrubbing them with quartz sand (Fluka) and rinsing thoroughly with pure deionised water and isopropanol. A similar method was employed by Harrison et al. (2016) who investigated less ice-active minerals (plagioclase 197 198 feldspars) and found that contamination from the cleaning process was not observed. Atkinson quartz (the same 199 quartz sample as used by Atkinson et al. (2013)) and Fluka quartz were supplied as a powder, although Atkinson 200 quartz was originally ground via the same milling process (Atkinson et al. 2013).

These samples were reground to ensure all samples initially had freshly exposed surfaces for ice nucleation experiments. The milling process was used to break down mineral crystals/powders to a sufficient size so that they may be suspended in water. We argue that these freshly milled samples are relevant in that they represent the fresh surfaces which are likely produced by mechanical processes in nature as rocks are broken down and particles aerosolised through the saltation process (see Figure 1 and discussion in the introduction). We therefore suggest that the results from these freshly ground samples of quartz represent an upper limit to the icenucleating ability of quartz in atmospheric mineral dust since ageing processes may reduce this activity.

208 The specific surface areas of the quartz samples were measured using the Brunauer-Emmett-Teller (BET) N2 209 adsorption method with a Micromeritics TriStar 3000 instrument (Table 1). Heating of the sample at 100 °C 210 overnight was performed under a steady flow of dry nitrogen to evaporate any moisture in the sample before the 211 surface area measurement. After BET analysis, 1 wt% suspensions for all the samples were prepared 212 gravimetrically by suspending a known amount of material in purified water (18.2 M $\Omega$  cm at 25 °C) in a 10 mL 213 214 glass vial. In some instances we had small amounts of sample and so the sample used for BET analysis was subsequently used for the succeeding ice-nucleation experiments. As quartz is a hard mineral the use of magnetic 215 stirrer bars was avoided when suspending the material as preliminary experiments showed the potential for the 216 Teflon coating to abrade off the stirrer bars and become mixed with the suspension. We also chose not to use glass 217 stirrer bars, partly because glass is softer than quartz and partly because we have noted in the past that is can be a 218 source of contamination. Therefore particles were suspended by vortexing for 5 mins prior to ice nucleation 219 experiments. Only small amounts of sample were available for Mexico quartz and Uruguay amethyst and so the 220 powder used for BET analysis was then used to prepare the suspensions for ice nucleation experiments. The BET 221 analysis and subsequent suspension in water was carried out within a week of grinding the sample.

#### 222 3.2 Ice nucleation experiments

The microlitre Nucleation by Immersed Particle Instrument (μL-NIPI) was employed to test the ice-nucleating ability of the various quartz samples in the immersion mode (Whale et al., 2015). This technique has been used in several previous ice nucleation studies e.g. (Atkinson et al., 2013;O'Sullivan et al., 2014;Harrison et al., 2016). 226 In brief, 1 µL droplets of a suspension were pipetted onto a hydrophobic glass cover slip atop a cold plate (EF600, 227 Asymptote, UK). During pipetting, the suspension was vigorously shaken<u>manually</u> every 10 droplets (with 228 roughly 40 droplets per experiment) to keep the quartz particles suspended and to ensure that the amount of 229 mineral in each droplet was similar. The cold plate and glass slide were then enclosed within a Perspex chamber 230 and a digital camera was used to image the droplets. The temperature of the cold plate was decreased at a rate of 5 °C min<sup>-1</sup> to 0 °C (from room temperature), then at 1 °C min<sup>-1</sup> until all the droplets were frozen. Whilst cooling 231 232 the system, a gentle flow of zero grade dry nitrogen (<0.2 L min<sup>-1</sup>) was passed across the cold plate to reduce 233 condensation onto the glass slide, which can cause interference between freezing droplets and the surrounding 234 unfrozen droplets (Whale et al., 2015). As the droplets were cooled, images were recorded with the digital camera 235 and freezing events identified in post analysis to calculate the fraction of droplets frozen as a function of 236 temperature  $\pm 0.4$  °C. A second run for each sample suspension, with a fresh array of droplets, was performed 237 238 immediately after the first experiment with approximately 1 hour between the two runs. Prior to the start of each experimental day droplets of pure water (no dust) were used to determine the background freezing signal. Umo et 239 al. (2015) compiled a large collection of background freezing results to create a fit which represents the variability 240 of the background in the uL-NIPL instrument. The background signal measured in this study was in line with the 241 lower bound set by Umo et al. (2015).

242 We assume that nucleation on quartz occurs at specific active sites, as supported by the work of Holden et al. 243 (2019) who showed that nucleation occurs preferentially at specific sites on  $\alpha$ -quartz and feldspar using high-244 speed cryomicroscopy of ice crystal growth on thin sections of mineral. The cumulative ice-nucleating active site 245 density  $n_s(T)$ , on cooling from 0 °C to a temperature, T, was determined for each quartz sample. Standardising the 246 active site density to the surface area of nucleant allows for comparison of the ice-nucleating ability of different 247 materials (Connolly et al., 2009; Vali et al., 2015). It should be noted that this model neglects the time dependence 248 of nucleation, which can have some influence on the nucleation temperature (Herbert et al., 2014;Holden et al., 249 2019).  $n_s(T)$  is calculated using:

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

where n(T) is the cumulative number of frozen droplets on cooling, N is the total number of droplets in the experiment. A is the\_surface area of nucleant per droplet calculated based on the mass of quartz per droplet (assumed to be the same as in the bulk suspension) and the <u>specific</u> surface area determined via BET analysis.

(1)

254 We conducted Monte Carlo simulations to estimate the error in  $n_s(T)$  as a result of the randomness of the 255 distribution of active sites in the droplet freezing experiments. These simulations consider the possible distribution 256 of active sites throughout the droplets that explain each fraction frozen and quantify this uncertainty, which is 257 then combined with the uncertainty in the pipetting and BET measurements. This methodology was based on the 258 work of Wright and Petters (2013).

#### 259 4 Results and discussion

#### 260 4.1 The variable ice-nucleating ability of α-quartz

261 The cumulative fraction of droplets frozen (n(T)/N) on cooling is shown in Fig. 3 a for arrays of droplets containing 262 the quartz samples. Comparison of these curves with the fraction frozen curves for droplets without added particles 263 in the µL-NIPI system (Umo et al., 2015), shows that all quartz samples heterogeneously nucleate ice since the 264 freezing temperatures for droplets containing quartz are always much higher than the pure water droplets. These 265 fraction frozen curves are then translated into  $n_s(T)$  in Fig. <u>3</u>b-c. In Fig. <u>3</u>b we show  $n_s$  for freshly prepared samples 266 where the particles were suspended in water for ~10 minutes before carrying out an experiment. The variability in the ice-nucleating ability of these α-quartz samples is striking. Bombay chalcedony and Atkinson quartz are 267 268 substantially more active than the other samples with the activity spanning roughly 10 °C at  $n_s(T) = 10 \text{ cm}^{-2}$ . While 269 the overall spread is large, it is also notable that the droplet freezing temperatures of 8 out of 10 of the samples 270 fall between -17 °C and -20 °C at  $n_s(T) = 10 \text{ cm}^{-2}$ .

**271** In Fig. <u>3</u>c we show  $n_s$  for both the first (fresh) run and a subsequent run performed approximately one hour after the first experiment for each quartz sample. In the cases of Bombay chalcedony, Brazil amethyst and Smokey quartz, the first and second runs where identical within the uncertainties, whereas in the other cases there was a systematic decrease in freezing temperature. For example, the temperature at which Atkinson quartz had an  $n_s(T)$ of 1 cm<sup>-2</sup> decreased by ~3 °C between the first experiment and the second experiment run. In the past, using this technique with mineral particles of a similar grain size has mostly resulted in consistent results from run-to-run (e.g. Atkinson et al., 2013; Whale et al., 2015). This suggests that the decrease in activity seen for some quartz samples is a real change in the activity of the quartz rather than artefacts such as, for example, the settling of particles out of suspension leading to less surface area in each droplet. The finding that the activity of many of the a-quartz samples decrease with time spent in water is perhaps surprising given quartz is typically regarded as an inert material. We come back to this issue of ageing of active sites in water and air in section 4.2 where we describe a dedicated set of experiments to explore this issue.

283 The Bombay chalcedony sample stands out as being one of the most active quartz samples. For  $n_s = 10$  cm<sup>-2</sup> the 284 Bombay chalcedony nucleates ice at -9 °C which is comparable to K-feldspar (see section 5.1, for a comparison 285 with other minerals). As described in section 2, chalcedony is a microcrystalline form of  $\alpha$ -quartz and commonly 286 has micropores. It is possible that these micropores contain ice nucleation active sites or create zones of weakness which allow defects to be created when ground. In order to test if the superior ice-nucleating ability of Bombay 287 288 chalcedony is inherent to chalcedony, we located, characterised and tested a second chalcedony sample. Grape 289 chalcedony has a similar microcrystalline form to Bombay chalcedony, but behaves more like the other quartz 290 samples we have tested, both in having a lower ice-nucleating activity, but also in the decrease in its activity with 291 time spent in water. One possibility is that the Bombay chalcedony sample is contaminated with another very 292 active ice-nucleating component. The X-ray diffraction results suggest that there is not enough inorganic 293 crystalline material, for example K-feldspar, to account for the result. In addition, we washed a ~2 g sample of 294 unground Bombay chalcedony in 10 mL pure water (shaking vigorously for ~2 minutes) and tested the water. A 295 droplet freezing assay with this washing water indicated that there was no significant detachable contamination. 296 This suggests that the ice-nucleating activity of the Bombay chalcedony is inherent to the material rather than 297 associated with an impurity, although the presence of an ice-nucleating impurity cannot be categorically excluded. 298 These results suggests that a subtle difference between the two chalcedony samples causes the Bombay 299 chalcedony to be much more active.

300 The second most active quartz sample, fresh Atkinson quartz, does not have any obvious differences with the 301 other less active quartz samples which might explain its activity. It is almost entirely pure α-quartz with only a 302 minor component of calcite (0.2%). It is unlikely that the calcite component is responsible for nucleation since 303 Uruguay amethyst contains the same percent impurity of calcite and is much less ice active.

B04 Overall, the results in Fig. <u>3</u> show a surprising diversity in ice nucleation behaviour. As mentioned above, quartz 305 is a relatively uniform material which is chemically and physically stable, hence we might have expected its ice-B06 nucleating ability to be uniform and insensitive to ageing processes (in fact, this was our original hypothesis when 307 we started this project). However, the results clearly demonstrate neither of these expectations is correct. Since 308 all these quartz samples are  $\alpha$ -quartz we might have expected all of these quartz samples to exhibit similar 309 nucleating properties. This variability indicates that these quartz samples do not nucleate through a lattice 310 matching mechanism. This is consistent with the recent observation that nucleation on quartz occurs at active sites 311 (Holden et al., 2019). Our results suggest that these active sites have diverse properties, with different activities. 312 different site densities and some being sensitive to ageing processes where others are not. In the next section we 313 present a set of experiments designed to further probe the ageing of the ice nucleation sites on quartz samples.

#### 4.2 The sensitivity of ice-nucleating activity with time spent in water and air

B15 The results presented in Fig. 3 clearly indicate that the activity of many of the samples of quartz decreases by 316 several degrees within an hour (Fig. 3b). In initial experiments we also showed that the quartz powder used by 317 Atkinson et al. (2013) had lost its activity since it was initially tested. The sample had been stored in air within a 318 sealed glass vial under dark conditions for ~5 years. However, milling of the powder dramatically increased its 319 activity, which suggests that milling can (re)expose surfaces with the most effective active sites. This observation 320 is similar to that described by Zolles et al. (2015) who noted that two out of three quartz samples increased in 321 activity by up to 5 °C on milling. This supports the hypothesis that fresh surfaces are often key to maximising a 322 quartz sample's ice-nucleating ability. Very recently, Kumar et al. (2018) have also observed that milling quartz 323 increases its ice nucleation activity and suggest that this may be a result of defects created during the process.

324 In order to further explore the stability of active sites we tested how the activity of three samples of quartz varied 326 when exposed for a range of times to water and air.\_For this investigation we tested: i) Smoky quartz, as it is a 326 representative quartz in terms of its ice-nucleating ability, lying within the middle of the spread of  $n_s(T)$ ; ii) 327 Bombay chalcedony, as it was the most active sample and iii) Atkinson quartz, since initial experiments indicated 328 it was highly sensitive to ageing in both water and air. The dry powder and suspension samples were stored at 329 room temperature in a dark cupboard in sealed glass vials. Prior to the droplet freezing experiment, wet samples 330 were agitated to re-suspend the particles and the dry powders were added to water in the standard manner 331 described above. The  $n_s(T)$  of the various quartz samples aged in both water and in air for varying times are 332 displayed in Fig. 4.

333 Each of the three samples responded in a distinct manner to time spent in water. Inspection of Fig. 4 (a, c and e) 334 reveals that while the ice-nucleating ability of Smoky quartz did not significantly decrease after ~1 h, its activity 335 decreased by about 3 °C after four months in water\_which is well outside the uncertainties of the experiment. 336 Bombay chalcedony was far more stable in water, with no substantial change in the  $n_s(T)$  curve after four months, 337 being within 1 °C of the fresh sample (close to the uncertainties of the experiment). In contrast, the activity of 338 Atkinson quartz decreased dramatically on exposure to water. Even after only ~1 hour in suspension the  $n_s(T)$ 339 curve decreased by 2 °C, but after 16 months in water the activity decreased by 12 °C. These results point to 340 populations of very different active sites on these three different quartz samples.

β41 We also found that the activity of some quartz samples decreased even when they were stored in air (Fig. 4b, d and e). Dry Smoky quartz and Bombay chalcedony powders were tested after being left in a glass vial for 20 months and showed no decrease in activity. In contrast the activity of Atkinson quartz decreased by ~5 °C in half of this time period (10 months). Fig. 4f also shows the initial freezing temperatures obtained using the same sample from the Atkinson *et al.* (2013) study which had been stored for ~5 years in a glass vial. This sample was ~10 °C less active compared to the freshly ground powder.

#### 347 4.3 Discussion of the nature of active sites on quartz

348 These results paint a complex picture of the properties of the active sites on quartz samples. Not only is the 349 absolute activity of the samples variable, but the sensitivity of the sites to time spent in water and air is also highly 350 variable. The active sites of the Atkinson quartz are far more susceptible to ageing in water and air than both the 351 Smoky quartz and Bombay Chalcedony. The sites on Bombay chalcedony are stable in both air and water, whereas 352 those on Smokey quartz are somewhat intermediate in stability, being sensitive to water only after an extended 353 period of time beyond 1 hour.

Very recently, Kumar et al. (2018) also described the deactivation of quartz in suspension over a period of five days. However, they noted that time series experiments carried out within glass vials showed deactivation of quartz in pure water whereas experiments within polypropylene falcon tubes did not. They suggested that silicic acid leached from the glass vial walls allows the quartz fragments to slowly grow and the active sites to be lost during the process. The explanation of Kumar et al. (2018) is consistent with our observation that the nucleating ability of many samples decreases with time spent in water. However, it is inconsistent with the stability of Bombay chalcedony and it cannot explain the loss of activity seen for Atkinson quartz when aged in air.

361 The physical and chemical characteristics which lead to the large variability in the properties of the ice nucleation 362 sites on quartz are challenging to define. Classical nucleation theory suggests that ice critical clusters at the 363 nucleation temperatures observed in this study are likely to be on the order of several nanometres across (Pummer 364 et al., 2015). It therefore seems reasonable to think that the relevant ice nucleation sites will be on a similar scale 365 but the nature of these sites remains unclear. A molecular dynamics study by Pedevilla et al. (2017) suggested 366 that surfaces with strong substrate-water interaction and high densities of OH groups (or other H-bonding groups) 367 give rise to effective sites for ice nucleation. However, sites with high densities of surface\_OH groups are also 368 inherently thermodynamically unstable and will have a tendency to either react with, for example, moisture in air, 369 or rearrange to a more stable configuration. Hence, it may be at defects in the crystal structure where such sites 370 become stabilised when the thermodynamic cost of having a nanoscale region with a high density of H-bonding 371 groups is outweighed by the gain from relaxing strain in a structure. For example, in K-feldspar, it has been 372 suggested that active sites are related to strain induced by exsolution into K and Na rich regions, which is known 373 to result in an array of nanoscale topographical features (Whale et al., 2017). Consistent with this idea, Kiselev 374 et al. (2016) reported that nucleation on K-feldspar was related to exposed patches of high energy (100) and 375 Holden et al. (2019) demonstrated that nucleation on K-feldspar always occurs within micrometre scale surface 376 imperfections. Holden et al. (2019) reports that topographic features were observed on quartz, at some of the 377 nucleation sites, but they have not been further characterised.

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Formatted: Highlight Formatted: Highlight B79 Larger nanoscale patches of surface H-bonding groups should be better at nucleating ice, but these larger high 380 energy patches will also be less energetically stable. Hence, one might expect that the sites responsible for 381 nucleation at the highest temperatures would also be the least stable and most sensitive to time spent in water or 382 air. But, this does not hold for Bombay chalcedony which is the most active quartz we studied and also the most 383 insensitive to exposure to water and air. This indicates that the sites in this case are either of a completely different 384 chemistry (perhaps a different high energy crystal plane), or the topography and strain associated with a defect 385 imparts a greater stability on these sites. The fact that Bombay chalcedony is distinct from the bulk of the samples 386 in being a microcrystalline quartz may be related to this, however, Grape chalcedony also has a similar 387 morphology and does not possess the population of very active sites.

388 The increased ice nucleation associated with milling may be caused by the mechanical fracturing of the quartz 389 leading to exposure of high energy but unstable sites, which decay away through a structural rearrangement 390 process when exposed to air or liquid water. Alternatively, milling may simply result in the removal of reaction 891 products to leave exposed active sites. Kumar et al. (2018) suggest the milling process causes the breakage of Si-392 O bonds which act as high energy sites for ice nucleation.\_Quartz does not exhibit a preferential plane of weakness 393 (cleavage) to break along and it therefore fractures. The presence of small impurities distributed throughout the 394 lattice, as described in sections 2 and 3, may influence the nature of fracturing and hence create differing defects 395 and high energy sites. Gallagher (1987) classified impurities as a form of structural weakness. The impurities can 396 create zones of weakness and stress within the crystal structure and therefore act as a pathway of least resistance 397 resulting in the breakage of bonds and development of microtexture. Alternatively, in some instances the 398 impurities may create areas of greater strength and so fracturing occurs around these zones. Hence, it is possible 399 that the presence of impurities influences the way in which individual quartz samples fracture and therefore 400 influence the presence of active sites.

401 Inherently, quartz is rather simple in terms of naturally occurring defects compared to other minerals, such as 402 feldspar. In fact, in the past quartz has been considered to be in the 'perfect crystal class', i.e. lacking 403 imperfections. However, quartz does have defects, albeit at a lower density than other minerals (Spencer and 404 Smith (1966)). Quartz minerals can be subject to varying conditions and stresses after their formation and so the 405 geological history of the quartz may also influence the degree of microtexture. For example, a quartz sample 406 which has undergone stress at a fault boundary is more likely to exhibit microtextural features than one that has 407 not (Mahaney et al., 2004). It may be these microtextural differences that lead\_to the observed variability ice-408 nucleating ability. This hypothesis might be tested in the future if quartz samples could be obtained with well 409 characterised geological histories.

410 It has also been observed in the past that, for other minerals, the specifics of the mineral formation mechanism are critical for determining its ice-nucleating ability. Whale et al. (2017) demonstrated that a sample of K-feldspar, 411 412 which had cooled sufficiently quickly during its formation that it did not undergo exsolution and therefore lacked 413 the associated microtextures, had very poor ice nucleation properties. This was in contrast to the more common 414 K-feldspars which do have exsolution microtexture and nucleate ice very effectively. Despite having very 415 different ice-nucleating properties, their crystal structures and compositions are very similar. A similar formation 416 pathway dependence may be true for quartz, such as strain introduced in geological fault systems. But one thing 417 is clear: while bulk mineralogy is a guide to ice-nucleating activity, in some cases details of the formation pathway 418 may be more important.

#### 419 5 The importance of quartz relative to feldspar for ice nucleation in the atmosphere

#### 420 5.1 Comparison to the literature data for quartz and feldspar

421 The data from the present study are contrasted with literature active site density data for quartz (Zolles et al., 422 2015;Atkinson et al., 2013;Losey et al., 2018) in Fig. 5. This data is also compared with  $n_s(T)$  parameterisations 423 for desert dust samples (Niemand et al., 2012;Ullrich et al., 2017) and K-feldspar (Atkinson et al., 2013). The 424 variability within the  $\alpha$ -quartz samples that we report is also reflected in the literature data for quartz. It is striking 425 that two of the quartz samples in this study, Bombay chalcedony and Atkinson quartz, have an activity 426 approaching or equal to K-feldspar. Nevertheless, it is apparent that quartz is never substantially more active than 427 K-feldspar or desert dust in terms of  $n_s(T)$ .

428 Since one of our objectives is to determine how effective quartz is at nucleating ice in comparison to feldspars,
 429 we contrast the literature active site density data for feldspars and quartz in Fig. 6. The feldspars have been colour

430 coded into the plagioclase (blue), albite (green) and the K-feldspar (orange-reds) groups. We note that, by 431 convention, albite is considered part of the plagioclase solid solution series. However, Harrison et al. (2016) 432 demonstrated that albites had a distinct nucleating activity and therefore we plot them here as a separate group. 433 The K-feldspars presented here represent the K-rich samples from the alkali feldspar group (i.e. >10 % K). Overall 434 there is a general trend in that plagioclase feldspars are the least active of the four mineral groups and K-feldspar 435 is the most active. Both albite and quartz show similar, intermediate, activities, K-feldspars from Whale et al. 436 (2017) which did not exhibit the common phase separation were excluded from this plot as they are 437 unrepresentative of common K-feldspars and are rare in nature. Although quartz is an ice active mineral, Fig. 6 438 supports the consensus that it is the K-feldspars that are the most active mineral for ice nucleation that is commonly 439 found in mineral dusts in the atmosphere.

#### 440 5.2 New parameterisations for the ice-nucleating activity of quartz, K-feldspar, plagioclase and albite

441 In order to be able to determine which mineral is most important in the atmosphere we need the activity of each 442 mineral (expressed as  $n_s(T)$ ) in combination with estimates of the abundance of each mineral in the atmosphere.

443 In this section we produce new  $n_s(T)$  parameterisations for quartz, K-feldspar, plagioclase and albite using data 444 from the present study in addition to literature data.

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445 The new set of parameterisations are shown in Fig. 7. In order to derive these parameterisations we compiled 446 data for representative samples of quartz. K-feldspar, plagioclase and albite. To create these parameterisations we 447 binned the data within each dataset into 1 °C intervals and then fitted a polynomial line through the log averages 448 of the data. We binned the data in an attempt to remove bias towards datasets with relatively high data density. In 449 addition, we only applied a fit in the temperature range where multiple datasets were present (with the exception 450 of plagioclase, where the available data is so sparse in some temperature regimes that we had to relax this criterion 451 in order to produce a parameterisation). We used polynomial fits to represent the data since the data is quite 452 complex and alternatives such as a straight line would produce a very poor representation of the data. These fits 453 454 were constrained at the warmest and coldest temperatures in order to obtain a reasonable representation of the data at these limits. We stress that these fits must not be extrapolated to higher and lower temperatures. The 455 standard deviation for each parameterisation was calculated by taking the average of the standard deviations of 456 the log  $n_s(T)$  values for each 1 °C temperature interval. The corresponding value was then used to approximate the 457 standard deviation from each fit, which is represented by the dashed lines and shaded area in Fig. 7.

458 For the quartz fit, the chalcedony samples were excluded given these microcrystalline minerals are 459 unrepresentative of most quartz in nature and that they are therefore likely to be in negligible abundances in the 460 atmosphere. We also only include the runs with freshly made quartz suspensions in the parameterisation since the 461 second runs often showed signs of deactivation in suspension. By only using the relatively fresh suspension data, 462 our parameterisation is representative of freshly milled quartz dust. The new parameterisation can be seen in Fig. 463 <u>7</u>a-b and covers a temperature range of -10.5 °C to -37.5 °C and nine orders of magnitude in  $n_s(T)$ . This is the first 464 robust  $n_s(T)$  parameterisation developed for this mineral that can be used to determine its role as an INP in the 465 atmosphere.

466 The K-feldspar parameterisation developed by Atkinson et al. (2013) has been used extensively within the ice 467 nucleation community. However, this parameterisation was created with data from one K-feldspar sample and 468 does not reflect the variability we now know to exist. The parameterisation developed as part of this study can be 469 seen in Fig. 7c-d. We excluded K-feldspar samples which did not exhibit phase separation from the Whale et al. 470 (2017) study from this parameterisation as these types of alkali feldspar are rare and unlikely to be found in 471 472 significant quantities in the atmosphere. The data included in these plots includes all three polymorphs of Kfeldspar (microcline, orthoclase and sanidine), although most of the data is for microcline. The strongly 473 hyperactive TUD #3, examined by Harrison et al. (2016) and Peckhaus et al. (2016), was excluded as it exhibited 474 extremely high activity and appears to be an exceptional case which is generally unrepresentative of the K-felds par 475 group of minerals. With this in mind we have developed a parameterisation which represents K-feldspars that 476 possess exsolution microtexture. It should be noted that all of the studies used BET derived surface areas for the 477 calculation of n<sub>s</sub>(T) other than DeMott et al. (2018) and Augustin-Bauditz et al. (2014) who used geometric surface 478 areas. However, while the difference between BET and geometric surface areas is substantial for clay samples 479 (Hiranuma et al., 2015), the discrepancy is much smaller for materials with larger grain sizes like feldspar 480 (Atkinson et al. 2013). When the new K-feldspar parameterisation is compared to the literature data it represents 481 the variability of K-feldspar, as well as the curvature in the datasets. In particular, the new parameterisation captures the observed plateau in  $n_s(T)$  below about -30 °C. In addition, the new parameterisation produces higher 482

483  $n_s(T)$  values at temperatures warmer than -10 °C relative to that of Atkinson et al. (2013). Below -10 °C this new 484 parameterisation gives lower values of  $n_s(T)$ . The temperature range of the parameterisation is also extended, 485 covering -3.5 °C to -37.5 °C.

486 The parameterisation proposed here to represent plagioclase feldspar is shown in Fig. 7e-f. The parameterisation 487 spans a temperature range of -12.5 °C to -38.5 °C. Only one dataset was available to represent the plagioclase 488 feldspars in the lowest temperature regime (Zolles et al., 2015), hence this parameterisation needs to be used 489 cautiously, but it is nonetheless a best estimate at present given the current data available. A similar caution must 490 be accepted when using the albite parameterisation displayed in Fig. 6g-h which spans a range of -6.5 °C to -35.5 491 °C. For the albite parameterisation, the hyperactive Amelia albite from the Harrison et al. (2016) study was 492 excluded due to its exceptional ice-nucleating ability making it unrepresentative of the other five albite samples. 493 Hence, this parameterisation is representative of the non-hyperactive albites.

494 The parameterisations are summarised in Fig.  $\underline{8}$  and are then combined with a typical abundance of each mineral 495 to estimate the INP concentration ([INP]<sub>T</sub>) associated with each of the four minerals in Fig. 8 b. On average, 496 roughly 3±6 % (by mass) of atmospheric transported mineral dust particles are K-feldspar whereas 16±15 % are 497 quartz and 8±3 % are plagioclase (see compilations of measurements in (Atkinson et al., 2013), which are 498 consistent with more recent measurements (Boose et al., 2016b)). Albite is often grouped with plagioclase 499 feldspars when determining the mineralogy of atmospheric mineral dusts rather than being reported on its own. 500 For the purposes of this estimate we have assumed that albite has a concentration equal to 10 % of that of 501 plagioclase.  $[INP]_T$  was derived from the  $n_s(T)$  parameterisations assuming a surface area concentration of mineral 502 dust of 50  $\mu$ m<sup>2</sup> cm<sup>-3</sup> (a moderately dusty environment) and assuming that the mass fraction of each mineral is 503 equivalent to its surface area fraction. In order to approximate the size distribution of dust, a lognormal size 504 distribution centred around particles of 1 µm in diameter with a standard deviation of 0.3 was used. We have also 505 assumed that each mineral is externally mixed (see Atkinson et al. (2013) for details of how to treat the mixing 506 state of mineral dust), which is the assumption that has been made when modelling the global distribution of INP 507 in the past (Atkinson et al., 2013 and Vergara-Temprado et al., 2017). In reality, desert dust aerosol will be 508 somewhat internally mixed. The opposing assumption of full internal mixing produces 1-2 orders more INP at the 509 lowest temperatures, but produces the same INP concentration above about -25°C (Atkinson et al. 2013). The 510 upper and lower bounds for each line in Fig 8 b are derived from the range of mineral mass concentrations.

511 The [INP]<sub>T</sub> curves in Fig. 8 b confirm that under most atmospheric situations K-feldspar has the main contribution 512 to the ice-nucleating particle population in desert dust. Quartz is the next most important mineral, with plagioclase 513 the least important. The contribution of pure albite is rather uncertain given the amount of pure albite in desert 514 dust is poorly constrained, but it is unlikely to compete with K-feldspar. Nevertheless, while K-feldspar is the 515 most important contributor to the INP population, the estimates in Fig. 8b do suggest that quartz may make a non-516 negligible contribution to the INP budget at temperatures between about -20 and -12.5 °C. This is particularly so 517 when we consider the variability in the ice-nucleating ability of the K-feldspar and quartz groups. It is possible 518 that in a desert dust aerosol that if the K-feldspar was at the bottom end of the activity, whereas the quartz were 519 at the top end of its activity range, then the quartz would contribute more INP than K-feldspar. However, it should 520 also be considered that the estimated  $[INP]_T$  curves in Fig. <u>8</u>b are also based on the assumption that quartz has the 521 activity of fresh quartz. We know from the work presented above that the activity of quartz is sensitive to ageing 522 processes. We cannot quantify ageing of atmospheric quartz, but the parameterisation we present here probably 523 represents an upper limit to its activity. In contrast, the activity of K-feldspar does not decrease with time spent in 524 water or air (Kumar et al., 2018;Harrison et al., 2016;Whale et al., 2017). Overall, we conclude that K-feldspar 525 contributes the bulk of the INPs associated with desert dust, because it is more active and it is less sensitive to 526 ageing processes. However, we should not rule out quartz making a significant contribution to the INP population 527 in a minority of cases.

#### 528 5.3 Testing the new parameterisations against literature laboratory and field measurements of the ice-529 nucleating ability of desert dust

530 We now test the quartz and K-feldspar parameterisations to see if they are consistent with literature data of the 531 ice-nucleating ability of desert dust (Fig. 9). In Fig 9a we contrast the predicted  $n_s(T)$  values, based on the quartz 532 and K-feldspar parameterisations, against a variety of literature datasets for desert dust. For the K-feldspar based 533 prediction, we have presented lines where 20 %, 1 % and 0.1 % of the surface area of dust is made up of K-534 feldspar. For the 20 % prediction, which is consistent with measurements in Cape Verde (Kandler et al., 2011),

535 we have also shown the natural variability in K-feldspar activity as the shaded region. The line assuming quartz

is the dominant ice-nucleating mineral in desert dust is for 12 % quartz which again is consistent withmeasurements made in Cape Verde (Kandler et al., 2011).

538 From Fig.  $\underline{9}_{a}$  it is clear that quartz does not account for the  $n_s(T)$  measurements of desert dusts sampled directly 539 from the atmosphere and suspended in laboratory studies. However, the new K-feldspar parameterisation is 540 consistent with the ice-nucleating activity of dusts over a wide range of temperatures. The K-feldspar 541 parameterisation reasonably represents the majority of mineral dust measurements when taking into account that 542 typically ~1 % to 25 % of atmospheric desert dust can be attributed to K-feldspar (Atkinson et al., 2013) and that 543 there is a natural variability in the ice-nucleating ability of K-feldspar (as presented by the shaded area around the 544 20 % K-feldspar prediction). The shape of the parameterisation represents the bulk of the data well and plateaus 545 at the lowest temperatures in agreement with the observations.

546 Fig. 2b shows INP concentrations measured from an aircraft in the eastern tropical Atlantic (Price et al., 2018) 547 plotted with the predicted INP concentrations based on the K-feldspar parameterisation developed by Atkinson et 548 al. (2013) (in black dashed lines), the parameterisation for desert dust by Niemand et al. (2012) (blue dashed lines) 549 and the K-feldspar parameterisation proposed here (red solid lines). The parameterisations were calculated 550 assuming an externally mixed scenario (although both internal and external mixing assumptions produce a similar 551 result in the regime where the measurements were made). The upper and lower bounds were calculated by 552 incorporating the maximum and minimum in the aerosol surface area concentrations corresponding to the various 553 aircraft measurements (23.8  $\mu$ m<sup>2</sup> cm<sup>-3</sup> to 1874  $\mu$ m<sup>2</sup> cm<sup>-3</sup>) (Price et al, 2018). K-feldspar was assumed to represent 554 20 % of the aerosol surface area, based on measurements by Kandler et al. (2011). Note that the small number of 555 data points above ~-11°C have a very high uncertainty due to Poisson counting issues and should be regarded as 556 upper limits. Price et al. (2018) and Sanchez-Marroquin et al. (2019) have described a sub-isokinetic sampling 557 bias in the aircraft inlet which results in an enhancement of aerosol surface area by roughly a factor of 2.5 for the 558 used sampling conditions. We have therefore corrected the Price et al. (2018) data downwards by a factor of 2.5 559 (although on the log scale this makes a relatively small difference).

We can see that the Atkinson et al. (2013) parameterisation is a relatively poor predictor of the INP concentration, especially at temperatures colder than about -15 °C. The parameterisation by Niemand et al. (2012) tends to overpredict INP concentrations relative to the Price et al. (2018) data by about one order of magnitude. The K-feldspar parameterisation proposed here better represents the magnitude, the range and the slope of the aircraft data. Overall, the new K-feldspar parameterisation provides a good representation of the ice-nucleating activity of dust from field and laboratory studies and it is also clear that quartz is of second order importance for desert dust's icenucleating ability.

#### 567 568 2 Conclusions

569 We have studied 10 quartz samples for their ice-nucleating ability in order to better understand and define the iceactivity of this abundant mineral. The chosen samples were all a-quartz, the most common silica polymorph 570 571 found at the Earth's surface, but included a variety of  $\alpha$ -quartz types with varying degrees of impurities and 572 different crystal habits. We found that the ice-nucleating activity of these samples is surprisingly variable, 573 spanning about 10 °C. Eight out often of the quartz samples lay within -17 °C to -20 °C at  $n_s(T) = 10 \text{ cm}^{-2}$ , with 574 two quartz samples, Bombay chalcedony and Atkinson quartz, being much more active (as active as K-feldspar). Overall, the quartz group of minerals tend to be less active than the K-feldspars, slightly less active than albite, 575 576 but more active than the plagioclase feldspars. In the future it would be interesting to probe the nature of the active 577 sites on the two most active samples and to try to contrast these sites to those on the less active samples in order

578 to further understand the nature of active sites and why they have such strongly contrasting characteristics.

Although quartz is regarded as a relatively chemically inert mineral the activity of some samples decreases with time spent in air and water. Most of the samples were sensitive to time spent in water, but interestingly, the most active sample's activity did not change significantly even after many months in water. We note that the sensitivity to time in water displayed by most of the quartz samples studied here is in strong contrast to K-feldspars, which tend to be much more stable. Related to this, we also note that solutes can alter the ice\_nucleating ability of mineral samples (Whale et al., 2018;Kumar et al., 2018;Kumar et al., 2019a, b). Sensitivity to these ageing processes and solutes could be very important in determining the dominant INP types globally\_(Boose et al., 2019). Hence, we

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**Deleted:** (Boose et al., 2019) and may also offer a window into an improved fundamental understanding ofice nucleation by minerals in general.

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590 suggest further studies aim to build a better understanding of the relationship between the experimental 591 observations and field collected samples to determine the role of ageing in the atmosphere. 592 To investigate the relative importance of quartz to feldspars in the atmosphere we have proposed new active site 593 density parameterisations for quartz, K-feldspar, plagioclase and albite. These parameterisations are based on a 594 combination of the data presented here for quartz along with data available in the literature. Sparse data sets 595 available for the albite and plagioclase mineral groups lead to lower confidence when creating parameterisations 596 for these mineral groups. It is suggested that future studies expand on the current datasets of the ice-nucleating 597 behaviour of minerals to improve these parameterisations. When using the newly developed parameterisations to 598 predict INP concentrations in combination with typical atmospheric abundances of minerals, it is found that K-599 feldspar typically produces more INP than milled quartz (or any other mineral). Also note that the parameterisation 600 for quartz is for freshly milled quartz and the ageing results presented here and elsewhere (Zolles et al., 601 602 2015;Kumar et al., 2019a) suggest that the active sites on quartz are removed on exposure to air and water. Therefore the parameterisation for milled quartz should be regarded as an upper limit. Even with this upper limit, 603 quartz is of secondary importance relative to K-feldspars which appear to be less sensitive to ageing processes. In 604 addition, we find that the newly developed K-feldspar parameterisation is consistent with  $n_s(T)$  literature 605 measurements on desert dusts and better represents field measurements of INP concentrations in the dusty tropical 606 Atlantic compared to the parameterisations by Atkinson et al. (2013) and Niemand et al. (2012). We hereby 607 propose the use of this new K-feldspar parameterisation when predicting INP concentrations related to mineral 608 dusts. 609 610 611 Data availability. Data for the various quartz samples presented in this paper are available at 612 http://dx.doi.org/10.5285/171726739bb54d0ba84cdde15c5b17ae. 613 Author contributions. ADH designed the experiments with help from scientific discussions with BJM, TFW and 614 JBM. Both KL and ADH performed the experiments. AS completed the calculations for the external mixing 615 assumption used in figures 8b and 2a and assisted in the calculation of errors for the active site density 616 measurements. MAH carried out Raman analysis of the chalcedony samples and MDT helped in the assembly of 617 the literature data. ADH prepared the manuscript with contributions from all co-authors. 618 Acknowledgements. We would like to take the opportunity to thank Lesley Neve for her contribution in the XRD 619 analysis. The authors acknowledge the European Research Council (ERC, Marinelce: 648661), Engineering and Physical Sciences Research Council (EPSRC, EP/M003027/1) and the Natural Environment Research Council 620 621 (NERC, NE/M010473/1) along with Asymptote Ltd. (now part of GE Healthcare) for funding this research. 622 7 References 623 Ansmann, A., Tesche, M., Seifert, P., Althausen, D., Engelmann, R., Fruntke, J., Wandinger, U., Mattis, 624 I., and Müller, D.: Evolution of the ice phase in tropical altocumulus: SAMUM lidar observations over Cape Verde, J. Geophys. Res. Atmos., 114, D17208, 10.1029/2008jd011659, 2009. 625 626 Applin, K. R., and Hicks, B. D.: Fibers of dumortierite in quartz, Am. Mineral., 72, 170-172, 1987. 627 Atkinson, J. D., Murray, B. J., Woodhouse, M. T., Whale, T. F., Baustian, K. J., Carslaw, K. S., Dobbie, 628 S., O'Sullivan, D., and Malkin, T. L.: The importance of felds par for ice nucleation by mineral dust in 629 mixed-phase clouds, Nature, 498, 355-358, 10.1038/nature12278, 2013. Avila, A., Queralt-Mitjans, I., and Alarcón, M.: Mineralogical composition of African dust delivered by 630 631 red rains over northeastern Spain, J. Geophys. Res. Atmos., 102, 21977-21996, 10.1029/97jd00485, 632 1997. 633 Bagnold, R. A.: The Physics of blown sand and desert dunes, Dover publicationsm Inc., New York, 634 1941.

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becoming suspended in water or air. The particles smaller than ~10 µm in air can be transported for long distances and may interact with clouds, serving as INP, many 100s or 1000s of kilometres away from the source regions.

Sample	XRD analysis	BET surface area (m²g⁻¹)	Spherical equivalent diameter (μm)
Bombay	α -quartz: 100%	1.23 ± 0.01	1.88
chalcedony			
Grape	α -quartz: 100%	4.39 ± 0.01	0.53
chalcedony			
Smoky quartz	α -quartz: 98.3% Haematite: 0.1% Albite: 1.6%	1.23 ± 0.01	1.88
Rose quartz	α -quartz: 100%	1.13 ± 0.01	2.04
Atkinson quartz	α -quartz: 99.9% Calcite: 0.1%	4.20 ± 0.01	0.55
Fluka quartz	α -quartz: 100%	0.91 ± 0.01	2.54
Mexico quartz	α -quartz: 96.4% Dolomite: 3.6%	1.74 ± 0.01	1.33
LD1 quartz	α -quartz: 100%	0.94 ± 0.01	2.45
Uruguay amethyst	α -quartz: 99.9% Calcite: 0.1%	1.46 ± 0.01	1.58
Brazil amethyst	α -quartz: 100%	2.76 ± 0.01	0.84

**Table 1:** Table showing the relative concentrations of different minerals within each sample and the respective BET <u>specific</u> surface area of the ground sample and derived spherical equivalent average surface area. The uncertainty in the XRD analysis is on the order of 0.1 %, hence the identification of some trace constituents in some samples is tentative.



Figure 2: Pictures of the various quartz samples explored in this study showing their varying appearances and characteristics.
 Samples supplied in a <u>milled</u> state are not shown.





Figure 3: Fraction frozen and active site densities for ten quartz suspensions (1 wt%). a) The fraction frozen versus temperature for the different quartz samples investigated in this study. The range of freezing for the baseline is highlighted in the grey shaded region (Umo et al., 2015). (b) The active site density (n<sub>s</sub>) for the range of quartz samples in this study. In this plot only the first run of each sample is displayed. These samples are considered to be fresh as they have only spent roughly 10 minutes in suspension. (c) The active site density (n<sub>s</sub>) versus temperature for the quartz samples on their initial runs and their corresponding second runs. The second runs were carried out roughly an hour after the first run. A sample of the error bars are shown in Fig. 2b/c.



931 932 933 **Figure 4:** Plots showing the sensitivity of quartz activity, expressed as  $n_s$ , to time spent in water and air. Data are shown for (a and b) Smok y quartz, (c and d) Bombay chalcedony and (e and f) Atkinson quartz. Error bars for the first run of each time series are shown, but omitted for the other datasets for clarity. The  $n_s$  values for the fresh (~10 min) and one hour  $suspensions were taken from Fig.\,2.$ 

![](_page_38_Figure_0.jpeg)

![](_page_38_Figure_1.jpeg)

**P38Figure 5:** Plotof $n_s$  versus temperature for the available literature data for quartz compared to the data collected in this**939**study. The symbols for this study's data are displayed the same as in Fig. 2 and only the first runs (fresh samples) from this**940**study are plotted. The data from Zolles et al. (2015) has been split into quartz samples which were milled for fresh surfaces

and all the combined data (both milled and un-milled quartz).

![](_page_39_Figure_0.jpeg)

![](_page_39_Figure_2.jpeg)

![](_page_39_Figure_3.jpeg)

![](_page_40_Figure_0.jpeg)

![](_page_40_Figure_1.jpeg)

![](_page_41_Figure_0.jpeg)

1	Deleted: concentration
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![](_page_42_Figure_0.jpeg)