

Answer to Reviewer 1:

We thank Reviewer T. Zolles for his constructive comments. We reproduce reviewer comments in blue in the following. Amended versions of the paper are given in *italics* for new sections and smaller red text for the original text. We have numbered the reviewer comments for clarity.

As major changes, we have

- renamed the “Namib sample” to “Etosha sample” throughout the manuscript to be more consistent with Kaufmann et al. 2016
- replaced “IN” with “ice nucleation” throughout the manuscript to avoid confusion with “ice nuclei”
- deleted p.9,l. 24-29 because the size distribution of the Australia sample was re-measured using an SMPS and APS. The mean surface area was very close to the original one (within 3%). The n_s values in the revised manuscript include the updated surface area but have changed insignificantly
- binned the IMCA-ZINC FF and n_s data into 1 K bin for visual clarity in Fig. 4
- split up the original Table 5 into Tables 5 and 6 in the revised manuscript
- re-calculated Tables 5 (and 6) after we realized that it was incorrect to correlate the mineralogical fraction with n_s . Instead we correlated the fractions now to $\ln(n_s)$. The trends did not change but the R values changed (typically by 0.03-0.1).
- added sample numbers in Tables 1 and 4 which we refer to in Tables 5 and 6
- added scatter plots (Figure 1 and 2) to the supplementary material corresponding to the correlation analysis in 3.3
- added Figure 3 to the supplementary material, showing the correlation of freezing temperatures with mineralogical fraction which were taken from Kaufmann et al. 2016

1) Sampling and sample treatment The decision to sample and compare air-born and ground samples is very well justified. As was stated the mineralogical composition between the used <2.5 μm fraction and the bulk (<32) that was analyzed with XRD may vary, but the general findings are very likely not influenced as neither mineral will be totally absent. This may influence the correlations in 3.3. Nevertheless, natural dusts and minerals are rather often found to have organic and biological material absorbed on their surface. It cannot be excluded that some are left on the dust particle surface. Gently heat treatment could have been used to destroy all organic material.

We agree with the reviewer’s comment (see also response to SC by Russ Schnell). We had performed parallel measurements of particle fluorescence as a proxy of biological material, but due to a failure of the xenon lamps these data were not useable. Unfortunately due to the small sample amounts, we are limited in repeating or performing additional measurements. We were able to repeat some of the deposition/condensation measurements with heat treatment as suggested by Reviewer Zolles. We will include the results of these in the part 2 paper associated with this manuscript (Boose et al., 2016). The experiments were performed using the portable ice nucleation chamber PINC with the original samples as well as samples heated at 300°C (573 K) for 10h. PINC, which works like ZINC but is shorter, has a

shorter residence time and sampled particles which were dry rather than pre-activated as droplets as was done in the present work. Therefore, the results are not necessarily comparable to the immersion mode results from the current manuscript because full droplet activation prior to freezing is not guaranteed.

Figure 1 shows the condensation mode n_s at 240 and 242 K. Filled symbols refer to unheated, open symbols to heated samples. Heating had little to no effect on the ice nucleation activity of the Australia, the Atacama milled and Peloponnese samples. Only the Etosha sample lost most of its ice nucleation activity after heating, which is the sample for which we could not relate the comparably high ice nucleation activity to its mineralogy as it consisted mostly of minerals with low ice nucleation activity. This is consistent with the manuscript conclusions that the ice nucleation activity is mainly caused by the mineralogy of the dust samples. The situation may be different at the warmer temperatures in the manuscript (> 250 K) but unfortunately we cannot do investigations at these conditions due to the small remaining sample size. The full data from these additional measurements and further analysis will be shown in the second paper of the series (Boose et al. 2016).

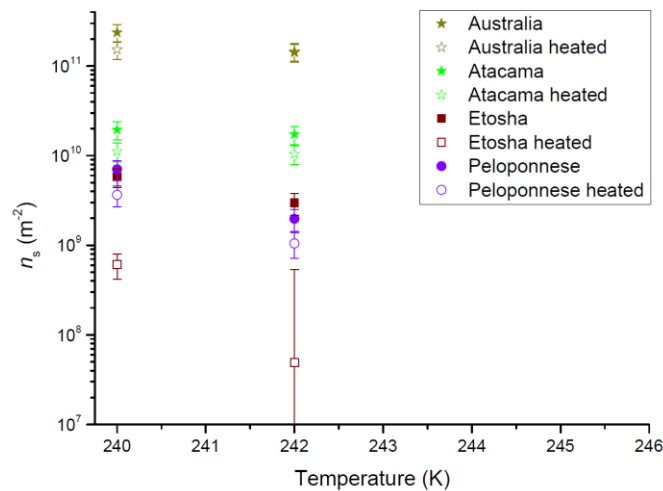


Figure 1: Condensation mode n_s for selected heat treated samples.

In the current manuscript we have added a paragraph on non-mineral matter mixed with the dust and its potential effects on the ice nucleation ability of the dust (p.4,l.15-20 of the revised manuscript):

“Non-mineral matter, which can become internally or externally mixed with the mineral dust before or after emission, may affect the ice nucleating behavior of the dust. Sulfuric acid (Sullivan et al., 2010; Augustin-Bauditz et al., 2014) or secondary organic aerosol coating (Möhler et al., 2008a) has been observed to decrease the ice nucleating ability while exposure to ozone (Kanji et al., 2013) or the presence of ammonium sulfate (Boose et al., 2016b) has been suggested to improve it. Biological material can adsorb to mineral dust, enhancing its ice nucleating ability (Schnell, 1977; Conen et al., 2011; O’Sullivan et al., 2016).”

We have rephrased p.5,.15-16 (now p.5,l.28-30 of the revised manuscript):

“All natural dust samples are expected to be very heterogeneous, i.e. external and internal mixtures of different minerals and potentially biological material (Meola et al., 2015).”

“The composition of natural dust samples is presumed to be heterogeneous, i.e. external and internal mixtures of different minerals and potentially containing organic or biological material (Meola et al., 2015).”

We have replaced p.14, l.22-23:

“If this is due to reasons other than mineralogy such as coating as suggested by Kaufmann et al. (2016) or if the present minerals ankerite, dolomite or muscovite can lead to a high IN activity at $T < 243$ K under certain circumstances is not known.”

with (now p.15, l.27-28 of the revised manuscript):

“Measurements in the condensation mode, which are the subject of part 2 of this study, suggest that the ice nucleation activity of this sample is in large part related to organic or biological material mixed with the dust.”

2) Secondly the dusts did undergo different treatments to produce sufficiently small grains. The surface samples were sieved or milled and with the Israel and Atacama sample two fractions were created. It is clear that the Australia and Morocco samples had to be milled due to not small enough dust fraction, but the authors give no reason why not of all other samples a milled and a sieved fraction was created. There is no clear explanation why in particular the Atacama and Israel samples were chosen. To study the effect of milling a few samples are probably sufficient, but this may lead to an increased uncertainty in the correlations in 3.3. If certain sample sites have an increased importance due to a milled and a sieved fraction.

We agree that it would be preferable if all ground-collected samples could have been treated the same way. Unfortunately, this was not possible since the volume – fraction of particles $< 32 \mu\text{m}$ was typically only on the order of 1/1000 or less of the initial, pre-preparation sample. Only the Israel sample had a large enough mass fraction of particles smaller than $32 \mu\text{m}$ to allow the direct comparison of a milled sieved fraction to the unmilled sieved fraction. The Atacama sample also had a small fraction of $< 32 \mu\text{m}$ but enough to do a comparison between a milled non-sieved fraction and an unmilled sieved fraction. For none of the other samples the amount of particles $< 32 \mu\text{m}$ was large enough to allow further comparisons.

We have added on p.5, l.27-28 of the revised manuscript:

“The sub- $32 \mu\text{m}$ size fraction of the other samples was too small to investigate the milling effect.”

We have repeated the correlations in section 3.3. including only either the sieved or milled Atacama and Israel samples. The trends stayed consistent with those presented in section 3.3. Therefore, an overrepresentation of these two sampling sites does not affect the conclusions presented in the paper.

*3) **Mineralogy analysis** The authors give a good description of the shortcomings of the analysis method as well as that the composition may not be valid for the particle sizes used in the freezing experiment.*

Page 4/30: Similarly, the milling of the Israel sample likely interfered with the preferred direction of the minor components in the sieved samples, leading to an observed reduction of these mineral fractions (e.g. illite, kaolinite, plagioclase) in the milled compared to the sieved sample.

There is a reduction in every relative fraction apart from the very soft calcite which, as the authors state, is probably increasing due to its softness upon milling. Why are these minor components of particular interest? What is the potential explanation of the observation?

For the ice nucleating behavior of the dust samples all components are of interest due to the unknown mixing state of the particles. In theory it could be that a minor component by weight is present on all particles and responsible for the ice nucleation. The minor components are mentioned here in regard to the preferred orientation during XRD to explain the differences between the Israel milled and sieved sample. In theory the mineralogy should be the same because the milled Israel sample was derived from milling the sieved Israel sample.

Preferred orientation of minerals can lead to an over- or underestimation of some minerals, which we suggest (p.7, l.10-14 of the revised manuscript) explains the difference between the milled and unmilled Israel sample.

4) Page 7/14: Natural mechanical weathering thus likely has enhanced the clay mineral and calcite content in the smaller particle fraction whereas feldspars and quartz tend to be found in the larger size fraction. Is the same expected for the sieved and milled samples in this study? In respect to the above mentioned part, it would be important to conduct milling on all ground samples.

The milling breaks up hard minerals such as quartz and feldspar and grinds them to smaller sizes. Therefore it changes the size distribution and size dependent mineralogy of the milled sample compared to the sieved sample. In this regards, the milled samples may show a different size dependent mineralogy compared to unprocessed dust. However, all unmilled samples, including the airborne ones, contain quartz and (except the Etosha (Namib) sample) also feldspar. Furthermore, as described on p.4, l.6-14 of the revised manuscript, quartz and feldspar are commonly found in airborne dust samples. Thus, the milled samples differ from the sieved samples but contain the same minerals found also in sieved or airborne samples.

Milling of all ground samples would allow a better overlap of particle sizes accessible with XRD and IMCA-ZINC. This would help answer one of our scientific questions, i.e. the correlation between mineralogical composition and ice nucleation activity. However, the studied samples would probably be less atmospherically relevant than the ones derived sieving the surface-collected samples.

5) Page 7/20: Hence, the Atacama and Israel milled, Australia, Crete, Peloponnese and Tenerife samples consisted mainly of particles smaller than 2.5 μm and the mineralogy is representative for the particles on which ice nucleation was studied.

I suggest adding the word milled to Australia here also: Hence Atacama, Israel and Australia milled as well as the airborne samples . . . to clarify and emphasize the origins.

We have deleted this sentence to avoid repetition. Instead, we rephrased the sentence on p.7,l. 28-30 of the original manuscript (now p. 8, l. 8-10):

“In summary, the identified mineralogical composition is well representative for the particle size fraction used for IN experiments on the Atacama milled and sieved, Israel milled, Australia, Crete, Peloponnese and Tenerife samples.”

“In summary, the identified mineralogical composition is well representative for the particle size fraction used for ice nucleation experiments on the Atacama milled and sieved, sieved Etosha, Israel milled, milled Australia, and the airborne Crete, Peloponnese and Tenerife samples.”

6) The authors found a bimodal fit for all samples. As a none-expert in the field of particle shapes figure 3 seems to me that this could be a result of the two used measurement techniques? Is there an explanation for the two modes based on hardness or mineral composition?

We did not find a combination of shape factor and density that is realistic for dust particles which would lead to a size distribution of the dust samples with only one mode (p.9,l.14-15 of the original manuscript). It is reasonable that there is a very broad peak with two, sometimes even three shoulders related to the high inhomogeneity of the samples with respect to hardness and fracture. The majority of the mineral composition tends to be soft (e.g. calcite and clays), giving smaller particles, or hard (e.g. quartz and feldspar) resulting in larger particles.

We have added on p.10,l.2-3 (revised manuscript): *“They are likely related to the high inhomogeneity of the samples with respect to hardness and fracture.”*

7) The whole section is very well written and the authors highlight new results.

Page 10/28: As a consequence of the large mean surface area of the Great Basin sample its n_s is shifted to the lowest values.

A shift can be misunderstood, maybe just: “shows the lowest n_s values.”

Agreed. We have rephrased p.10,l.27-29:

“The Israel milled and the Peloponnese sample show a low IN activity. Overall, the airborne Saharan samples belong to the lower half of all n_s curves. As a consequence of the large mean surface area of the Great Basin sample its n_s is shifted to the lowest values.”

now p.10,l.32-33 of the revised manuscript:

“The n_s of the Great Basin sample, which has one of the highest FFs, is amongst the lowest, due to its coarse particle sizes.”

and p.11,l.6-7 of the revised manuscript:

“The Israel milled, the Great Basin, and the Peloponnese sample show a low ice nucleation activity.”

8) Role of mineralogy

The first part is very well written and points out the difficulties with single minerals in case of micas, muscovite and ankerite. The authors again emphasize well that surface collected samples may not be

representative for the atmosphere. In the following paragraphs the study tries to correlate n_s with the mineral fractions. The aim of this is clear and the general findings may still hold true, but the statistical significance of the reported correlations is questionable. Firstly, the Pearson correlation coefficients (R) should not be used as the only statistical measure indicating the correlation. It is furthermore not clear from the text and table 5 which minerals were used at which temperature for obtaining the correlation coefficient. This information should be added to the manuscript. Including more statistical measures is probably out of scope of this study, but the regressions and plots yielding to the correlations should be added to the supplement.

We have indicated now with an asterisk which R - values are significant at the 0.05 level for each correlation in Table 5 and the new Table 6. We have added the most important scatter plots yielding the correlations as Figure 1 to the supplement. These are the correlations of n_s at 243 K, 245 K and 253 K with quartz, calcite, K-feldspars and kaolinite, respectively. Furthermore, we have added the following lines at p.14, l.6-9 of the revised manuscript:

“Table 5 shows the Pearson correlation coefficients (R) between the mineral fractions and the n_s at five temperatures. Only a few of the correlations are statistically significant, owing to the low number of samples. Nevertheless, the overview of the correlation coefficients gives an idea of the effect of certain minerals on n_s . The related scatter plots are given in Figure 1 of the supplementary material.”

To clarify which samples were used at which temperature we have added sample numbers in Tables 1 and 4 and provide these sample numbers in Table 5 and the new Table 6 as “samples included”. We have split the original Table 5 in two: the new Table 5 contains the former first five columns and the new Table 6 the former last three columns. Furthermore, we clarify on p.14, l.2-5 of the revised manuscript:

“For each temperature, all samples which showed a FF between 0.1 and 0.9 were used for the correlations. The Etosha sample was excluded from the correlations with feldspars, quartz and clays, as it does not contain any significant amount of these minerals. However, it was included for the comparison with calcite.”

9) In respect to the content I find the term anti-correlation of n_s for illite and other clays rather confusing, independent of the fact that the values of $|R| < 0.5$ have a low significance. Anti-correlation could be understood as an anti-freezing behavior. By increasing the content of example illite you reduce the n_s at the given temperature, but in fact this is depending on the other mineral components.

Rather than being relative to the fundamental process of freezing, the mineralogy correlation coefficients calculated are relative to the mean mineralogy of the samples. This means that if a sample has increased levels of (presumably) ice nucleation inactive minerals such as illite and calcite, it will have a correspondingly lower concentration of the (presumably) ice nucleation active quartz and feldspars. This produces the anticorrelation between these minerals and n_s . To avoid any confusion we have replaced “**anticorrelation**” with “**negative correlation**” and “**anticorrelated**” with “**negatively correlated**”.

10) The study reports that at 253K there is a good correlation between n_s and the Kfeldspar content, while 245K the correlation with quartz alone is better than with feldspars and quartz. The question arising is: how much of the total n_s is still available at 245K to be explained by quartz if it had been already partly by K-feldspar at the higher temperature? By including a different amount of samples in the correlations at every temperature the relations are harder to identify. In my perspective it is necessary to also have a look at the correlations for the same 3 samples that were used at 253K alone at 245K and if they are better explained by quartz alone or joined by quartz and feldspar. The authors do conduct a manual selection of which samples are included to obtain the correlation coefficient. I therefore want to emphasize once more to state which samples are taken for which correlation and to add this correlation plots to the supplement.

In response to comment 8, we added sample numbers to Tables 1 and 4 and provide the sample numbers for each correlation (Table 5 and Table 6).

We abstained from presenting correlations at $T < 253$ K for only three samples due to the even lower significance. However, we have included them now as Figure 2 in the supplement. The correlations for only Taklamakan, Egypt, and Atacama milled at $T < 250$ K are consistent with the correlations given for all relevant samples. Since none of the three samples contains any illite and only one sample contains kaolinite, the addition of clays to the correlation is meaningless. At 245 K the sum of quartz and all feldspar is the best predictor for n_s ($R = 0.97$) compared to the K-feldspars ($R = 0.68$) or the sum of all feldspars ($R = 0.85$). At $T=240$ K and 243 K, the sum of quartz and feldspar correlates best with n_s . At $T = 238$ K finally, quartz alone leads to the best correlation ($R = 0.72$) with n_s .

We have added on p.14, l.23-26 of the revised manuscript:

“To exclude a bias from varying numbers of samples at different temperatures, we have repeated the correlations at 245, 243, 240 and 238 K for the Atacama milled, Egypt and Taklamakan samples only. The corresponding scatter plots are provided as Figure 2 of the supplementary material and confirm the observations that quartz plus feldspar yield the best correlations at $T < 245$ K.”

11) Minor adjustments: In figure 5 the great basin sample for me does not appear in the same color in the plot and the legend below 150

Corrected.

12) In table two what is the order of the minerals. It does not seem to be milled, sieved or airborne neither are they alphabetically sorted. Do you want to have the Israel samples on the same page?

We have sorted the samples now alphabetically in all tables.

References:

Boose, Y., et al.: Heterogeneous ice nucleation on dust particles sourced from 9 deserts worldwide - Part 2: Deposition and condensation freezing, in prep., 2016

Chou, C., Stetzer, O., Weingartner, E., Jurányi, Z., Kanji, Z. A., and Lohmann, U.: Ice nuclei properties within a Saharan dust event at the Jungfraujoch in the Swiss Alps, *Atmos. Chem. Phys.*, 11, 4725–4738, doi:10.5194/acp-11-4725-2011, 2011.

Kaufmann, L., Marcolli, C., Hofer, J., Pinti, V., Hoyle, C. R., and Peter, T.: Ice nucleation efficiency of natural dust samples in the immersion mode, *Atmos. Chem. Phys.*, 16, 11177–11206, doi:10.5194/acp-16-11177-2016, 2016

Answer to Reviewer 2:

We thank Reviewer 2 for their constructive comments. We reproduce reviewer comments in *blue* in the following. Amended versions of the paper are given in *green italics* for new sections and *smaller red text* for the original text.

As major changes, we have

- renamed the “Namib sample” to “Etosha sample” throughout the manuscript to be more consistent with Kaufmann et al. 2016
- replaced “IN” with “ice nucleation” throughout the manuscript to avoid confusion with “ice nuclei”
- deleted p.9,l. 24-29 because the size distribution of the Australia sample was re-measured using an SMPS and APS. The mean surface area was very close to the original one (within 3%). The n_s values in the revised manuscript include the updated surface area but have changed insignificantly
- binned the IMCA-ZINC FF and n_s data into 1 K bin for visual clarity in Fig. 4
- split up the original Table 5 into Tables 5 and 6 in the revised manuscript
- re-calculated Tables 5 (and 6) after we realized that it was incorrect to correlate the mineralogical fraction with n_s . Instead we correlated the fractions now to $\ln(n_s)$. The trends did not change but the R values changed (typically by 0.03-0.1)
- added sample numbers in Tables 1 and 4 which we refer to in Tables 5 and 6
- added scatter plots (Figure 1 and 2) to the supplementary material corresponding to the correlation analysis in section 3.3
- added Figure 3 to the supplementary material, showing the correlation of freezing temperatures with mineralogical fraction which were taken from Kaufmann et al. 2016

1. Kaufmann et al. vs. Boose et al.: One of the major conclusions from this study (that is, mineralogy matters for dust IN) goes in the opposite direction of that from the study done by Kaufmann et al. (2016, AMTD; K16 hereafter), which points out the similar freezing behavior amongst multiple surface dust samples despite the difference/variation in mineralogy. Does this difference appear due to the technical issue/limitation (i.e., IMCA-ZINC-IODE vs. DSC) or totally something different? I am missing such discussion in this manuscript. Please elaborate to the extent of the community-wide scale. Providing a solid answer with respect to this point would be potentially important for modelers to consider if they require a computationally expensive mineralogy-resolved parameterization for their future simulation works or not.

We do not agree with the reviewer’s statement that the results of our study go in the opposite direction of the study by Kaufmann et al. (K16 hereafter) which is in ACP, not AMTD. On p. 11197 of K16, the authors clearly state: “However, mineralogical composition does matter.”

Furthermore, in the abstract of K16: “In summary, the mineralogical composition can explain the observed freezing behaviour of 5 of the investigated 12 natural dust samples, and partly for 6 samples,

leaving the freezing efficiency of only 1 sample not easily explained in terms of its mineral reference components.”

However, the abstract of K16 also states:

“All natural dusts, except for the Antarctica and ATD samples, froze in a remarkably narrow temperature range with the heterogeneously frozen fraction reaching 10% between 244 and 250 K, 25% between 242 and 246 K, and 50% between 239 and 244 K.”

This statement is not in conflict with our results. The maximum temperature range found by K16 for the natural dust samples excluding the Antarctica and ATD samples is 6 K (frozen water fraction reaching 10 %) while the maximum T -range at the same n_s in our data is 10 K. The larger spread is probably due to the larger number of dust samples and a greater variety in the dust mineralogy in our study, particularly in the quartz content (K16: 1-26 wt%, our study: 1-91 wt%), the K-feldspar content (K16: 0-10 wt%, our study: 0-30 wt%) and the sum of all feldspars (K16: 0-23 wt%, our study: 0-65 wt%).

In addition, the resolution of the latent heat release peaks in the differential scanning calorimetry (DSC) may result in masking of the variability in freezing. In the DSC a droplet can contain more than one particle while IMCA-ZINC works on a single particle basis. If several particles are contained in a droplet, the particle with the most active site will initiate freezing. K16 studied droplets of about 2 μm which contain only a few particles. This curtails the effects but could still cause some of the variability not being observed with the DSC compared to the IMCA-ZINC.

Both studies conclude that as a first approximation, a parameterization like the one by Niemand et al. 2012 is applicable but a more sophisticated parameterization should rely on the mineralogical composition of dust (p.11198 in K16 and p.17,l.21-23 in our revised manuscript).

To clarify this point we have rephrased the following sentence on p.3,l.27-33 of the revised manuscript:

“A recent study by Kaufmann et al. (2016) investigated the ice nucleation ability of surface-collected samples from eight different arid regions worldwide and several single-mineral reference samples using differential scanning calorimetry. The authors found at maximum a 6 K spread in freezing temperatures of emulsion experiments amongst surface-collected samples from different atmospheric-dust source regions. They confirmed the exceptional freezing ability of microcline but found only a minor fraction (4 wt%) in one of the samples from the dust source regions studied. Their samples contained quartz fractions between 1 and 26 wt%, K-feldspar fractions between 0 and 10 wt%, and plagioclase fractions between 0 and 22 wt%.”.

Furthermore, we show in Figure 1 of this document correlation plots of T_{het} at 10 and 50 % frozen water fraction of 0.5 and 1 wt% suspensions with the quartz, calcite, plagioclase, microcline and smectite fraction, all taken from K16. The highest correlation coefficient is found for microcline ($R = 0.93, 0.85$ and 0.93). The correlation with microcline however also suffers from a low number of samples. Microcline is followed by quartz ($R = 0.75, 0.72$, and 0.79) and plagioclase ($R = 0.53, 0.27$, and 0.4) as best predictors for ice nucleation activity (here in terms of T_{het} at 10 and 50 % frozen water fraction). These results show that our method works well and the conclusions are supported by K16.

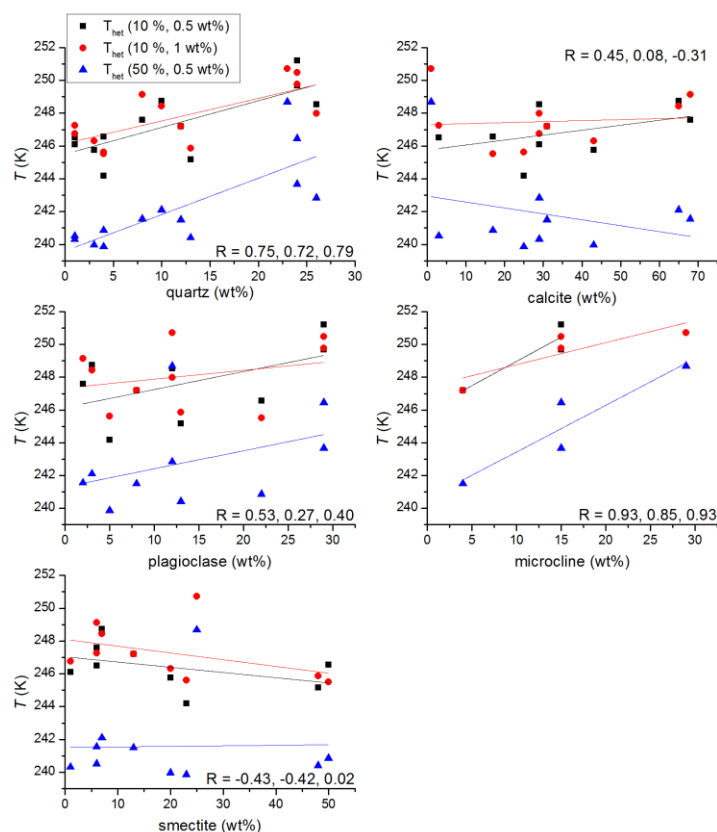


Figure 2: Correlation of freezing temperature of 10 and 50 % frozen water fraction of a 0.5 and 1 wt% solution with six different minerals for the data from Kaufmann et al. 2016

Along similar lines, K16 suggests that microcline-containing particles are not abundant in the atmosphere and, hence, may have overall small contributions to atmospheric ice nucleation (IN) and glaciation (e.g., P20 L22-25 of K16). Do the authors agree with that statement? The reviewer thinks that microcline is in general an important dust composition that can contribute to efficient IN of material composites. Anyhow, it is somehow puzzling for the reviewer to see that two papers from the same institute report opposite things...

We already addressed this point in the original manuscript (p.12, l.10-12):

“We find microcline in at least three of the surface-collected (Great Basin and both Israel) and also in the airborne Tenerife sample. In the samples from Australia and Morocco both phases orthoclase and microcline seem to be present.”

and on p.14, l. 6-10:

“We find microcline in some of our natural dust samples and also in one of the airborne samples. However, we cannot confirm a superior role of microcline over orthoclase for ice nucleation as in most samples microcline was found to be less than 8 wt%. The Great Basin sample contained 30 wt% microcline in the bulk sample but likely significantly less in the size fraction < 2.5 μm . The highly polyminerall nature of our samples and the effect of differences in the size distributions prevent a further investigation of the role of microcline.”

We have merged the two parts above in the revised manuscript (now p.13,l.10-13):

“We find less than 8 wt% microcline in the sieved and milled Israel and the airborne Tenerife samples. In the samples from Australia and Morocco both K-feldspars orthoclase and microcline seem to be present. The surface-collected Great Basin sample contained 30 wt% microcline in the bulk sample but likely much less in the size fraction $< 2.5 \mu\text{m}$. ”

We have added a paragraph on the role of microcline in the conclusions (p.16,l.14-19 of the revised manuscript):

“Microcline was found in one airborne sample (6 wt%) and in surface-collected samples from four different locations. We could not confirm a superior role of microcline over orthoclase, in-part because a differentiation of the two minerals was often difficult and partly because their content was too low in the size range investigated for ice nucleation to cause an effect detectable with the IMCA-ZINC experiment. We cannot therefore conclude that microcline is generally atmospherically not relevant because even in low amounts of a few percent it could glaciate clouds at temperatures warmer than 253 K.”

We cannot confirm or negate a superior role of microcline over orthoclase due to the described limitations in the ice nucleation and mineralogy measurements in terms of concentration and temperature. We therefore abstain from any further speculation on the role of microcline in the atmosphere.

2. n_s , geo vs. n_s , BET: As the authors may be aware, there are two sub-metrics in n_s , namely geometric-based n_s and BET based n_s (Hiranuma et al., 2015, ACP; H15 hereafter). It appears to me that both n_s metrics co-exist in Fig. 5 - Atkinson, Murray and Broadley seem BET-based, while Niemand and all of your data are geometric-based. This is an apples-to-oranges comparison. Note that the difference in these two n_s metrics could be more than an order magnitude (e.g., for illite NX in H15), which would have a substantial effect on your stats presented in Table 5 & P13 L5-33. I strongly urge the authors to select either one metric (the conversion method is introduced in H15), re-evaluate your stats and re-visit your statement in P1 L21-23. Your conclusion may change.

Figure 5 is a comparison between our results (all in $n_{s,\text{geo}}$) to literature curves to give an overview on the ice nucleation ability of mineralogical components. Furthermore, we do not use the literature values in our statistical analysis, so the conversion of the literature data to $n_{s,\text{geo}}$ doesn't have any effect on Table 5 (and now also Table 6) or the interpretation. Keeping this in mind, we agree with the reviewer, that a conversion of all n_s curves into the same metric is a fairer comparison to the literature, despite the uncertainties inherent to such a conversion, particularly where values needed for such a conversion aren't reported. To acknowledge this uncertainty, we do not show single $n_{s,\text{geo}}$ curves in the revised Fig. 5 but instead the area between $n_{s,\text{BET}}$ and the calculated $n_{s,\text{geo}}$ curves.

To calculate $n_{s,\text{geo}}$ curves we have done the following:

-In the case of Atkinson et al. 2013 (A13 in the following), we have converted the K-feldspar $n_{s,\text{BET}}$ curve into $n_{s,\text{geo}}$ using a factor of 3.5 as given in the Supplementary Material of A13.

-In the case of Broadley et al. 2012 (B12 in the following), we have converted the illite $n_{s,\text{BET}}$ curve following Hiranuma et al. 2015, using the specific surface area of $104.2 \text{ m}^2/\text{g}$ given in B12 and a ratio of

the total surface area to total mass of $6.54 \text{ m}^2/\text{g}$ given in Hiranuma et al. 2015 for the same illite NX sample.

- For the Murray et al. 2011 (M11 in the following) case, we converted the kaolinite $n_{s,BET}$ curve into $n_{s,geo}$, following Hiranuma et al. 2015, using a specific surface area of $11.8 \text{ m}^2/\text{g}$ (M11), a density of 2.63 g/cm^3 (M11) and a mean mass-weighted diameter of 674 nm (Hudson et al. 2008). This yielded a correction factor of 3.49. It should be kept in mind that taking the mean mass-weighted diameter from another study leads to a high uncertainty, given that the size distribution might well be different from M11.

- For the newly added quartz curves we could not infer the total surface area to total mass ratio. Given that quartz is somewhat similar to feldspar however, we use the same factor of 3.5 also for quartz. This comes with high uncertainty as well, as the size distribution and also the particle shape of quartz are likely to be different from K-feldspar. The area shown in the plot covers the $n_{s,geo}$ curves calculated from the $n_{s,BET}$ curves from Zolles et al. 2015 and that calculated from the $n_{s,BET}$ curve for quartz from A13 and like the other areas stretches from the original $n_{s,BET}$ curves to the calculated $n_{s,geo}$ curves.

We have added the following paragraph on p.11, l.7-22 of the revised manuscript:

“For comparison, the n_s fits for K-feldspar from Atkinson et al. (2013), for kaolinite KGb-1b from Murray et al. (2011), for Illite NX from Broadley et al. (2012), data for quartz from Atkinson et al. (2013) and Zolles et al. (2015) and the n_s parameterization curve from Niemand et al. (2012) are shown. The K-feldspar, kaolinite, illite and quartz curves and data points were provided as $n_{s,BET}$, i.e. the surface area of the particles was measured with the Brunauer, Emmett and Teller (BET) nitrogen adsorption method (Brunauer et al., 1938). This method yields typically a higher surface area than that based on volume equivalent diameter. The literature $n_{s,BET}$ was converted to n_s using a conversion factor of 3.5 in case of K-feldspar as given in the supplementary material of Atkinson et al. (2013). For illite, we followed Hiranuma et al. (2015), using a specific surface area (SSA) of $104.2 \text{ m}^2 \text{ g}^{-1}$ (Broadley et al., 2012) and a ratio of total surface area to total mass of $6.54 \text{ m}^2 \text{ g}^{-1}$ (Hiranuma et al., 2015). Similarly, for kaolinite we used $SSA = 11.8 \text{ m}^2 \text{ g}^{-1}$, a density of 2.63 g cm^{-3} and a mean mass-weighted diameter of 674 nm (Hudson et al., 2008), yielding a correction factor of 3.49. For the same $n_{s,BET}$ values, the three quartz samples from Zolles et al. (2015) were active over a range of 10 K. No SSA values were provided therefore we used also a conversion factor of 3.5 given that feldspar is somewhat similar to quartz. This comes with a very high uncertainty, as the size distribution and particle shape of quartz are likely to differ from the K-feldspar of Atkinson et al. (2013). The K-feldspar, kaolinite, illite and quartz n_s areas cover the range from the $n_{s,BET}$ as provided in the literature and the calculated n_s to show the uncertainty inherent to the conversion. It can be seen that all desert dust samples fall between the K-feldspar and the clay mineral and quartz fits at all temperatures.”

3. Your n_s vs. Niemand's n_s : The parameterization described in Niemand et al. (2012; N12 hereafter) is essentially based on the observed ice number normalized to the measured “total” surface area (see Eqn. 1-4 in N12), while your parameterization introduces another approximated parameter, the weighted mean aerosol surface area ($A_{ve,w}$; P6 L11). Are these two n_s values apples-to-apples? The performance comparison of IMCA-ZINC-IODE to the AIDA chamber, where the N12 study was conducted, with a

reference IN material seems available in H15. The authors may extend the discussion given in H15 a bit more to justify the use of $A_{ve,w}$ in its first appearance.

The weighted mean aerosol surface area is the area corresponding to the mean of the surface area distribution. We chose to use this value because it is impossible in our case to use the total surface area, due to the fact that the frozen fraction FF is always larger than 0.1. Therefore Equation 2 of Niemand et al. 2012 cannot be approximated and we would have to consider each size bin separately. This on the other hand is not possible because we don't know which particles acted as INPs. Therefore we use the mean of the surface area distribution (which we call weighted mean aerosol surface area), which is the most comparable value to the Niemand et al. 2012 parameterization.

We agree with the reviewer that the wording "weighted mean aerosol surface area" which we used to distinguish the area from the area calculated by the mean diameter of the number concentration distribution, was confusing. We are now simply referring to it as "mean particle surface area".

Furthermore, we have rephrased p.6,l.9-11

"The surface area-weighted mean diameter ($d_{ve,w}$) was calculated from the resulting fit for each sample (see Table 1) as well as the surface area corresponding to this weighted average diameter ($A_{ve,w}$)."

to now p.6,l.22-23 of the revised manuscript:

"The mean particle surface area ($A_{ve,w}$) was calculated from the resulting fit for each sample (see Table 1) as well as the corresponding surface area-weighted mean diameter ($d_{ve,w}$)."

In addition, the general discussion of the ns concept seems scattered over the multiple sections and somehow cumbersome (i.e., P11 L3-6, P9 L 4-7 and P10 L12-16). For clarity, I suggest the authors to briefly describe the following two things within one section (any):

1) Three assumptions of the ns parameterization, which is relevant to the immersion freezing characterization, include i) the probability of ice nucleation is proportional to the available surface area of immersed aerosols, ii) ice nucleation active sites are uniformly distributed over individual particle surfaces and iii) ice nucleation occurs at specific site in a deterministic manner (predominantly T dependent).

We have added on p.9,l.9-12 of the revised manuscript:

"Earlier studies have shown that the probability of a particle to act as INP scales with the surface area of the particle immersed in a droplet (Archuleta et al., 2005; Welti et al., 2009; Kanji and Abbatt, 2010). So-called ice-active sites (Vali, 1966) are assumed on the surface of an INP in the deterministic concept (Langham and Mason, 1958). The probability of such a site to be present on a particle increases with the surface area."

And rephrased p.9,l.4-5

"It should be kept in mind that the assumption that ns stays constant with particle size most likely has limitations for complex polymineral samples such as desert dust particles."

to now p.9,l.21-22 of the revised manuscript:

“The assumption that active sites are uniformly distributed over individual particle surfaces, and therefore that n_s stays constant with particle size, most likely has limitations for complex polymineral samples such as desert dust particles. “

2) The use of the weighted mean aerosol surface area ($A_{ve,w}$) is something unique in this study (and different from N12).

As described above, we have rephrased p.6,l.9-11 to now p.6,l.22-23 of the revised manuscript to avoid any confusion:

“The surface area-weighted mean diameter ($d_{ve,w}$) was calculated from the resulting fit for each sample (see Table 1) as well as the surface area corresponding to this weighted average diameter ($A_{ve,w}$).”

“The mean particle surface area ($A_{ve,w}$) was calculated from the resulting fit for each sample (see Table 1) as well as the corresponding surface area-weighted mean diameter ($d_{ve,w}$).”

Accordingly, I suggest revising the conclusion (P 16 L15-17).

As described above, the way we calculated n_s is the method most comparable to N12. Therefore, we leave the conclusions unchanged.

4. The effect of milling: The discussion regarding the effect of milling is misleading. Specifically, the reviewer’s concerns are as follows:

P1 L18-20: This statement is misleading as it sounds like the milling process generally deteriorates IN efficiency of any composite materials. In fact, this statement contradicts to the IN results of the Atacama samples ($n_{s,milled} > n_{s,sieved}$) presented in Sect. 3.4. (i.e., P14 L29-30). I suggest rephrasing this sentence to be more specific (adding the “may” word would not help).

We have rephrased the sentence, to now (p.1, l.18-21 new manuscript):

“Furthermore, we find that under certain conditions milling can lead to a decrease in the ice nucleation ability of polymineral samples, due to the different hardness and cleavage of individual mineral phases causing an increase of minerals with low ice nucleation ability in the atmospherically relevant size fraction.”

P15 L11-13: Without any evidence of the alternation in defect densities on the Isralel dust surface or calcite surface per milling, this statement (morphology vs. mineralogy) seems too ambitious/strong. It is likely the micro pores on the surface (Subramanyam et al., 2016, Appl. Mater. Interfaces, doi:10.1021/acsami.6b01133) that enhance the IN activity of particles due to the inverse Kelvin effect (Marcolli et al., 2014, ACP). If calcite etc. is breaking up but maintaining smooth surface, there is no reason for its fragments to enhance IN activity. The authors may be aware, but the nature of active sites

is still uncertain and under investigation. Concerning these points, I suggest the authors to soften the tone of this statement.

We believe that we have made clear that this statement is valid only for the Israel sample and we do not generalize this finding (p.15, l11-12 of the original manuscript: “Thus, we conclude for the Israel sample that a morphology effect is small in comparison to the change in mineralogical composition caused by the milling in the analyzed size range.”). Furthermore, we have stated that we were not able to investigate properties like the defect density, surface irregularities etc. and base our conclusion on the finding of earlier studies which all found an increase in ice nucleation activity with an increase in defect density etc. Since the Israel sample lost ice nucleation activity with milling, an increase in defect density therefore is unlikely (except if defects are not really active sites). At least its effect on ice nucleation activity must be small. Hence, the change in mineralogy, which is expected for the sub 2.5 μm particles, likely explains the increase in ice nucleation activity. We have modified the respective sentence to make it more clear that we only refer to the Israel sample in this case. p.16, l.4-6 of the revised manuscript:

“As milling reduced the ice nucleation activity for the Israel sample, we conclude for this specific sample that any morphology effect is small in comparison to the change in mineralogical composition of the analyzed size range caused by the milling.”

5. Airborne vs. Surface: To me, the essence of this paper is summarized in P10 L9-10. This single statement and the method to reach this point would be worth a paper. The authors have already provided a great conclusion (P16 L8-10 & P1 L9-10). Focus your story along with this line. I have some questions regarding airborne dust vs. surface-collected dust as follows:

We thank the reviewer for the remarks above.

P11 L9-10: Interesting. The authors are right - according to Table 4, airborne samples in general seem having larger α ($0.48 \pm 0.07 \text{ K}^{-1}$) as compared to the average of the rest ($0.38 \pm 0.16 \text{ K}^{-1}$), suggesting high T dependency of the airborne samples. But, this is not all about T dependency. This may be rather an indication that the airborne particles miss certain active sites that can be activated at high T (owing to the difference in mineralogy??). The authors may discuss and clarify this point. This observation seems important.

We agree with the reviewer that a steep n_s curve, having a high α value in Table 4 can, in the active site concept, be described as missing certain active sites which activate at warm temperature. These two aspects (warm T active sites and T -dependency) do not contradict each other but are descriptions of the same observations. We have added on p.11, l.32-33 of the revised manuscript:

“This can be seen as an indication of active sites, which activate at warmer temperatures, being more frequent on the surface-collected samples compared to the airborne samples.”

P12 L26-27: This is another important statement. Elaborate a bit further by discussing the atmospheric relevancy of the minerals uniquely found in the airborne samples. Put clear emphasis if your bulk measurements at least suggest the atmospheric relevance of quartz/K-feldspar. According to P7 L14-15

and P7 L20-22, I have a feeling that there would be reduced amount of quartz/K-feldspar in air. Any comments? This argument seems the core research question of this manuscript.

All airborne samples stem from North Africa whereas the surface-collected samples are from sources all over the globe. Hence, the direct comparison of airborne to surface-collected samples might be biased by location dependent differences in mineralogy. This is why we don't focus on this comparison alone.

We have discussed in the original manuscript that harder minerals such as feldspar and quartz are more likely to be found in larger grain sizes whereas softer minerals such as calcite and clays tend to be found more often in the small grain sizes. (P.3, L.30-31). Furthermore, we have described in the introduction the mineralogical composition of airborne dust samples over the North Pacific, Morocco and Israel, all indicating that quartz and feldspar are commonly found in atmospheric dust particles (p.3,l.34-p.4,l.6).

To stress the atmospheric relevance of quartz further, we have added on p.3,l.26-27 of the revised manuscript:

“Quartz is commonly (5-50 wt%) found in atmospherically transported Saharan dust samples (Avila et al., 1997; Caquineau et al., 1998; Alastuey et al., 2005; Kandler et al., 2009).”

Our analysis of the six samples where the mineralogy analysis was directly representative of the particles on which we measured ice nucleation, i.e. which were in the size range smaller than 2.5 μm and therefore also likely to be lifted by wind, suggested also that feldspars plus quartz are the best predictors of ice nucleation activity. Out of these six samples, three were airborne. If the analysis is done on the airborne samples alone the same trend is seen.

We further stress the importance of feldspar and quartz even in low concentrations on p. 15, l.9-10:

“However, our results indicate that feldspar or quartz present in the bulk dust will dominate its freezing behavior down to 238 K.”

and in the conclusions on p.16, l.21-28:

“Keeping in mind that quartz is ubiquitous in atmospheric desert dust, this suggests that quartz plays a more prominent role for atmospheric ice nucleation than previously thought. The clay mineral (illite and kaolinite) and calcite content of the dust samples negatively correlated with n_s at all studied temperatures, suggesting a minor importance of these minerals for the ice nucleation activity of natural dust samples in the immersion mode, especially if quartz or feldspar are present. Atkinson et al. (2013) suggested that the global mineral dust INP concentration down to a temperature of about 240 K is dominated by feldspar. At temperatures between the homogeneous freezing limit and 240 K, where quartz is an active INP, it dominates the total INP concentration as it is much more abundant than feldspar. Our experiments on natural dust confirm this suggestion.”

and on p.17, 1-4:

“For all desert dust samples we found a high correlation of the ice nucleation activity of particles smaller than 2.5 μm with the quartz content of the dust samples. This shows that despite the dominance of the

clay minerals in the small size fraction, quartz is an important atmospheric INP component and also found in the particle size fraction with the longest atmospheric residence time. ”

Table 3: It is really bothering me that the Tenerife sample (6% microcline!) is not showing any superb IN behavior as compared to other airborne dusts. The authors said that the mineralogy inferred by XRD is representative of the aerosolized Tenerife sample (P7 L28-30). The authors disregard the contribution of atmospheric processes (P14 L17-19). Then, what is limiting the IN of this particular dust?

Mineralogy analysis is a bulk measurement, hence we cannot infer the mixing state and therefore don't know, if a) 6% of all particles are pure microcline particles or b) all particles contain 6% microcline or c) an intermediate mixing state. In case a): even if all microcline particles would activate as INP, this would not reach the lower detection limit of IMCA (10 %). In case b): it may well be that the 6% microcline aren't on the surface of each single dust particle but covered by less active minerals (e.g. Zhu et al 2006). For case c) both effects could play a role.

6 % microcline is clearly at the lower end of K-feldspar content in our samples. An effect on ice nucleation from the 6 % of microcline should be detectable at warmer temperatures but unfortunately no FRIDGE measurements are available for this sample. The microcline fraction is included in the K-feldspar fraction used for the correlations in section 3.3.

6. Table 5 (P13 L5-P14 L24): This part includes a number of flaws (i.e., n_s , geo vs. n_s , BET) and needs substantial improvements. In fact, with given limitations/assumptions in P14 L6-24, I am not convinced that these 'relative' correlations add much meaning to the manuscript. Do the authors really require this part to draw their conclusion? This whole statistics part of the manuscript could be deleted?

The conversion of the literature $n_{s, \text{BET}}$ to $n_{s, \text{geo}}$ has no effect on the correlations because the whole analysis was consistently done using $n_{s, \text{geo}}$. We believe that this approach of directly correlating the mineralogical components with the ice nucleation ability (n_s) is a novel approach and the results are valuable. We have added the correlation plots in the supplementary material and have added if the correlations are statistically significant in Table 5 and the new Table 6. We agree that the method has limitations due to the low number of samples and the comparison of a volume property (mineralogy) to a surface property (ice nucleation ability). Therefore, the correlations are often statistically not significant. Both limitations have already been discussed in the original version of the manuscript. Despite these limitations, the results shed new light on the importance of mineralogy and in particular of quartz for ice nucleation of atmospheric dust. We believe this part is clearly required to draw the conclusion that quartz seems to play a more important role for ice nucleation of natural desert dust samples at the investigated temperatures than believed so far and much more than do clays or any other minerals apart from feldspar. This has been suggested by Atkinson et al. 2013 based on mineralogical maps and n_s of single minerals. Our study confirms this now for airborne and surface-collected natural dust samples. Since single mineral studies of the ice nucleation ability of quartz have yielded inconsistent results and focus has been placed on the role of clays and in recent years on feldspar, this is an important new finding. We have added on p.16, l.25-28 of the revised manuscript:

“Atkinson et al. (2013) suggested that the global mineral dust INP concentration down to a temperature

of about 240 K is dominated by feldspar. At temperatures between the homogeneous freezing limit and 240 K, where quartz is an active INP, it dominates the total INP concentration as it is much more abundant than feldspar. Our experiments on natural dust confirm this suggestion. ”

Again, I generally agree that quartz and microcline are IN active and may have potential importance in the atmospheric IN. What would be more valuable to see is if there is any ‘absolute’ relation between mineralogy and IN. For example, the authors may explore if the natural dust n_s (or FF) can be optimized/predicted by its composition and associated individual n_s scaled to the surface fraction (SF) of each component ($x_1, x_2 \dots$ to x_i) [i.e., $n_{s,dust} = (n_{s,x1} \times SF_{x1}) + (n_{s,x2} \times SF_{x2}) + \dots + (n_{s,xi} \times SF_{xi})$]. Note that H15 attempted, but no success. Give more in-depth thoughts regarding the role of particular mineral IN.

This is an interesting suggestion. Please note that the method of correlating the sum of minerals that are assumed to contribute to the ice-nucleation activity at the investigated temperatures with n_s is a simplified version of the proposed method. However, we do not have surface specific mineralogical information, therefore no surface fraction of each component can be determined. As a first attempt one could assume surface fraction to equal volume fraction (see O’Sullivan et al. 2014). But given the uncertainty related to the surface-specific mineralogy, the conversion from $n_{s, BET}$ to $n_{s, geo}$, the polydisperse size distribution of our sample, the wide spread of n_s of minerals that are supposed to be the same within one single study (e.g. plagioclase and K-feldspar in Harrison et al. 2016, quartz in Zolles et al. 2015) or between studies (comparison provided in Harrison et al. 2016 of their own study and Zolles et al. 2015, Emersic et al. 2015 and Atkinson et al. 2013 for feldspars) and the failed attempt of H15 for a rather simple dust sample, we believe that the method proposed by the reviewer is too ambitious to give meaningful results for our dust samples at the moment. This however would be an excellent suggestion for the future, when monodisperse natural dusts are measured with the same instrument/method at the same temperatures as reference minerals and the surface fraction of each component can be determined with reasonable accuracy.

Specific comments/suggestions

Introduction

P2 L22: Briefly explain what the authors mean for ‘contradicting results’.

We have replaced

“The IN ability of soot (Brooks et al., 2014; Kulkarni et al., 2016) and secondary organic aerosol (Prenni et al., 2009; Ignatius et al., 2015) at heterogeneous freezing temperatures is still debated as contradicting results have been observed.”

with (p.2,L.21-25 of revised manuscript):

“The ice nucleation ability of soot (Brooks et al., 2014; Kulkarni et al., 2016) at heterogeneous freezing temperatures is still debated as contradicting results were observed, spanning from hardly any ice nucleation ability at $T > 236$ K (Kanji et al., 2011) to up to 3 % of soot particles active in the immersion mode (DeMott, 1990). Similarly, the reported freezing behavior of secondary organic aerosol particles varies from inefficient to comparably efficient (Möhler et al., 2008a; Prenni et al., 2009; Wang et al., 2012; Ladino et al., 2014; Ignatius et al., 2016).”

P2 L24: Briefly describe ‘certain minerals’.

“Recently, also certain minerals have been identified to nucleate ice at temperatures up to 271 K (Harrison et al., 2016).”

has been replaced by (p.2,l.27-28 revised manuscript):

“Recently, the K-feldspar microcline and the Na-feldspar albite, both minerals found in atmospheric dust, have been identified to nucleate ice at temperatures up to 271 K (Harrison et al., 2016).”

P2 L25: “For the implementation...” - I suggest starting a new paragraph here regarding the IN parameterizations. This way, the previous paragraph (L18-25) reads more like a general introduction of atmospheric INPs and their diversity (biological and non-biological).

done

P3 L19: The authors may mention that the abundance of quartz in atmospheric dusts is consistently high (i.e., ~10% in volume) in the size range of ~1 to 35 μm geometric diameter (see Table 1 of Kandler et al., 2009, Tellus; cited in this paper), which would add the atmospheric relevance and general importance of quartz. Such information could also fit in P4 L1-3.

We added (p.3,l.26-27 of the revised manuscript):

“Quartz is commonly (5-50 wt%) found in atmospherically transported Saharan dust samples (Avila et al., 1997; Caquineau et al., 1998; Alastuey et al., 2005; Kandler et al., 2009).”

and (p.3,l.32-33):

“Their samples contained quartz fractions between 1 and 26 wt%, K-feldspar fractions between 0 and 10 wt%, and plagioclase fractions between 0 and 22 wt%.”

Methods

P5 L26-27: Does the size distribution of particles in the chamber change over 3.5 hours (i.e., the filter sampling period; P8 L15-16)? Large particles settle down faster than the smaller ones, and the authors infer that certain mineral compositions are large in their sizes (e.g., P15 L33). Please clarify and discuss potential consequences, if any.

We state on p.6, l. 11-13 of the original manuscript (now p.6, l.14-16), and in Table 1, the mean surface area varied by 6-24 % over the course of a day of experiments (which lasted typically between 5-12h), except for the Great Basin sample (64 %). Since the 3.5h filter sampling period is lower, the variation is also smaller. Nevertheless, this maximum error has been used when calculating the uncertainty of n_s (see p.10, l.18-19 of original and p.10, l.21-22 of revised manuscript). Since the uncertainty resulting from this decrease in surface area is small compared to the uncertainty in the INP concentration, we do not discuss potential consequences. We have added on p.10,l.29-30 of the revised manuscript:

“The error bars in n_s are derived by error propagation from the error in FF and ($A_{ve,w}$) and are dominated by the error in FF.”

P5 L28: This background (~10%) seems high for the IN research. Any justification or measurements that this much background particles have no substantial contributions to heterogeneous freezing?

We agree that the value is comparably high. But since we only consider frozen fractions between 10-90% in the IMCA-ZINC experiments, we have no influence of the background in our analyses even if all background particles would act as INP and none of the sample particles were INPs. Furthermore, it is expected that the residual particles are of the smallest sizes and hence least ice nucleation active. Nevertheless, in case of the FRIDGE measurements there could be an influence even though the observed results suggest there was hardly any: The order of measurements was Egypt, then Atacama milled, then Etosha, and at last Taklamakan. The Atacama milled sample had an order of magnitude higher n_s than the other samples. So, the influence of residuals from the Egypt sample on the Atacama milled measurements (which would decrease the Atacama milled n_s) would be less than 1 % if the n_s of the Egypt sample residuals was the same as during the actual experiment. Due to their higher n_s , residual particles from the Atacama milled sample could have increased the observed n_s of the Etosha sample, even though less than 6 % of the particles were residuals. This could potentially explain why we found a comparably high ice nucleation activity which cannot be related to any of the known ice nucleation activities of the mineral components. As shown in Figure 2 of this document however, the ice nucleation activity at 240-242 K seems to be related to organic/biological material. This does not rule out a large influence of the Atacama milled residual particles on the Etosha sample in the FRIDGE measurements but makes it unlikely.

The Etosha and the Taklamakan sample finally show similar n_s in the FRIDGE data. This is in line with the results from the IMCA-ZINC measurements at lower temperature, suggesting that there is only negligible influence if any.

P5 L30: Briefly describe "coincidence effects" or cite proper papers.

We have added (p.6, l.12 of the revised manuscript)

"For the IMCA-ZINC measurements the particle concentration was diluted to about 60 cm^{-3} to avoid coincidence effects in the detector which occur if more than one particle is present in the laser beam of the detector Nicolet et al. 2010."

P7 L2: According to Table 3 of K16 (Kaufmann et al.), the Israel sample contains some sanidine. Moreover, sanidine in the natural surface samples seems non-negligible as 6 out of 12 natural surface samples examined in K16 shows the presence of sanidine. Was your sample totally different from K16? Or the the sample may not be completely homogeneous in terms of mineralogical distribution even within a same batch? Was the XRD data interpretation method somewhat different from K16? Please clarify.

The Israel and the Namib (Etosha) samples are the same as studied by K16 as we stated on p.5, l.7-8 (now p.5, l. 17 of the revised manuscript): *"The Israel sample and the Namib sample are from the same batch as those studied in Kaufmann et al. (2016)."*

The XRD data interpretation method was done slightly differently from K16. K16 used in addition to AutoQuan the software EVA, whereas we used AutoQuan and only for unidentified minerals used EVA. The Israel sample only contains about 2 % K-feldspar. Due to this low fraction and since the feldspar

analysis is one of the most challenging part of the mineralogical composition analysis of a polymineral sample, the different results are reasonable.

We have replaced (p.7,l.2 of the old manuscript):

“No sanidine feldspar was found in any of the samples.”

with (p.7,l.15-17) of the new manuscript:

“In case of a low K-feldspar content of a few wt% it was not possible to determine if K-feldspar was present as microcline, orthoclase or sanidine or a mixture of the different phases. Values are given for the K-feldspar with the best Rietveld fit result.”

P7 L20-22: Doesn't this just mean that a majority of large particles (up to 32 μm) break up by the RBG milling? I mean that RBG may do more than just aerosol dispersion, correct? Long story short, is it really fair to assume that those aerosolized particles are identical to the sieved bulk used for XRD as the authors mention in P13 L20-23? Further clarification seems necessary. Accordingly, the authors may consider rephrasing the relevant text in the conclusion (i.e., P15 L29-32). 2.5 μm sounds like a magic number as it is right now.

The RBG may deagglomerates but does not break up or grind particles as the residence time is low and it is a stainless steel brush not a mill or balls. Even if particles would break up during generation, their mineralogical composition would remain the same. If the mineralogical composition is representative depends only on the fraction of particles that make it into the tank reservoir compared to those that are left behind in the cyclone. This fraction has been semi-quantified as described in the manuscript.

The 2.5 μm is simply the D_{50} of the cyclone used during aerosol generation (p.5, l26 of the original manuscript). There is nothing magical about this number, but it is the size cut-off we used consistently for particle generation.

P7 L28-30: For the reason given above, I am not sure if the authors can asset like this.

We hope we could convince the reviewer of the plausibility of the method.

Results & Discussion

P10 L3: The homogeneous freezing regime presented in this manuscript is based on CNT? Or anything different? I suggest adding proper reference(s) here at least.

The homogeneous freezing regime indicated in Figure 4. a) - c) is derived from CNT for 10 μm droplets using formulae and constants given in Ickes et al. 2015. Reference experiments on homogeneous freezing with the IMCA-ZINC setup can be found in Hoyle et al. 2011 Fig.5. We add a reference to Hoyle et al. 2011 and Ickes et al. 2015 to the figure caption.

P10 L9-10: I encourage the authors to clearly state that the same trend holds true for another metric, $ns(T)$.

We have added on p.10,l.33-34 of the revised manuscript:

“Like their FF, the range of n_s of the Saharan samples is comparable to those of the non-Saharan ones (Fig. 4f).”

P11 L2-3: It looks to me that the Niemand parameterization falls in the middle of your 15 $n_s(T)$ spectra. Please clarify what “rather at the lower end” means quantitatively.

We have added on p.11,l.26 of the revised manuscript as subclause:

“(a factor of 3 to 4 below the average $n_s(T)$ of all measured curves, not shown).”

P11 L13-14: The word “overpredicts” implies that the Niemand parameterization (N12) is wrong. The authors may want to soften the tone and rephrase. Your assumption vs. assumption made in N12 would be discussed here.

We have rephrased the sentence to (p.12,l.1-3 of the revised manuscript):

“The parameterization from Niemand et al. (2012) predicts one to two orders of magnitude higher n_s than measured by FRIDGE. Only for the Atacama milled sample at $T = 251 - 256$ K the parameterization shows about 30 % higher values than the measurements.”

We believe that a parameterization cannot be right or wrong. At first it is simply representative for the samples which were used to define it. Even for those, there is an uncertainty related to the parameterization because of the scattering of the data points included. It must be tested if the parameterization also represents other samples and if not, why not. This is what is done in our manuscript.

P11 L11-20: I do not find the scientific significance of having FRIDGE data included in this manuscript. The authors briefly discuss about the FRIDGE results in this part and only a bit more afterward. The reviewer does not find that the FRIDGE results are complementing IMCA-ZINC-IODE, vice versa. In addition, no proper justification for why FRIDGE was conducted for a subset of samples is provided. Does the authors' conclusion change without the FRIDGE data?

The scientific significance of having FRIDGE data included is given on p.4, l.18-19 of the original manuscript:

“This allowed examination of immersion freezing at temperatures between 250 and 262 K, hence covering a wide range of heterogeneous freezing temperatures.”

We have rephrased it to p.4, l.31-32 of the revised manuscript:

“This allowed examination of immersion freezing at temperatures between 250 and 262 K, covering a wider range of heterogeneous freezing temperatures than would otherwise be possible with IMCA-ZINC alone.”

IMCA-ZINC is not sensitive enough to measure FF below 10 % reliably. Therefore, FRIDGE was used to extend the covered temperature range. This was not initially planned as a part of the dust measuring

campaign and for logistical reasons, the particle collection for FRIDGE was only done at the end of the campaign. Therefore only four samples were collected. We don't see a value of adding this information to the manuscript.

The authors' conclusions on K-feldspar determining mainly the ice-nucleation behavior of natural dust at $T > 250\text{K}$ (p.15, l.18-20 of the original manuscript) is entirely based on the FRIDGE data. We therefore see a high value in keeping the FRIDGE data.

Fig. 5: Adding quartz reference spectrum (Atkinson et al., 2013) would be nice.

We did not show a reference spectrum for quartz in the original manuscript because different authors found very different results even within a single study (Zolles et al. 2015, Atkinson et al. 2013). However, since we are now showing areas of n_s than lines, we have included an area of n_s for quartz.

Fig. 5 Cont'd: Having another panel depicting the highest-median-lowest spectra of airborne n_s vs. those of surface-collected n_s would add some clarity and strengthen the paper.

We agree, that's a great suggestion. We have added such a Figure (6a) in the revised manuscript. Furthermore, we have added the following paragraph on p.12,l.9-18:

"Figure 6a shows the median and minimum to maximum $n_s(T)$ range of the airborne and surface-collected samples. This illustrates that the n_s range of the airborne samples falls in the lower half of the n_s range of the surface-collected samples or even below. It shows that for immersion mode ice nucleation surface-collected dust samples are not representative for airborne dust samples, which all stem from North Africa, the world's largest source of atmospheric dust. This might be caused by a non-representative surface-dust collection, e.g. soil rather than dust is collected which has a different size distribution and composition, or dust from a location where threshold wind velocities for dust lifting are not reached. Another cause could be that atmospheric processes taking place during or after particle lofting may alter the particle surface and decrease the ice nucleation ability which has been suggested to occur in the field (Cziczo et al. 2013) and laboratory (Sullivan et al. 2010, Augustin-Bauditz et al. 2014). The potential effects of mineralogy on the ice nucleation activity at different temperatures is investigated in the following section."

P12 L4-9: The discussion given here makes the review think something other than minerals (e.g., P5 L15-17) are competing for IN at given T range. The reviewer is aware that the focus of the current work is on mineralogy vs. IN (and no biological INP perspective at all). That said, the authors should extend the discussion regarding the potential bioaccessibility of dust surface (Augustin-Bauditz et al., 2016, ACP; O'Sullivan et al., 2016, ACP) and other IN species that might be present in soil (O'Sullivan et al., 2014, ACP; Tobo et al., 2014, ACP; Pummer et al., 2015, ACP). Such information would strengthen the manuscript.

We agree with the reviewer's comment. We performed parallel measurements of particle fluorescence as a proxy of biological material, but due to technical reasons these data were not useable. We were able to repeat some of the deposition/condensation measurements, which will be included in the part 2 paper associated with this manuscript (Boose et al., 2016). The experiments were performed using the portable ice nucleation chamber PINC with the original samples as well as samples heated to 300°C (573 K) for 10h. PINC, which works like ZINC but is shorter, has a shorter residence time and sampled particles which were dry rather than pre-activated. Therefore, the results are not necessarily comparable to the immersion mode results from the current manuscript because full droplet activation prior to freezing is not guaranteed.

Figure 2 shows the condensation mode n_s at 240 and 242 K and at the highest RH_w sampled (100 – 105 %) to mimic immersion freezing (Hiranuma et al. 2015). Filled symbols refer to unheated, open symbols to heated samples. Heating had little to no effect on the ice nucleation activity of the Australia, the Atacama milled and Peloponnese samples. The Etosha sample lost most of its ice nucleation activity after heating, which is the sample for which we could not relate the comparably high ice nucleation activity to its mineralogy as it consisted mostly of calcite and dolomite, which have a low ice nucleation activity (Atkinson et al. 2013, Kaufmann et al. 2016), and ankerite, of which the ice nucleation activity is not known (Kaufmann et al. 2016). This is consistent with the manuscript conclusions that the ice nucleation activity is mainly caused by the mineralogy of the dust samples. The situation may be different at warmer temperatures but unfortunately we cannot repeat investigations at these conditions due to the small remaining sample size. The full data from these additional measurements and further analysis will be shown in the second paper of the series (Boose et al. 2016).

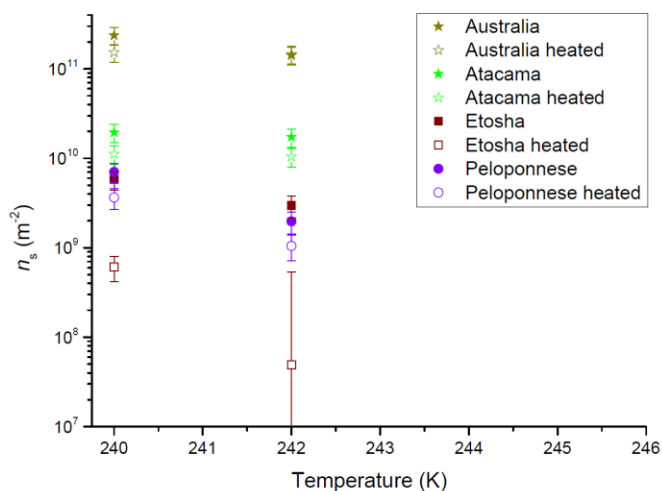


Figure 2: Condensation mode n_s for selected heat treated samples.

In the revised manuscript we have added a paragraph on non-mineral matter mixed with the dust and its potential effects on the ice nucleation ability of the dust (p.4,l.15-20 of the revised manuscript):

“Non-mineral matter, which can become internally or externally mixed with the mineral dust before or after emission, may affect the ice nucleating behavior of the dust. Sulfuric acid (Sullivan et al., 2010; Augustin-Bauditz et al., 2014) or secondary organic aerosol coating (Möhler et al., 2008a) has been observed to decrease the ice nucleating ability while exposure to ozone (Kanji et al., 2013) or the presence of ammonium sulfate (Boose et al., 2016b) has been suggested to improve it. Biological material can adsorb to mineral dust, enhancing its ice-nucleating ability (Schnell, 1977; Conen et al., 2011; O’Sullivan et al., 2016).”

We have rephrased p.5, l.15-16 (now p.5, l.28-30 of the revised manuscript):

“All natural dust samples are expected to be very heterogeneous, i.e. external and internal mixtures of different minerals and potentially biological material (Meola et al., 2015).”

“The composition of natural dust samples is presumed to be heterogeneous, i.e. external and internal mixtures of different minerals and potentially containing organic or biological material (Meola et al., 2015).”

We have replaced p.12, l.8-9 (now p.13, l.7-9 of the revised manuscript):

“No study so far has investigated the IN behavior of pure ankerite. Thus it remains unclear what leads to the observed high IN activity at $T < 242$ K of the Namib sample.”

“Thus, the high ice nucleation activity at $T < 242$ K of the Etosha sample is not explainable by the known ice nucleation ability of its mineral components. To our knowledge, no study so far has investigated the ice nucleation behavior of pure ankerite.”

We have replaced p.14, l.22-23:

“If this is due to reasons other than mineralogy such as coating as suggested by Kaufmann et al. (2016) or if the present minerals ankerite, dolomite or muscovite can lead to a high IN activity at $T < 243$ K under certain circumstances is not known.”

with (now p.15, l.15-16 of the revised manuscript)

“Measurements in the condensation mode, which are the subject of part 2 of this study, suggest that the ice nucleation activity of this sample is in large part related to organic or biological material mixed with the dust.”

Conclusion

P15 L18-19: Which data infers the FF and $n_s(T)$ results at temperatures above 250 K? I do not see them in Fig. 4. FRIDGE?

The n_s of FRIDGE at $T > 250$ K is shown in Fig 5b). We have deleted “the FF” on p.15, l.19 (original manuscript). The sentence reads now (p.16, l.12-13 in the revised manuscript):

“The comparison showed that at temperatures above 250 K the highest n_s is related to the highest fraction of K-feldspars in the sample...”

P16 L2-4: Your data presented in Tables 2 and 3 (i.e., Atacama milled vs. sieved; Israele milled vs. sieved) seem contradicting to this statement. For instance, I do not see any increase in the quartz fraction.

It is correct that for the Israel and the Atacama sample, the milling did not lead to an increase in the quartz fraction. This has the following reasons: For the Israel sample, the milled and the sieved sample should have the same mineralogy because the batch which was already sieved to below 32 μm was further milled. In the case of the Atacama sample, were the original pre-processed sample was milled and compared to the < 32 μm sieved fraction, the quartz fraction actually is slightly lower in the milled compared to the sieved sample. However, one can see that the K-feldspar (orthoclase) fraction is 10.5 % higher than in the sieved sample. As feldspar is also hard and in addition due to its reactivity less common in the small particle fraction, the milling increased the feldspar fraction, resulting in a reduction of the quartz fraction.

We refer here mostly to the Morocco and Australia samples which had almost no particles in the size range < 32 μm and therefore needed to be milled. They consisted both mainly of quartz and feldspar.

P16 L6-8: This part seems contradicting to the previous statement (that is, P15 L33).

We have now changed the sentence on p.15,l.33:

“Quartz is a comparably hard mineral and thus less common in the smallest dust size fractions. Since we measured IN activity of particles smaller than 2.5 μm and found a high correlation with the quartz content of the dust samples we show that quartz is nevertheless an important atmospheric INP component ”

to p.17,l.1-4 of the revised manuscript:

“For all desert dust samples we found a high correlation of the ice nucleation activity of particles smaller than 2.5 μm with the quartz content of the dust samples. This shows that despite the dominance of the clay minerals in the small size fraction, quartz is an important atmospheric INP component and also found in the particle size fraction with the longest atmospheric residence time.”

With this change we now in the revised manuscript want to say that one could expect that quartz should be only found in the larger size fraction of dust particles because of its hardness (rather than stating that as a fact as previously done so). We then follow this with a discussion demonstrating that in our results quartz can be indeed found in the atmospheric size fraction and can be important to predicting ice nucleation behavior.

Technical comments/suggestions

P1 L1-2: “Traditionally, clay minerals were assumed to determine...” → “Since natural dusts are composite in nature, clay minerals were typically used as a proxy to determine...”

We prefer to leave the sentence as it is. We base this statement on early publications on ice nucleation, e.g. Kumai 1961. Furthermore clays were used as a proxy because clays can form a substantial component of natural dust.

P1 L14: "...activity in a given sample above 253 K that can be attributed to..."

We prefer to keep the wording "at 253 K" because we did our analysis of correlating n_s with mineralogy only at 253 K and not at warmer temperatures. Hence, "above 253 K" would be speculative.

P1 L17 and hereafter: Use the Italic font for T throughout the manuscript.

done

P2 L3: "determine" → "influence" - Besides primary ice nucleation, secondary ice processes can also contribute to the lifetime of clouds.

done

P2 L20: Pummer et al. missing as INM references

"Pummer et al. 2012" was added

P2 L21: DeMott et al. missing as soot IN references

"DeMott et al. 1990" was added.

P2 L32: ", respectively"

A comma was inserted.

P2 L32-P3 L1: Too many things packed in a single sentence. Split into two sentences.

done (p.3, l.2-4 of the revised manuscript)

P2 L33: between → amongst

done

P3 L13: "K-feldspars (microcline, orthoclase and sanidine) were..."

done

P3 L20-22: Redundant (P3 L4-6)

We have deleted the first half of the sentence (p.3,l.24-26 of the revised manuscript):

"It has been proposed that differences in the surface structure can lead to different IN abilities of quartz samples and it is suspected that functional groups on the surface of feldspars and quartz are responsible for their higher IN ability (Zolles et al., 2015)."

“It is suspected that functional groups on the surface of feldspars and quartz are responsible for their higher ice nucleation ability (Zolles et al., 2015) but it is unknown where the high variability stems from.”

P3 L27: Delete “hence”. Size and composition are inherently related. Is that what the authors want to say? If so, state so.

The sentence

“It has been observed that the size distribution and hence mineralogical composition of dust changes during its emission and transport compared to that on the surface (D’Almeida and Schütz, 1983; Murray et al., 2012; Knippertz and Stuut, 2014). The reason for this is a size dependent mineralogical composition caused by differences in the hardness, cleavage and shape of minerals.”

has been changed to (p.3, l.34 - p.4, l.2 of the revised manuscript):

“It has been observed that the size distribution of dust changes during its emission and transport compared to dust on the surface. This leads to variations in the mineralogical composition of the dust, (D’Almeida and Schütz, 1983; Murray et al., 2012; 35 Knippertz and Stuut, 2014) as the mineralogical composition is size dependent due to differences in the hardness, cleavage, shape and reactivity of minerals.”

P3 L31: No “hence”

done

P4 L29: “The GPS coordinates of our collection sites...”

done (p. 5, 7-8)

P5 L15-16: “The composition of all natural samples are presumably heterogeneous...”

done (p.5, l. 28-30)

P6 L10: “... sample (see ...)”

done (p.6, l. 23)

P6 L15: “... (sieving/milling)”

done (p.6, l. 29)

P8 L5: “The cloud droplets” → “The simulated cloud droplets” or “The activated droplets”

We have deleted “cloud” (p.8,l.16 of the revised manuscript).

P8 L15: “subsequent” → “independent”

done (p.8, l. 29)

Eqn. 4: Missing negative sign on the RHS of Eqn.4?

done (p. 9)

P9 L4-5: Awkward sentence. I suggest rephrasing.

The sentence

“It should be kept in mind that the assumption that n_s stays constant with particle size most likely has limitations for complex polymineral samples such as desert dust particles.”

has been rephrased to (p.9,l.21-22 of the revised manuscript):

“The assumption that active sites are uniformly distributed over individual particle surfaces, and therefore that n_s stays constant with particle size, most likely has limitations for complex polymineral samples such as desert dust particles.”

P9 L14-15: Awkward sentence. Simply say something like our measurements are valid with χ in the range of 1.1 to 1.6.

We have rephrased this and the preceding sentence

“Since one mode was detected in each instrument’s size range, a variation of the shape factor χ was tested to check if a better overlap of the two size distributions could be achieved. Within realistic limits ($1.1 \leq \chi \leq 1.6$) for shape factors of atmospheric dusts (Alexander, 2015) the two modes remained distinguishable and are thus assumed to be real.”

to (p.9,l.32-p.10,l.3 of the new manuscript):

“Since one mode was detected in each instrument's size range, the shape factor χ was optimized to give the best overlap of the two size distributions. For any shape factor within realistic limits for atmospheric dusts ($1.1 \leq \chi \leq 1.6$, Alexander 2015) the two modes remained distinguishable.”

P9 L21-22: Awkward sentence. Simply say ...because of the presence of predominantly large particles... or something similar.

done (p.10, l.9-10)

P 10 L12-13: “Due to the heterogeneous and possibly size-dependent particle compositions, a partial step function like activation spectrum could be...”

done (p.10, l.23-24)

P10 L27-28: two consecutive “overalls” are bothering.

The second “**overall**” was deleted. (p.11, l. 6)

P11 L2: “The comparison between the Niemand parameterization and our parameterizations based on...”

We have rephrased the sentence to (p.11,l.24-26 of the revised manuscript):

“For $T < 250\text{ K}$ the parameterization falls in the lower end of the range of n_s observed for our broader collection of global surface collected and airborne dust samples (a factor of 3 to 4 below the average $n_s(T)$ of all measured curves, not shown).”

P11 L5: “polydisperse nature” → “heterogeneous properties”

We have replaced “**nature**” with “*size distribution*” (p.11, l.28 of the revised manuscript)

P11 L23-24: This sentence does not fit in here. I suggest deleting.

We have added another sentence to create a smoother transition (p.12, l.20-21) of the revised manuscript:

“By analyzing the bulk mineralogy we investigate if the different natural dust's mineralogical composition explains the observed ice nucleation activity.”

P14 L34: The authors may want to remind the reader that $2.5\text{ }\mu\text{m}$ is D_{50} of your cyclone.

We added “(*the D_{50} cut-off of the particle generation system used*)” after “ $2.5\text{ }\mu\text{m}$ ” on p.16, l.5 of the revised manuscript.

P15 L10-13: “However... Thus...” - Awkward transition. Rephrase.

The sentences have been rephrased to (p.16, l.3-6 of the new manuscript):

“However, an increase in defect density and surface irregularities has been shown to increase the IN activity of monomineral or single compound samples. Thus, we conclude for the Israel sample that a morphology effect is small in comparison to the change in mineralogical composition caused by the milling in the analyzed size range.”

“An increase in defect density and surface irregularities has been shown to increase the ice nucleation activity of monomineral or single compound samples. As milling reduced the ice nucleation activity of the Israel sample, we conclude for this specific sample that any morphology effect is small in comparison to the change in mineralogical composition of the analyzed size range caused by the milling.”

P15 L22 above or below?

We have deleted the respective sentence.

P15 L27-28: I do not understand this sentence. Rephrase.

The sentence

“The size dependent enrichment of different minerals leading to differences in n_s highlights the interplay between IN ability and atmospheric relevance of certain mineral phases.”

was replaced by (now p.16, l.29):

“The variation in mineralogy with particle size leads to variations in n_s .”

P15 L29-32: Awkward sentence. Rephrase.

Sentence rephrased (p.16, l.33-p.17, l.1 of the revised manuscript):

“The focus of earlier IN studies on the clay mineral IN behavior is supported by the observation that three of the four airborne samples (Crete, Peloponnese and Tenerife), which had been long-range transported and were almost entirely in the size range < 2.5 μm , had the highest clay mineral fraction.”

“Three of the four airborne samples (Crete, Peloponnese and Tenerife) had the highest clay mineral content and were amongst the least ice nucleation-active samples.”

P16 L 12: “can not” → “cannot” (to be consistent with the rest of the manuscript)

done

P16 L 21-22: Redundant (P4 L22)

We deleted the sentence.

References:

Boose, Y. et al.: Heterogeneous ice nucleation on dust particles sourced from 9 deserts worldwide - Part 2: Deposition and condensation freezing, in prep., 2016

Hiranuma, N., Augustin-Bauditz, S., Bingemer, H., Budke, C., Curtius, J., Danielczok, A., Diehl, K., Dreischmeier, K., Ebert, M., Frank, F., Hoffmann, N., Kandler, K., Kiselev, A., Koop, T., Leisner, T., Möhler, O., Nillius, B., Peckhaus, A., Rose, D., Weinbruch, S., Wex, H., Boose, Y., DeMott, P. J., Hader, J. D., Hill, T. C. J., Kanji, Z. A., Kulkarni, G., Levin, E. J. T., McCluskey, C. S., Murakami, M., Murray, B. J., Niedermeier, D., Petters, M. D., O’Sullivan, D., Saito, A., Schill, G. P., Tajiri, T., Tolbert, M. A., Welti, A., Whale, T. F., Wright, T. P., and Yamashita, K.: A comprehensive laboratory study on the immersion freezing behavior of illite NX particles: a comparison of 17 ice nucleation measurement techniques, Atmos. Chem. Phys., 15, 2489–2518, doi:10.5194/acp-15-2489-2015, 2015.

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Zhu, C., Veblen, D.R., Blum, A. E., Chipera, S. J.: Naturally weathered feldspar surfaces in the Navajo Sandstone aquifer, Black Mesa, Arizona: Electron microscopic characterization, *Geochim. Cosmochim. Acta*, 70, 18, 4600-4616, doi: 10.1016/j.gca.2006.07.013, 2006.

Answer to Short Comment by Russ Schnell:

We thank Russ Schnell for his interactive comment. We reproduce reviewer comments in blue in the following. Amended versions of the paper are given in *italics* for new sections and smaller red text for the original text. We have numbered the reviewer comments for clarity.

As major changes, we have

- renamed the “Namib sample” to “Etosha sample” throughout the manuscript to be more consistent with Kaufmann et al. 2016
- replaced “IN” with “ice nucleation” throughout the manuscript to avoid confusion with “ice nuclei”
- deleted p.9,l. 24-29 because the size distribution of the Australia sample was re-measured using an SMPS and APS. The mean surface area was very close to the original one (within 3%). The n_s values in the revised manuscript include the updated surface area but have changed insignificantly
- binned the IMCA-ZINC FF and n_s data into 1 K bin for visual clarity in Fig. 4
- split up the original Table 5 into Tables 5 and 6 in the revised manuscript
- re-calculated Tables 5 (and 6) after we realized that it was incorrect to correlate the mineralogical fraction with n_s . Instead we correlated the fractions now to $\ln(n_s)$. The trends did not change but the R values changed (typically by 0.03-0.1)
- added sample numbers in Tables 1 and 4 which we refer to in Tables 5 and 6
- added scatter plots (Figure 1 and 2) to the supplementary material corresponding to the correlation analysis in 3.3
- added Figure 3 to the supplementary material, showing the correlation of freezing temperatures with mineralogical fraction which were taken from Kaufmann et al. 2016

Mineral aerosol particles in the atmosphere and on the surface of soils rarely, if ever, do not contain associated biological material. As is well known, biological materials are the warmest IN observed in nature. Desert dusts are most readily generated in playas that are deposited by water that has concentrated small mineral particles and associated biological material into lower level areas. Desert dusts that travel appreciable distances rarely are sourced from the tops of sand (mineral) dunes. In this paper, it may be disingenuous to ascribe the measured IN content solely on the mineral content of the particles. The authors may consider heating the desert dusts in a furnace and boiling samples before and after the immersion IN freezing tests to remove the organics. If the sample IN contents are unchanged, the authors and their audience may be somewhat assured that the mineral components of the samples are the IN source and not organic passengers. Russ Schnell, NOAA, Boulder, CO

At the comparably low investigated temperatures (≤ 253 K), the role of biological particles is expected to be rather secondary (O’Sullivan et al. 2015) since some minerals are known to be efficient INP at these temperatures (e.g. Atkinson et al. 2013) and the concentration of dust particles compared to biological material is likely high (e.g. Fig. 19 of Murray et al. 2012). The focus of our study was therefore mineralogical composition of natural (airborne and surface-collected) dust samples and its role for ice

nucleation. The small post-processing amount of most samples (particularly of the airborne ones) does not allow a systematic study on the effect of heating of the samples on the ice nucleation properties with the same instrumentation (there is simply not enough dust left to repeat the measurements with heated samples). However, we were able to heat some of the samples at 300°C (573 K) for 10h and perform measurements in the condensation mode with the portable ice nucleation chamber, PINC (Chou et al. 2011), at a temperature of 240 K and 242 K (Fig. 1 below). We show here the results at $RH_w = 102$ -105 (240 K) and 100-103% (242 K), the highest measured RH_w . The measurements are not directly comparable to the immersion freezing results obtained with IMCA-ZINC since these RH_w values do not guarantee complete droplet activation prior to freezing during the residence time of the particles in PINC (about 5 s). Nevertheless, they give an indication of the effect heating has on the ice nucleation ability of the particles.

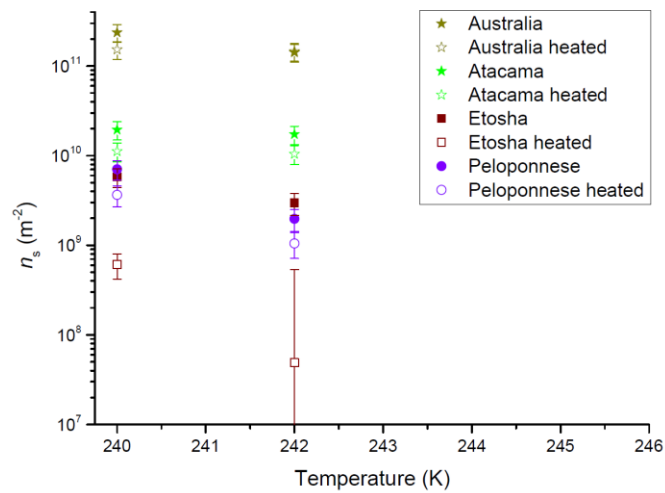


Figure 3: Condensation mode n_s for selected heat treated samples.

Figure 1 shows the condensation mode n_s at 240 and 242 K. Filled symbols refer to unheated, open symbols to heated samples. Heating had little to no effect on the ice nucleation activity of the Australia, the Atacama milled and Peloponnese samples. The Etosha sample lost most of its ice nucleation activity after heating, which is the sample for which we could not relate the comparably high ice nucleation activity to its mineralogy as it consisted mostly of calcite and dolomite, which have a low ice nucleation activity (Atkinson et al. 2013, Kaufmann et al. 2016), and ankerite, of which the ice nucleation activity is not known (Kaufmann et al. 2016). This is consistent with the manuscript conclusions that the ice nucleation activity is mainly caused by the mineralogy of the dust samples. The situation may be different at warmer temperatures but unfortunately we cannot repeat investigations at these conditions due to the small remaining sample size. The full data from these additional measurements and further analysis will be shown in the second paper of the series (Boose et al. 2016).

We have added a paragraph on non-mineral matter mixed with the dust and its potential effects on the ice nucleation ability of the dust (p.4,l.15-20 of the revised manuscript):

“Non-mineral matter, which can become internally or externally mixed with the mineral dust before or after emission, may affect the ice nucleating behavior of the dust. Sulfuric acid (Sullivan et al., 2010;

Augustin-Bauditz et al., 2014) or secondary organic aerosol coating (Möhler et al., 2008a) has been observed to decrease the ice nucleating ability while exposure to ozone (Kanji et al., 2013) or the presence of ammonium sulfate (Boose et al., 2016b) has been suggested to improve it. Biological material can adsorb to mineral dust, keeping its ice nucleating ability and lead to an increased ice-nucleating ability of the dust (Schnell, 1977; Conen et al., 2011; O'Sullivan et al., 2016)."

We have rephrased p.5, l.15-16: "All natural dust samples are expected to be very heterogeneous, i.e. external and internal mixtures of different minerals and potentially biological material (Meola et al., 2015)."

to now p.5, l.28-20 of the revised manuscript:

"The composition of natural dust samples is presumed to be heterogeneous, i.e. external and internal mixtures of different minerals and potentially containing organic or biological material (Meola et al., 2015)."

We have replaced p.14, l.22-23:

"If this is due to reasons other than mineralogy such as coating as suggested by Kaufmann et al. (2016) or if the present minerals ankerite, dolomite or muscovite can lead to a high IN activity at $T < 243$ K under certain circumstances is not known."

with now p.15, l.15-16 of the revised manuscript:

"Measurements in the condensation mode, which are the subject of part 2 of this study, suggest that the ice nucleation activity of this sample is in large part related to organic or biological material mixed with the dust"

We have replaced p.14, l.17-19:

"The results suggest that potential coating of the particles only plays a secondary role for the immersion freezing ability of the mineral dusts as the majority of the results can be explained by the mineralogy as has also been observed by Kaufmann et al. (2016)."

with now p.15, l.10-13 of the revised manuscript:

"While the correlations do not exclude an influence of non-mineral material, the results suggest that potential coatings or mixing of the particles only play a secondary role for the immersion freezing ability at the studied temperatures of the mineral dusts. The majority of the results can be explained by the mineralogy as also observed by Kaufmann et al. (2016)."

References:

Boose, Y., et al.: Heterogeneous ice nucleation on dust particles sourced from 9 deserts worldwide - Part 2: Deposition and condensation freezing, in prep., 2016

Chou, C., Stetzer, O., Weingartner, E., Jurányi, Z., Kanji, Z. A., and Lohmann, U.: Ice nuclei properties within a Saharan dust event at the Jungfraujoch in the Swiss Alps, *Atmos. Chem. Phys.*, **11**, 4725–4738, doi:10.5194/acp-11-4725-2011, 2011.

Murray, B. J., O’Sullivan, D., Atkinson, J. D., and Webb, M. E.: Ice nucleation by particles immersed in supercooled cloud droplets, *Chem. Soc. Rev.*, **41**, 6519, doi:10.1039/c2cs35200a, 2012.

O’Sullivan, D., Murray, B. J., Ross, J. F., Whale, T. F., Price, H. C., Atkinson, J. D., Umo, N. S. and Webb, M.E.: The relevance of nanoscale biological fragments for ice nucleation in clouds, *Sci. Rep.* **5**, 8082, doi: 10.1038/srep08082, 2015.

Answer to Co-Editor Comment and list of relevant changes made in the manuscript:

We thank the co-editor Hinrich Grothe for his comment. We reproduce his comment in *blue* in the following.

Comments to the Author:

You might consider to change the abbreviations INP and IN, since in former papers these shortings have been used with a different meaning: INP was "ice nucleating protein" and IN was "ice nuclei". My suggestion is to wave INP and use IN instead and to use INA for "ice nucleation activity (or ability)".

We have kept "INP" as abbreviation for ice nucleating particle, following Vali et al. 2015. We believe that this abbreviation is common enough to not confuse the reader. We have avoided the abbreviation "IN" in the revised manuscript to avoid confusion with "ice nuclei" and we now always write out "ice nucleation" and "ice nucleation activity".

As other major changes, we have

- renamed the "Namib sample" to "Etosha sample" throughout the manuscript to be more consistent with Kaufmann et al. 2016
- deleted p.9,l. 24-29 because the size distribution of the Australia sample was re-measured using an SMPS and APS. The mean surface area was very close to the original one (within 3%). The n_s values in the revised manuscript include the updated surface area but have changed insignificantly
- binned the IMCA-ZINC FF and n_s data into 1 K bin for visual clarity in Fig. 4
- split up the original Table 5 into Tables 5 and 6 in the revised manuscript
- re-calculated Tables 5 (and 6) after we realized that it was incorrect to correlate the mineralogical fraction with n_s . Instead we correlated the fractions now to $\ln(n_s)$. The trends did not change but the R values changed (typically by 0.03-0.1).
- added sample numbers in Tables 1 and 4 which we refer to in Tables 5 and 6
- added scatter plots (Figure 1 and 2) to the supplementary material corresponding to the correlation analysis in 3.3
- added Figure 3 to the supplementary material, showing the correlation of freezing temperatures with mineralogical fraction which were taken from Kaufmann et al. 2016

References:

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Heterogeneous ice nucleation on dust particles sourced from 9 deserts worldwide - Part 1: Immersion freezing

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Abstract. Desert dust is one of the most abundant ice nucleating particle types in the atmosphere. Traditionally, clay minerals were assumed to determine the ice nucleation ability of desert dust and constituted the focus of ice nucleation studies over several decades. Recently some feldspar species were identified to be ice-active at much higher temperatures than clay minerals, redirecting studies to investigate the contribution of feldspar to ice nucleation on desert dust. However, so far no study has shown the atmospheric relevance of this mineral phase.

For this study four dust samples were collected after airborne transport in the troposphere from the Sahara to different locations (Crete, the Peloponnese, Canary Islands and the Sinai Peninsula). Additionally, eleven dust samples were collected from the surface from nine of the biggest deserts worldwide. The samples were used to study the ice nucleation behavior specific to different desert dusts. Furthermore we investigated how representative surface-collected dust is for the atmosphere by comparing to the ice nucleation activity of the airborne samples. We used the IMCA-ZINC set-up to form droplets on single aerosol particles which were subsequently exposed to temperatures between 233 - 250 K. Dust particles were collected in parallel on filters for offline cold stage ice nucleation experiments at 253 - 263 K. To help the interpretation of the ice nucleation experiments the mineralogical composition of the dusts was investigated. We find that a higher ice nucleation activity in a given sample at 253 K can be attributed to the K-feldspar content present in this sample whereas at temperatures between 238 - 245 K it is attributed to the sum of feldspar and quartz content present. A high clay content on the other hand is associated with lower ice nucleation activity. This confirms the importance of feldspar above 250 K and the role of quartz and feldspars determining the ice nucleation activities at lower temperatures as found by earlier studies for monomineral dusts. The airborne samples show on average a lower ice nucleation activity than the surface-collected ones. Furthermore, we find that under certain conditions milling can lead to a decrease in the ice nucleation ability of polymineral samples, due to the different hardness and cleavage of individual mineral phases causing an increase of minerals with low ice nucleation ability in the atmospherically relevant size fraction. Comparison of our data set to an existing desert dust parameterization confirms its applicability for climate models. Our results suggest that for an improved prediction of the ice nucleation ability of desert dust in the atmosphere, the modelling of emission and atmospheric transport of the feldspar and quartz mineral phases would be key while other minerals are only of minor importance.

1 Introduction

Predicting the occurrence and evolution of clouds at temperatures (T) below 273 K remains a challenge for global and regional climate models (Boucher et al., 2013). One source of uncertainty is the effect of certain aerosol particles which influence the cold cloud microphysics by acting as ice nucleating particles (INPs). Ice formation affects precipitation, cloud life time and radiative properties of these clouds and by that global climate (Lohmann and Feichter, 2005). Mineral dust particles have been known as efficient INPs at $T \leq 253$ K for more than 60 years (e.g. Isono 1955, and references given in Hoose and Möhler 2012; Murray et al. 2012) and have been observed to nucleate ice in the atmosphere in various regions worldwide (Kumai, 1976; DeMott et al., 2003; Chou et al., 2011; Boose et al., 2016a, b). However, the molecular mechanisms and particle properties triggering ice nucleation on atmospheric mineral dusts are still subject of ongoing research. Supercooled cloud droplets can freeze homogeneously at temperatures below 235 K, without the aid of an INP (Schaefer, 1946; Mason and Ludlam, 1950). At higher temperatures the surface of an INP is required to overcome the energy barrier of freezing. Traditionally, four pathways of ice nucleation are differentiated (Vali et al., 2015):

- 1) deposition nucleation where ice forms on an INP directly from the vapor phase;
- 2) condensation freezing, in which ice forms during the process of water condensing on an INP;
- 3) immersion freezing where an INP immersed in a supercooled cloud droplet initiates freezing;
- 4) contact freezing where the interaction of an INP with the surface of a supercooled droplet either from the outside or inside of the droplet leads to freezing.

Ice formation in clouds with top temperatures above 263 K is often observed (Hobbs and Rangno, 1985) but only very few aerosol particle types have been identified to nucleate ice at these warm temperatures. These are mainly biological particles, such as certain bacterial strains or macromolecules (Schnell and Vali, 1976; Krog et al., 1979; Möhler et al., 2008b; Pummer et al., 2012). The ice nucleation ability of soot (Brooks et al., 2014; Kulkarni et al., 2016) at heterogeneous freezing temperatures is still debated as contradicting results were observed, spanning from hardly any ice nucleation ability at $T > 236$ K (Kanji et al., 2011) to up to 3 % of soot particles active in the immersion mode (DeMott, 1990). Similarly, the reported freezing behavior of secondary organic aerosol particles varies from inefficient to comparably efficient (Möhler et al., 2008a; Prenni et al., 2009; Wang et al., 2012; Ladino et al., 2014; Ignatius et al., 2016). Aerosol particles from marine sources are believed to be important INP at remote locations and are subject of current research (Knopf et al., 2011, 2014; DeMott et al., 2015a; Wilson et al., 2015). Recently, the K-feldspar microcline and the Na-feldspar albite, both minerals found in atmospheric dust, have been identified to nucleate ice at temperatures up to 271 K (Harrison et al., 2016).

For the implementation of ice nucleation into climate models, a simplistic description of ice formation on different INP types is required. Existing parameterizations for dust can be based on laboratory experiments using commercially available dusts such as Arizona Test Dust (ATD) including mostly pure clay mineral samples such as illite, kaolinite or montmorillonite (Lüönd et al., 2010; Murray et al., 2011; Niedermeier et al., 2011), dust samples collected from the surface (Niemand et al., 2012) or on in-situ measurements in the atmosphere at locations often distant from major dust sources (DeMott et al., 2010; Tobo et al., 2013). One recent study by DeMott et al. (2015b) combines laboratory data of two surface-collected dust samples with

results from two flight campaigns over the Pacific Ocean and the Caribbean Sea within dust layers that underwent long-range transport from Asia and the Sahara, respectively. The authors found relatively good agreement amongst the different samples. They concluded that both a parameterization from Niemand et al. (2012) as well as one adapted from Tobo et al. (2013) were applicable for predicting atmospheric mineral dust INP concentrations.

- 5 For laboratory ice nucleation experiments, dust samples collected from the surface typically have to be sieved or milled, which may break up larger agglomerates and alter the size-dependent mineralogy (Perlwitz et al., 2015). This could significantly alter the ice nucleation ability of these dust particles in laboratory experiments compared to their ambient ice nucleation ability. It has been shown that milling of hematite or quartz particles leads to an increase in ice nucleation efficiency compared to the unmilled samples (Hiranuma et al., 2014; Zolles et al., 2015). It has been speculated that this is also part of the reason for ATD,
- 10 a commercially available dust sample that is washed and milled after collection from a certain desert area in Arizona, being more ice nucleation active than natural unprocessed dust samples (Möhler et al., 2006).

Due to their high abundance, for many decades the immersion freezing behavior of atmospheric dust was attributed largely to clay minerals and ice nucleation on relatively pure clay mineral samples were often studied in more detail (Hoffer, 1961; Lüönd et al., 2010; Murray et al., 2010, 2011; Broadley et al., 2012; Pinti et al., 2012; Welti et al., 2012; Hiranuma et al., 2015).

- 15 Recently, Atkinson et al. (2013) showed that compared to other minerals feldspar particles are more efficient immersion mode INP at temperatures above 245 K. The K-feldspars (microcline, orthoclase and sanidine) were found to be more ice nucleation-active than the Na/Ca-feldspars albite, anorthite and other plagioclase feldspars (Atkinson et al., 2013; Zolles et al., 2015; Peckhaus et al., 2016). Amongst the K-feldspars microcline appears to be the most ice nucleation-active (Augustin-Bauditz et al., 2014; Kaufmann et al., 2016), even nucleating ice at a temperature of 271 K (Harrison et al., 2016). Feldspar is a highly
- 20 complex group of minerals and, depending on the source, mineralogically similar samples can have different ice nucleation abilities (Harrison et al., 2016). Thus it remains an open question if and how feldspar is affecting the ice nucleation behavior of dust in the atmosphere and if it is causing ice nucleation in clouds at $T > 263$ K. A high variability in ice nucleation activity was found for quartz, with some quartz samples being more ice nucleation-active in the immersion mode than clay minerals but always less than the feldspars (Atkinson et al., 2013; Zolles et al., 2015; Kaufmann et al., 2016). It is suspected
- 25 that functional groups on the surface of feldspars and quartz are responsible for their higher ice nucleation ability (Zolles et al., 2015) but it is unknown where the high variability stems from. Quartz is commonly (5-50 wt%) found in atmospherically transported Saharan dust samples (Avila et al., 1997; Caquineau et al., 1998; Alastuey et al., 2005; Kandler et al., 2009). A recent study by Kaufmann et al. (2016) investigated the ice nucleation ability of surface-collected samples from eight different arid regions worldwide and several single-mineral reference samples using differential scanning calorimetry. The authors found at
- 30 maximum a 6 K spread in freezing temperatures of emulsion experiments amongst surface-collected samples from different atmospheric-dust source regions. They confirmed the exceptional freezing ability of microcline but found only a minor fraction (4 wt%) in one of the samples from the dust source regions studied. Their samples contained quartz fractions between 1 and 26 wt%, K-feldspar fractions between 0 and 10 wt%, and plagioclase fractions between 0 and 22 wt%.

It has been observed that the size distribution of dust changes during its emission and transport compared to dust on the surface. This leads to variations in the mineralogical composition of the dust (D'Almeida and Schütz, 1983; Murray et al., 2012;

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Knippertz and Stuut, 2014), as the mineralogical composition is size dependent due to differences in the hardness, cleavage, shape and reactivity of minerals. Hard minerals such as feldspar tend to be dominant in the large grains whereas soft minerals are concentrated in the small size fraction (e.g. clay minerals). Saltation and dust emission strength depends on several factors and is nonlinear in dust particle size (Knippertz and Stuut, 2014). During atmospheric transport, gravitational settling or wet deposition further alters the size distribution. Additionally, minerals which act as cloud condensation nuclei or INP are preferably lost.

Airborne dust particles smaller than 20 μm over the North Pacific have been found to contain 10 to over 50 wt% clay minerals such as illite, kaolinite or smectite, 4 - 40 wt% quartz and 4 - 75 wt% plagioclase feldspar (Leinen et al., 1994). Kandler et al. (2009) found that dust particles over Morocco consist of about 30 wt% clay minerals (illite, kaolinite, chlorite), less than 5 wt% plagioclase but over 20 wt% K-feldspar, less than 10 wt% quartz and less than 10 wt% calcite in the size range below about 20 μm geometric diameter. Other identified minerals in the airborne dust were rutile, gypsum, dolomite, hematite or halite. Similar results were found by Falkovich et al. (2001) over Israel. Caquineau et al. (1998) found a north-south gradient of the illite to kaolinite ratio of soil samples in the Sahara with higher values in the northern and western part of the Sahara and lower values in the southern and central Sahara.

Non-mineral matter, which can become internally or externally mixed with the mineral dust before or after emission, may affect the ice nucleating behavior of the dust. Sulfuric acid (Sullivan et al., 2010; Augustin-Bauditz et al., 2014) or secondary organic aerosol coating (Möhler et al., 2008a) has been observed to decrease the ice nucleating ability while exposure to ozone (Kanjani et al., 2013) or the presence of ammonium sulfate (Boose et al., 2016b) has been suggested to improve it. Biological material can adsorb to mineral dust, enhancing its ice nucleating ability (Schnell, 1977; Conen et al., 2011; O'Sullivan et al., 2016).

In this study we investigate the immersion ice nucleation properties of 15 dust samples from nine different deserts around the world. Four of the samples were collected directly from the air (Tenerife) or by deposition after atmospheric transport (Crete, Egypt, Peloponnese) for subsequent analysis in the laboratory without additional treatment such as sieving or milling. Based on back trajectory analysis, the four airborne samples originate from different parts of the Sahara. The ice nucleation ability of these airborne dusts was compared to that of several samples collected in the desert. The effect of sieving and milling on the ice nucleation behavior of two surface-collected samples was investigated.

Immersion mode ice nucleation measurements at temperatures between 235 and 250 K were conducted with the combination of the Zurich Ice Nucleation Chamber, ZINC (Stetzer et al., 2008), and the Immersion Mode Cooling chamber, IMCA (Lüönd et al., 2010). Particles of four dust samples were collected on filters for subsequent offline analysis with the Frankfurt Ice Deposition Freezing Experiment (FRIDGE) counter operated in the droplet freezing mode as described by Ardon-Dryer and Levin (2014) and Hiranuma et al. (2015). This allowed examination of immersion freezing at temperatures between 250 and 262 K, covering a wider range of heterogeneous freezing temperatures than would otherwise be possible with IMCA-ZINC alone.

The aim of the current, and a follow-up study on deposition/condensation nucleation, is to investigate the link between ice nucleation and bulk mineralogy of desert dust as it is found in the atmosphere and to compare it to surface-collected samples. By using aeolian transported samples, the particle size distribution and sample composition are as realistic as possible. To our

knowledge this is the first study to investigate ice nucleation behavior of airborne desert dust in the laboratory, compare it with surface-collected natural dust samples and link it to the mineralogical composition of these complex samples. With samples from nine different deserts we present a data set covering most major global dust sources.

2 Methods

2.1 Dust sample origins and processing

The immersion mode freezing behavior of a total of 15 different dust samples was investigated. The collection sites are shown in Fig. 1 together with the major dust emission sources and common atmospheric transport pathways. GPS coordinates of the collection sites are provided in the supplementary material. It can be seen from Fig. 1 that the dust samples stem from most of the major atmospheric dust sources. The Tenerife sample was collected directly from the air over four days in August 2013 at the Izaña observatory on Tenerife, Spain, using a custom-made large cyclone (Advanced Cyclone Systems, S.A.: flow rate: $200 \text{ m}^3 \text{ h}^{-1}$, $D_{50} = 1.3 \text{ } \mu\text{m}$, the diameter at which the collection efficiency is 50 %). After deposition on a roof and on solar panels, dust samples were collected at the Aburdees observatory, Egypt on 10 May, 2010 and in Crete and the Peloponnese in Greece in April, 2014. The Crete sample was an integrated sample over several dust events whereas the Peloponnese sample was from one single dust event. Surface collection sites were (i) the Atacama desert in Chile; (ii) a location approximately 70 km from Uluru in Australia; (iii) the Great Basin in Nevada and (iv) the Mojave desert in California, USA; (v) a Wadi in the Negev desert, approximately 5 km from Sde Boker in Israel; (vi) dunes in the Sahara, close to Merzouga in Morocco; (vii) dunes in the Arabian desert in Dubai; (viii) the Etosha pan in Namibia, a dry salt pan; and (ix) the Taklamakan desert in China. The Israel sample and the Etosha sample are from the same batch as those studied in Kaufmann et al. (2016).

The surface-collected samples needed to be sieved to separate the grain sizes larger than $32 \text{ } \mu\text{m}$ from the remaining sample to avoid clogging of the aerosol generation system used for the ice nucleation experiments. Samples were sieved in a cascade of dry sieves with the smallest cut-off size being at $32 \text{ } \mu\text{m}$ diameter (Retsch Vibratory Sieve Shaker AS 200). Typically only a few weight percent of the sample was in this size range. The Australia and Morocco samples had no fraction in this size range and thus were milled using a vibratory disc mill (Retsch, model RS1). For the Morocco sample, particles of the lowest size bin (32 to $64 \text{ } \mu\text{m}$) were milled. The Australia sample was first sieved with a coarse, millimeter range sieve to separate any large material, and the remaining sand was milled. For the Atacama and Israel samples, both a milled and a sieved sample were compared to investigate the effect of milling on ice nucleation. In case of the Atacama sample, part of the unsieved sample was milled. The Israel sample was first sieved and part of the sieved sample with $d \leq 32 \text{ } \mu\text{m}$ was milled. The sub- $32 \text{ } \mu\text{m}$ size fraction of the other samples was too small to investigate the milling effect. The composition of natural dust samples is presumed to be heterogeneous, i.e. external and internal mixtures of different minerals and potentially containing organic or biological material (Meola et al., 2015). Additionally, they have probably undergone natural aging processes due to the exposure to the atmosphere of the surface-collected samples and actual atmospheric aging of the airborne samples (Dall'Osto et al., 2010). This could physically or chemically alter the surface of the dust particles, potentially changing the ice nucleation properties compared to the pure mineral dust particles. Effects of washing or heating of the samples, which could yield information on

coating or mixing, could not be investigated in this part of the study due to the small sample size of the airborne samples.

2.2 Dust particle generation

The dust samples were dry dispersed into a 2.78 m³ stainless steel aerosol reservoir tank (Kanji et al., 2013) using a Rotating Brush Generator (RBG, Palas, model RBG 1000) with N₂ (5.0) as carrier gas via a cyclone that confined the dust size distribution to below $D_{50} = 2.5 \mu\text{m}$. The maximum particle concentration in the tank was about 1200 cm⁻³ and decreased steadily to about 300 cm⁻³ over approximately 10 h. Before each experiment, the tank was cleaned by repeatedly evacuating and purging it with N₂ until the particle concentration decreased to 30 - 90 cm⁻³. The total particle concentration was monitored with a Condensation Particle Counter (CPC; TSI model 3772). The ice nucleating particle counters, the particle collection for offline FRIDGE experiments and the instruments measuring the particles' size distribution sampled directly from the tank. For the IMCA-ZINC measurements the particle concentration was diluted to about 60 cm⁻³ to avoid coincidence effects in the detector which occur if more than one particle is present in the laser beam of the detector (Nicolet et al., 2010).

2.3 Aerosol particle size distribution

The particle size distribution in the reservoir tank was monitored using a Scanning Mobility Particle Sizer (SMPS; TSI; DMA model 3081, CPC model 3010) for mobility diameters (d_m) between 12.2 - 615 nm and an Aerodynamic Particle Sizer (APS; TSI; model 3321) for aerodynamic diameters (d_{aer}) between 0.5 - 20 μm . After converting the mobility and aerodynamic diameter to volume equivalent diameter (d_{ve}) the size distributions were merged. A shape factor of $\chi = 1.36$ and a particle density of $\rho = 2.65 \text{ g cm}^{-3}$ were assumed for the conversion. These values lie in the range of natural dust samples analyzed in earlier studies, e.g. quartz: $\chi = 1.10\text{-}1.36$ (Hinds, 1999; Alexander, 2015), $\rho = 2.6 \text{ g cm}^{-3}$ (Hinds, 1999; Kandler et al., 2007), illite NX: $\chi = 1.49$ and $\rho = 2.65 \text{ g cm}^{-3}$ (Hiranuma et al., 2015). Assuming spherical particles, the area size distribution was calculated and fitted with a bimodal lognormal distribution. The mean particle surface area ($\overline{A_{\text{ve,w}}}$) was calculated from the resulting fit for each sample (see Table 1) as well as the corresponding surface area-weighted mean diameter ($\overline{d_{\text{ve,w}}}$). Over the course of a single experiment the size distribution changed as larger particles settle out of the volume faster than smaller ones. This effect was reduced by a fan inside the aerosol tank leading to $\overline{A_{\text{ve,w}}}$ varying by 6 to 24 % over the course of an experiment for the different samples, except for the Great Basin sample (64 %), which was coarser than the other samples and settled out faster.

Figure 2 shows a schematic of the different size fractions resulting from the different collection methods and post-treatment (sieving/milling) of the samples used for ice nucleation experiments in the tank and the mineralogical analysis. Due to the small amount of sample, a mineralogical analysis of the identical size fraction as in the tank ($< 2.5 \mu\text{m}$) was not possible. Instead, we used the entire size fraction of the airborne samples, the smallest size fraction of the sieved samples ($< 32 \mu\text{m}$), and of the milled samples the whole size distribution after milling.

2.4 Mineralogy analysis

The quantitative mineralogical composition of the bulk dust samples was investigated using the X-ray diffraction (XRD) Rietveld method (Rietveld, 1969) using a Bragg-Brentano diffractometer (Bruker AXS D8 Advance with CoK α -radiation). The qualitative phase composition was determined with the software DIFFRACplus (Bruker AXS). On the basis of the peak positions and their relative intensities, the mineral phases were identified in comparison to the PDF-2 data base (International Centre for Diffraction Data). The quantitative composition was calculated by means of Rietveld analysis of the XRD pattern (Rietveld program AutoQuan, GE SEIFERT, Bergmann et al. 1998; Bish and Plötze 2011).

The results and uncertainties for the mineralogy of each sample given from the Rietveld refinement are provided in Tables 2 and 3. For the Egypt sample the mineralogical composition is associated with a significantly higher uncertainty because the amount of sample was small and the measured intensity of the diffracted X-rays very low. In this case the grain statistics were poor and crystals more likely to be arranged in a certain, preferred orientation instead of randomly, leading to a potential over-estimation of some mineral fractions. Similarly, the milling of the Israel sample likely interfered with the preferred orientation of the minor components in the sieved samples, leading to an observed reduction of these mineral fractions (e.g. illite, dolomite, plagioclase) in the milled compared to the sieved sample. The differentiation between the microcline and orthoclase K-feldspar fraction was for some samples not possible (i.e. Morocco and Australia) where both phases were likely present. In case of a low K-feldspar content of a few wt% it was not possible to determine if K-feldspar was present as microcline, orthoclase or sanidine or a mixture of the different phases. Values are given for the K-feldspar with the best Rietveld fit result. As Rietveld fit results for the various Na-plagioclase feldspars (albite, oligoclase and andesine) were often insignificantly different, they are summarized as Na-plagioclase. The fraction of ankerite and dolomite are usually provided together because in some cases (especially Morocco) it was not possible to differentiate between them. Only for the Etosha sample they are provided separately because the fractions were large enough to be distinguishable (Kaufmann et al., 2016).

Due to the broader size range of particles studied with XRD, the mineralogy is not only describing the particles that were studied with the ice nucleation chambers but also the fraction between 2.5 - 32 μm . This could lead to differences between the measured mineralogy and the actual mineralogical composition of particles smaller than 2.5 μm due to differences in the hardness and cleavage or fracture, i.e. the breaking behavior, of different minerals. This is particularly true for softer minerals such as calcite, which has a Mohs hardness of 3 (standard scale of hardness between 1, talc and 10, diamond), and clay minerals (2 - 2.5) in contrast to feldspars (6) and quartz (7) as well as for minerals with a higher cleavage such as gypsum and calcite (perfect cleavage) compared to quartz (without cleavage, for information on mineral cleavage and hardness see www.mindat.org or www.webmineral.com). Natural mechanical weathering thus likely has enhanced the clay mineral and calcite content in the smaller particle fraction whereas feldspars and quartz tend to be found in the larger size fractions. For each filling of the reservoir tank a similar volume of dust sample was used ($\approx 0.2 \text{ cm}^3$) and the dust density is assumed to be comparable (about 2.65 g cm^{-3}). This allows to roughly approximate what fraction of particles was larger than 2.5 μm by the amount of dust sample left over in the 2.5 μm cut-off cyclone and the particle concentration reached in the tank. Hardly any particles were left over in the cyclone and maximum particle concentrations of 900 - 1200 cm^{-3} were reached by all milled

samples apart from the Morocco sample, and by all airborne samples apart from the Egypt sample. We suspect that the Egypt sample has a higher fraction of large particles because it originated from local sources within Egypt and thus the transport time was much shorter compared to the other airborne samples leading to the size distribution being shifted to larger particles. Of the sieved samples, the Dubai, Great Basin, Israel, Mojave and Taklamakan samples had a comparably high fraction of particles larger than $2.5 \mu\text{m}$ and particle concentrations of $400 - 970 \text{ cm}^{-3}$ were reached when filling the tank. For these samples the presented mineralogy may not be fully representative for the particles $< 2.5 \mu\text{m}$ investigated for ice nucleation. In contrast, particles of the Etosha and Atacama sieved samples were mainly smaller than $2.5 \mu\text{m}$ and thus the mineralogy is representative of the small particle fraction. In summary, the identified mineralogical composition is well representative for the particle size fraction used for ice nucleation experiments on the Atacama milled and sieved, sieved Etosha, Israel milled, milled Australia, and the airborne Crete, Peloponnese and Tenerife samples.

2.5 Immersion freezing experiments and data treatment

Immersion freezing experiments between 235 and 250 K were conducted by extending ZINC (Stetzer et al., 2008) with IMCA (Lüönd et al., 2010). ZINC is a vertically oriented continuous flow diffusion chamber (Rogers, 1988) with two flat parallel walls. The walls are ice-coated before an experiment, and by applying a temperature gradient between the two walls at supercooled temperatures supersaturation with respect to ice is established between the walls. To ensure droplet activation of all sampled particles before freezing, IMCA is installed upstream of ZINC. In IMCA a relative humidity of 120 % with respect to water at a temperature of 303 K is provided by humidified filter paper on the two parallel walls of the chamber. Under these conditions, all particles activate such that each droplet contains a single dust particle. The droplets are then cooled to the experimental temperature before they enter ZINC. For the immersion freezing experiments the relative humidity in ZINC is kept at water saturation. The IODE detector (Nicolet et al., 2010) measures the depolarization signal of a linearly polarized laser beam by the particles. This allows differentiation between spherical droplets, which nominally do not lead to a depolarization signal, and the non-spherical ice crystals which depolarize the laser light. The ratio of the detected ice crystal concentration (N_i) to the sum of ice crystals and detected droplet concentration (N_d) is called the frozen fraction (FF):

$$FF = \frac{N_i}{N_d + N_i}. \quad (1)$$

IODE can distinguish the depolarization signal of droplets and ice crystals between the limits of detection (LOD) of $FF = 0.1$ and $FF = 0.9$. Over the course of about 3 h the temperature is stepwise ramped up. Each data point represents 2000 - 3000 single detected particles.

For independent offline immersion freezing measurements between 250 - 263 K with FRIDGE, dust particles were collected by filtration from the tank over 3.5 h using Teflon membrane filters (Fluoropore PTFE, 47 mm, $0.2 \mu\text{m}$, Merck Millipore Ltd.). The particles were then extracted from the filters into vials with 10 ml of deionized water for 10 minutes in an ultrasonic bath. 150 drops of $0.5 \mu\text{l}$ each were randomly placed on a silicon plate on the cold stage of FRIDGE using an Eppendorff-pipette. At ambient pressure conditions the temperature of the cold stage was then lowered by 1 K min^{-1} and the number of drops

freezing as a function of temperature is recorded with a CCD camera. This process is repeated several times with fresh droplets until a minimum of 1000 droplets is exposed. The INP concentration is given by (Vali, 1971; Ardon-Dryer and Levin, 2014)

$$K'(T) = \frac{1}{V_{\text{drop}}} [\ln(N_0) - \ln(N(T))] \frac{V_{\text{water}}}{V_{\text{air}}} \quad (2)$$

where $K'(T)$ is the cumulative INP concentration, V_{drop} is the volume of a droplet, N_0 the number of droplets sampled, $N(T)$ the number of frozen droplets, V_{water} the volume of water used to wash off the particles from the filter and V_{air} the volume of air (N_2 in the current study) sampled through the filter. The temperature uncertainty is ± 0.2 K and the uncertainty in FF typically ± 30 % at $T \leq 260$ K and decreases with lower temperatures.

Due to the small sample amounts particularly of the airborne dust samples, generating monodisperse particles for the ice nucleation measurements was not possible. Earlier studies have shown that the probability of a particle to act as INP scales with the surface area of the particle immersed in a droplet (Archuleta et al., 2005; Welti et al., 2009; Kanji and Abbatt, 2010). So-called ice-active sites (Vali, 1966) are assumed on the surface of an INP in the deterministic concept (Langham and Mason, 1958). The probability of such a site to be present on a particle increases with the surface area. To compare the FF measured in IMCA from samples with different size distributions, the FF is normalized by the mean aerosol particle surface area. This yields the ice-active surface site density, n_s :

$$n_s = - \frac{\ln(1 - FF)}{A_{\text{ve,w}}} \quad (3)$$

In the case of FRIDGE it is calculated as:

$$n_s = - \frac{\ln(1 - \frac{N(T)}{N_0})}{A_{\text{t,drop}}} \quad (4)$$

with $A_{\text{t,drop}}$ being the total aerosol surface area present in each droplet and given as:

$$A_{\text{t,drop}} = \bar{N} V_{\text{air}} \bar{A}_{\text{ve,w}} \frac{V_{\text{water}}}{V_{\text{drop}}} \quad (5)$$

with the mean total aerosol concentration \bar{N} in the reservoir tank during the time of the particle collection as measured by the CPC. The assumption that active sites are uniformly distributed over individual particle surfaces, and therefore that n_s stays constant with particle size, most likely has limitations for complex polymineral samples such as desert dust particles. Therefore, the provided n_s values should not be treated as an exact parameter, valid at any particle size, but rather a normalization method for the bulk natural dust samples $< 2.5 \mu\text{m}$ which we investigated.

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3 Results and Discussion

3.1 Dust size distribution

Most of the size distributions of the different dust samples in the tank were bimodal. Figure 3 shows exemplary SMPS and APS surface area distribution data of four samples together with the bimodal fit. Since one mode was detected in each instrument's

size range, the shape factor χ was optimized to give the best overlap of the two size distributions. For any shape factor within realistic limits for atmospheric dusts ($1.1 \leq \chi \leq 1.6$, Alexander 2015) the two modes remained distinguishable. They are likely related to the high inhomogeneity of the samples with respect to hardness and fracture. Two airborne (Crete and Egypt), one surface-collected sieved and one surface-collected milled (both Israel) samples are shown. The Crete sample has a third small mode at $d_{ve} = 50$ nm. Since the smaller aerosol particles contribute only little to the average surface area, the distribution was also bi-modally fitted. The mean particle surface area values are given in Table 1 together with the relative error $\delta(\overline{A_{ve,w}})$ resulting from a change in distribution during the course of the experiment. All samples peak in number concentration between $d_{ve} = 200 - 400$ nm and a mean particle surface area of $\overline{A_{ve,w}} = 2 - 3.7 \mu\text{m}^2$ corresponding to a diameter of $\overline{d_{ve,w}} = 800 - 1100$ nm. Only the Great Basin sample differs strongly because of the presence of predominantly large particles leading to a high mean particle surface area ($\overline{A_{ve,w}} = 16.4 \mu\text{m}^2$, $\overline{d_{ve,w}} = 2133$ nm). The relative error $\delta(\overline{A_{ve,w}})$ is 64 % in the case of the Great Basin sample because two refills were necessary during the course of the experiment. For all other samples $\delta(\overline{A_{ve,w}})$ is less than 24 %.

3.2 Ice nucleation of desert dust

The plots on the left side of Fig. 4 show the FF as a function of temperature between 235 and 253 K, separately for non-Saharan and the Saharan samples. The majority of the non-Saharan FF curves (Fig. 4a and b) behave similarly, with two samples being distinctly different: the Australia sample shows significantly higher FF values at all temperatures whereas the milled Israel sample falls clearly below the other FF curves for all $T > 237$ K. Of the intermediately active samples, the Taklamakan and Great Basin samples are at the upper end whereas the Dubai sample shows the second lowest FF values. The remaining samples are mostly not significantly different, with FF values lying within each others error bars.

The five Saharan samples in Fig. 4c cover a comparable range of FF to the non-Saharan ones at any temperature. The only surface-collected Saharan sample (Morocco) has higher FF values compared to the airborne Saharan samples. All samples were fit with sigmoidal curves. None of the samples shows a stepwise FF owing to the polydisperse size distribution of the particles. Due to the heterogeneous particle composition, a partial step-like activation spectrum could be expected with decreasing temperature if the single mineral components were externally mixed and not present within one particle. Since ice nucleation activity is also dependent on the surface area of each particle (Archuleta et al., 2005; Connolly et al., 2009; Welti et al., 2009), larger particles will activate at higher temperatures than smaller ones, smoothing out the potential step function of different minerals.

n_s was calculated from the FF using $\overline{A_{ve,w}}$ in Eq. 3 to account for differences in the size distributions which may impact the ice nucleation behavior. The results are shown in the plots on the right side of Fig. 4. The error bars in n_s are derived by error propagation from the error in FF and $\delta(\overline{A_{ve,w}})$ and are dominated by the error in FF . Data points outside of $0.1 < FF < 0.9$ and in the homogeneous freezing regime are omitted. The n_s of the Australian sample remains the highest of all samples and that of the Israel milled sample one of the lowest. The n_s of the Great Basin sample, which has one of the highest FF s, is amongst the lowest, due to its coarse particle sizes. Like their FF , the range of n_s of the Saharan samples is comparable to those of the non-Saharan ones (Fig. 4f). Among the Saharan samples, the n_s of the Tenerife sample is similar to that of Crete,

whereas the Egypt sample is higher for $T > 238$ K. The n_s of the surface-collected and milled Morocco sample is distinctly higher at all temperatures.

To compare all dust samples, the n_s in m^{-2} was fitted using the exponential function:

$$n_s = \exp(-a(T - 273.15\text{K}) + b) \quad (6)$$

- 5 with the fit parameters a and b , which are given in Table 4 for each sample. The resulting fit lines from all samples are shown in Fig. 5a. Overall the Australian sample is by far the most ice nucleation active sample. The Israel milled, the Great Basin, and the Peloponnese sample show a low ice nucleation activity. For comparison, the n_s fits for K-feldspar from Atkinson et al. (2013), for kaolinite KGb-1b from Murray et al. (2011), for Illite NX from Broadley et al. (2012), data for quartz from Atkinson et al. (2013) and Zolles et al. (2015) and the n_s parameterization curve from Niemand et al. (2012) are shown. The
- 10 K-feldspar, kaolinite, illite and quartz curves and data points were provided as $n_{s,\text{BET}}$, i.e. the surface area of the particles was measured with the Brunauer, Emmett and Teller (BET) nitrogen adsorption method (Brunauer et al., 1938). This method yields typically a higher surface area than that based on volume equivalent diameter. The literature $n_{s,\text{BET}}$ was converted to n_s using a conversion factor of 3.5 in case of K-feldspar as given in the supplementary material of Atkinson et al. (2013). For illite, we followed Hiranuma et al. (2015), using a specific surface area (SSA) of $104.2 \text{ m}^2 \text{ g}^{-1}$ (Broadley et al., 2012) and a ratio of
- 15 total surface area to total mass of $6.54 \text{ m}^2 \text{ g}^{-1}$ (Hiranuma et al., 2015). Similarly, for kaolinite we used $SSA = 11.8 \text{ m}^2 \text{ g}^{-1}$, a density of 2.63 g cm^{-3} and a mean mass-weighted diameter of 674 nm (Hudson et al., 2008), yielding a correction factor of 3.49. For the same $n_{s,\text{BET}}$ values, the three quartz samples from Zolles et al. (2015) were active over a range of 10 K. No SSA values were provided therefore we used also a conversion factor of 3.5 given that feldspar is somewhat similar to quartz. This comes with a very high uncertainty, as the size distribution and particle shape of quartz are likely to differ from the K-feldspar
- 20 of Atkinson et al. (2013). The K-feldspar, kaolinite, illite and quartz n_s areas cover the range from the $n_{s,\text{BET}}$ as provided in the literature and the calculated n_s to show the uncertainty inherent to the conversion. It can be seen that all desert dust samples fall between the K-feldspar and the clay mineral and quartz fits at all temperatures.
- Similarly to our study the parameterization from Niemand et al. (2012) was based on the $n_s(T)$ of three polydisperse surface-collected dust samples from China, Egypt and the Canary Islands and one sample collected after deposition in Israel. For
- 25 $T < 250$ K the parameterization falls in the lower end of the range of n_s observed for our broader collection of global surface-collected and airborne dust samples (a factor of 3 to 4 below the average $n_s(T)$ of all measured curves, not shown). Given that the measurements were conducted with different instruments, which can lead to a systematic offset of up to three orders of magnitude in terms of n_s (Hiranuma et al., 2015), and the polydisperse size distribution of the dust samples, the agreement is considered reasonable. The maximum difference in temperature between the parameterization from Niemand et al. (2012) and
- 30 the average of all n_s curves from this study (not shown) is less than 3 K, while the spread in n_s curves across all samples in our study is up to 10 K. The parameterization has a slope close to that of all airborne samples, whereas most of the surface-collected samples show a more moderate slope, i.e. a lower temperature dependence. This can be seen as an indication of active sites, which activate at warmer temperatures, being more frequent in the surface-collected samples compared to the airborne samples.

The high temperature measurements from FRIDGE for four samples are shown in Fig. 5b together with those from IMCA and parameterizations. Again, the desert dusts fall between extrapolations of the clay mineral and K-feldspar fits. The parameterization from Niemand et al. (2012) predicts one to two orders of magnitude higher n_s than measured by FRIDGE. Only for the Atacama milled sample at $T = 251 - 256$ K the parameterization shows about 30 % higher values than the measurements. While at $T < 250$ K the n_s values of the four samples mostly overlap within error bars, at $T > 250$ K the Atacama milled sample has about one order of magnitude higher n_s than the other three samples. This shows that the fits of $n_s(T)$ are not constant over the whole temperature spectrum and are only valid for the given range. It indicates that the Atacama milled sample contains active sites at these temperatures which are missing in the other samples.

Figure 6a shows the median and minimum to maximum $n_s(T)$ range of the airborne and surface-collected samples. This illustrates that the n_s range of the airborne samples falls in the lower half of the n_s range of the surface-collected samples or even below. It shows that for immersion mode ice nucleation surface-collected dust samples are not representative for airborne dust samples, which all stem from North Africa, the world's largest source of atmospheric dust. This might be caused by a non-representative surface-dust collection, e.g. soil rather than dust is collected which has a different size distribution and composition, or dust from a location where threshold wind velocities for dust lifting are not reached. Another cause could be that atmospheric processes taking place during or after particle lofting may alter the particle surface and decrease the ice nucleation ability which has been suggested to occur in the field (Cziczo et al., 2013) and laboratory (Sullivan et al., 2010; Augustin-Bauditz et al., 2014). The potential effects of mineralogy on the ice nucleation activity at different temperatures is investigated in the following section.

3.3 Role of mineralogy

Various earlier studies have shown that the ice nucleation activity expressed by n_s varies by several orders of magnitude between different types of minerals. By analyzing the bulk mineralogy we investigate if the dust's mineralogical composition explains the observed ice nucleation activity. Tables 2 and 3 show the results of the mineralogical analysis of the dust samples. The distinct composition of the Australia sample is striking, consisting almost entirely of quartz (91.3 wt%) and K-feldspars (4.2 wt% orthoclase, 3.9 wt% microcline), which are highly ice-active minerals in the immersion mode (Atkinson et al., 2013; Zolles et al., 2015). The Morocco sample also has a high quartz content (63.8 wt%), followed by the Taklamakan sample (33.1 wt%), both being two of the most ice-active samples of this study. The remaining samples have a quartz content of 23 wt% or less. Another obvious difference is the high feldspar content of both Atacama samples (milled: 22.3 wt% orthoclase, 43.2 wt% Na-plagioclase, sieved: 11.8 wt% orthoclase, 39.3 wt% Na-plagioclase). The milled Atacama sample shows the highest n_s of the four investigated samples in FRIDGE at $T > 250$ K (Fig. 5b), close to the K-feldspar parameterisation by Atkinson et al. (2013) at $260 < T < 262$ K and also higher activities than the sieved sample at $T > 240$ K (Fig. 6b). The Israel samples have a distinctly high calcite content (milled: 81 wt%, sieved: 67.2 wt%), followed by Dubai (37.2 wt%) and Peloponnese (33 wt%). Calcite has been found to be a weakly ice-active mineral in the immersion mode (Atkinson et al., 2013; Zolles et al., 2015) and also in the condensation mode (Roberts and Hallett, 1969; Zimmermann et al., 2008). The Etosha

sample consists of about one quarter each of calcite (29 wt%), dolomite (27 wt%) and ankerite (23 wt%) with 10 wt% muscovite and no significant fraction of clay minerals, feldspars or quartz (1 wt% smectite and 1 wt% quartz were identified). This is surprising as the Etosha sample is one the most ice nucleation-active samples at $T < 242$ K. The ice nucleation ability of the mica muscovite is debated as some studies have found hardly any ice nucleation activity at heterogeneous freezing temperatures (Atkinson et al., 2013; Campbell et al., 2015; Kaufmann et al., 2016) while others found significant ice nucleation ability at $T < 243$ K (Steinke, 2013; Abdelmonem et al., 2015). Kaufmann et al. (2016) found little ice nucleation activity of a reference dolomite sample. Thus, the high ice nucleation activity at $T < 242$ K of the Etosha sample is not explainable by the known ice nucleation ability of its mineral components. To our knowledge, no study so far has investigated the ice nucleation behavior of pure ankerite.

The remaining samples are more complex mixtures of quartz, feldspars, clay minerals, micas and other minerals. We find less than 8 wt% microcline in the sieved and milled Israel and the airborne Tenerife samples. In the samples from Australia and Morocco both K-feldspars orthoclase and microcline seem to be present. The surface-collected Great Basin sample contained 30 wt% microcline in the bulk sample but likely much less in the size fraction $< 2.5 \mu\text{m}$. The Saharan samples show a great variety with the Tenerife sample having the highest content of clay minerals (illite + kaolinite + palygorskite: 43.3 wt%) of all dusts, similar to the findings of Alastuey et al. (2005). The other airborne Saharan samples (Egypt, Peloponnese and Crete) consist to about 50 wt% of quartz and calcite, likely due to different source regions within the Sahara. The mineral fraction of the main minerals in soil samples is not homogeneous throughout the Sahara (Nickovic et al., 2012). Based on air mass back trajectory calculations the Tenerife sample originated in Northern Mauritania or Morocco, whereas the Egypt sample stemmed from local sources in Egypt and the Peloponnese and Crete samples from Northern Saharan sources in Algeria, Tunisia and Libya. Schütz and Sebert (1987) found that the mineral composition of the size fraction $< 5 \mu\text{m}$ of surface-collected samples in the Sahara was very similar throughout the Sahara and concluded that this size fraction is already well mixed within the desert. The main differences were a higher calcite and palygorskite content in the Northern Sahara which is consistent with our findings for the Egypt, Peloponnese and Crete samples in the case of calcite. We find comparable amounts of palygorskite in the Crete, Peloponnese and Tenerife samples (4.5 - 5.3 wt%) but no palygorskite in the Egypt and Morocco samples. The differences with regard to mineralogical composition and ice nucleation ability found between the Morocco (higher quartz content) and Tenerife (higher clay mineral content) samples shows that, even if the source region of an airborne sample can be roughly localized, the mineralogy of surface-based and airborne samples can differ: surface-collected samples are not necessarily representative of the dust aerosol. This is supported by the fact that the Morocco sample consisted mostly of dust grains larger than $32 \mu\text{m}$, which sediment quickly before being transported long distances in the atmosphere.

In the following we investigate if the different n_s values of the dust samples can be attributed to their mineralogy. For this, we compare the fraction of single minerals to the n_s of our dust samples at five different temperatures, using the most prominent minerals which have been found to have n_s values in a range which is measurable with IMCA-ZINC (Atkinson et al., 2013; Hiranuma et al., 2015; Zolles et al., 2015; Harrison et al., 2016; Peckhaus et al., 2016). Those are quartz, illite, kaolinite, and calcite. Additionally, we compare the samples' n_s to the following sums of minerals: K-feldspars (microcline plus orthoclase); all feldspars (K-feldspars plus Na-plagioclase feldspars); sum of all feldspars plus quartz; sum of all feldspars plus quartz plus

illite and/or kaolinite. We do not differentiate between the different K-feldspar polymorphs because even the same type of feldspar can vary in n_s as shown by Harrison et al. (2016) due to the complex structure of feldspars. For each temperature, all samples which showed a FF between 0.1 and 0.9 were used for the correlations. The Etosha sample was excluded from the correlations with feldspars, quartz and clays, as it does not contain any significant amount of these minerals. However, it was included for the comparison with calcite.

Table 5 shows the Pearson correlation coefficients (R) between the mineral fractions and the n_s at five temperatures. Only a few correlations are statistically significant, owing to the low number of samples. Nevertheless, the overview of the correlation coefficients gives an idea of the effect of certain minerals on n_s . The related scatter plots are given in Figure 1 of the supplementary material.

At 253 K only three samples (Atacama milled, Egypt and Taklamakan) are available for comparison. For these, the K-feldspar content leads to a very high correlation ($R = 0.97$) and adding the Na-plagioclase to the feldspar sum reduces the R value to 0.87. At lower temperatures, no correlation is found between the K-feldspar content and n_s . At 245 K, the n_s correlates best ($R = 0.89$) with the quartz alone and adding feldspar, illite or kaolinite leads to a lower R value (0.67 - 0.81). This is in agreement with earlier studies showing the comparable high immersion mode ice nucleation activity of some quartz samples at this temperature (Atkinson et al., 2013; Zolles et al., 2015). Interestingly, this behavior stays the same at 243 K ($R = 0.91$). At 240 K and 238 K the quartz correlation is not as good and adding feldspars to the quartz improves the correlation (from $R = 0.52$ and 0.45 to 0.65 and 0.54 , respectively). Note that the Australia sample, which has the highest quartz content, is excluded at 240 K and 238 K from the correlation analysis because FF was > 0.9 . Illite alone shows a weak negative correlation with n_s at any of the investigated temperatures and leads to reduced or constant R values when added to the quartz plus feldspar sum. Also calcite and kaolinite are negatively correlated with n_s at all presented temperatures. This means that a higher ice nucleation activity in one sample can be attributed at 253 K to the K-feldspar content present in this sample whereas at temperatures between 238 - 245 K it is attributed to the sum of feldspar and quartz content present. A high clay mineral content on the other hand is associated with lower ice nucleation activity. To exclude a bias from varying numbers of samples at different temperatures, we have repeated the correlations at 245, 243, 240 and 238 K for the Atacama milled, Egypt and Taklamakan samples only. The corresponding scatter plots are provided as Figure 2 of the supplementary material and confirm the observations that quartz plus feldspar yield the best correlations at $T < 245$ K.

These results need to be treated carefully, because the mineralogy is derived from the full size range up to $32 \mu\text{m}$ and may be different to the studied size fraction ($< 2.5 \mu\text{m}$). Therefore, we do the same analysis exclusively for the samples for which the size fraction larger than $2.5 \mu\text{m}$ was small and the mineralogical composition determined by XRD can be assumed to be representative for particles $< 2.5 \mu\text{m}$. These samples are: the Atacama milled and sieved samples, the sieved Etosha, milled Israel and Australia, and the airborne Crete, Peloponnese, and Tenerife samples. From these samples only the ice nucleation ability of the Atacama milled and the Etosha sample was measured with FRIDGE at 253 K and only two of the samples show measurable n_s at 245 K in the IMCA data, thus those temperatures are excluded. The results for 243 K, 240 K, and 238 K are given in Table 6. The correlation with illite and kaolinite is still negative at any temperature despite the fact that some of the samples in this subset contain a comparably large amount of clay minerals (Tenerife: 38.5 wt%, Peloponnese: 20.2 wt%). At

- 243 K quartz shows the highest R value (0.99) for the selected samples. At 240 K and 238 K the sum of all feldspars ($R = 0.99$ and $R = 0.94$) and the sum of all feldspars plus quartz ($R = 0.96$ and $R = 0.94$) show the highest correlation with n_s . This is different to when all samples were included, where quartz exclusively led to the highest R values. The difference stems mainly from the exclusion of the Morocco, Taklamakan, Egypt and Great Basin samples, which all had a high quartz content.
- 5 It should be noted that XRD is a bulk analysis of the mineralogical composition whereas ice nucleation is a process sensitive to the particle's surface, including cracks, crevices or pores (Marcolli, 2014; Welts et al., 2014). Despite this difference in sensitivity, a high correlation between bulk mineralogy and ice nucleation activity is found in this study. As XRD does not allow any inference of the mixing state of different minerals it is not known, particularly for the small particles, if each particle contains some amount of quartz and/or feldspar or if pure calcite or clay mineral particles exist. However, our results indicate
- 10 that feldspar or quartz present in the bulk dust will dominate its freezing behavior down to 238 K. While the correlations do not exclude an influence of non-mineral material, the results suggest that potential coatings or mixing of the particles only play a secondary role for the immersion freezing ability at the studied temperatures of the mineral dusts. The majority of the results can be explained by the mineralogy, as also observed by Kaufmann et al. (2016). This may be due to a significant dilution of coating material in the droplets forming on each dust particle and may have a more prominent role in deposition nucleation.
- 15 Measurements in the condensation mode, which is the subject of part 2 of this study, suggest that the ice nucleation activity of this sample is in large part related to organic or biological material mixed with the dust.

3.4 Effect of milling

- Two of the dust samples have undergone two different treatments (sieving and milling) to compare the effect of milling on n_s of a polymineral sample. The Israel sample was first sieved and then part of the $d \leq 32 \mu\text{m}$ fraction was milled. For the Atacama sample, the original sample containing particles of all sizes was split, one part was sieved and one part milled. The resulting n_s curves are shown in Fig. 6b. Interestingly, the two sieved samples are very similar in n_s . The milling of the Atacama sample led to a slightly higher ice nucleation efficiency at $T > 240 \text{ K}$ compared to the sieved sample. Contrastingly, for the Israel sample milling led to a decrease in n_s at all studied temperatures above 237 K. The latter could be related to the high calcite content
- 25 of the Israel dust. Calcite is a rather soft mineral with a Mohs hardness of 3 and a perfect cleavage, and during the milling process it could be ground to a smaller grain size faster than compared to harder minerals such as quartz (Mohs hardness of 7) or feldspar (6). Thus the size fraction $d_{ve} \leq 2.5 \mu\text{m}$ (the D_{50} cut-off of the particle generation system used) could be enriched in calcite. Calcite has been found to be ice-active only very close to the homogeneous freezing regime (Atkinson et al., 2013; Zolles et al., 2015) and negatively correlated with n_s at all presented temperatures in this study (Tables 5 and 6). Similarly, the
- 30 slightly higher n_s at $T > 240 \text{ K}$ of the milled Atacama sample is likely due to more feldspar being present in the $d_{ve} > 32 \mu\text{m}$ fraction compared to the sieved sample, which then got milled into sizes $d_{ve} < 2.5 \mu\text{m}$. It can be seen from Tables 2 and 3 that the K-feldspar (orthoclase) content is higher in the Atacama milled sample (22 wt%) than in the sieved one (12 wt%). The milled sample mostly consisted of particles smaller than $2.5 \mu\text{m}$, whereas the sieved one had a large fraction of particles larger than $2.5 \mu\text{m}$. Thus, there was likely more orthoclase content in the milled Atacama sample particles smaller than $2.5 \mu\text{m}$

compared to those in the sieved sample, leading to higher n_s at warmer temperatures. Effects such as an increase in surface irregularities, defect density and functional groups due to the milling as reported by other authors (Hiranuma et al., 2014; Zolles et al., 2015), are not excluded but were not investigated in this study. An increase in defect density and surface irregularities has been shown to increase the ice nucleation activity of monomineral or single compound samples. As milling reduced the ice nucleation activity of the Israel sample, we conclude for this specific sample that any morphology effect is small in comparison to the change in mineralogical composition of the analyzed size range caused by the milling. This emphasizes the importance of mineralogy for the surface sensitive ice nucleation process.

4 Conclusions

- 10 The ice nucleation ability in the immersion mode of 15 natural desert dust samples was quantified by the frozen fraction and ice-active surface site density, and compared with the bulk dust mineralogy. A diverse mineralogical composition was found for the different desert dust samples which can be related to variable ice nucleation abilities. The comparison showed that at temperatures above 250 K the highest n_s is related to the highest K-feldspar content in the sample confirming earlier findings on the superior ice nucleation ability of K-feldspars compared to other minerals. Microcline was found in one airborne sample (6 wt%) and in surface-collected samples from four different locations. We could not confirm a superior role of microcline over orthoclase, in-part because a differentiation of the two minerals was often difficult and partly because their content was too low in the size range investigated for ice nucleation to cause an effect detectable with the IMCA-ZINC experiment. We cannot therefore conclude that microcline is generally atmospherically not relevant because even in low amounts of a few percent it could glaci-ate clouds at temperatures warmer than 253 K.
- 15 At temperatures below 250 K, the ice nucleation ability was mainly attributed to the quartz content of the samples, as well as to the sum of all feldspars (K-feldspars and Na-plagioclase feldspars). Keeping in mind that quartz is ubiquitous in atmospheric desert dust, this suggests that quartz plays a more prominent role for atmospheric ice nucleation than previously thought. The clay mineral (illite and kaolinite) and calcite content of the dust samples negatively correlated with n_s at all studied temperatures, suggesting a minor importance of these minerals for the ice nucleation activity of natural dust samples in the immersion mode, especially if quartz or feldspar are present. Atkinson et al. (2013) suggested that the global mineral dust INP concentration down to a temperature of about 240 K is dominated by feldspar. At temperatures between the homogeneous freezing limit and 240 K, where quartz is an active INP, it dominates the total INP concentration as it is much more abundant than feldspar. Our experiments on natural dust confirm this suggestion.
- 20 The variation in mineralogy with particle size leads to variations in n_s . The most ice nucleation-active mineral feldspar is less common in the smallest dust size fractions. Quartz is found in all size ranges but more common in the larger dust size fractions. The less ice nucleation-active clay minerals and calcite dominate the small size fraction. As the size distribution of dust changes during atmospheric transport, a resulting change in mineralogy will have implications for the atmospheric relevance of certain mineral components. Three of the four airborne samples (Crete, Peloponnese and Tenerife) had the highest clay mineral
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- 30

content and were amongst the least ice nucleation-active samples. For all desert dust samples we found a high correlation of the ice nucleation activity of particles smaller than $2.5\ \mu\text{m}$ with the quartz content of the dust samples. This shows that despite the dominance of the clay minerals in the small size fraction, quartz is an important atmospheric INP component and also found in the particle size fraction with the longest atmospheric residence time.

- 5 Milling of dust samples in the laboratory or by natural mechanical weathering processes can lead to more surface inhomogeneities and also to an enrichment of more ice nucleation-active minerals, such as quartz, in sizes relevant for atmospheric ice nucleation. This potentially explains the higher ice nucleation activity of Arizona test dust compared to desert dust samples found in earlier studies (Zolles et al., 2015; Kaufmann et al., 2016). The observed differences between the surface-collected and the airborne Saharan dust samples suggest that surface-collected dust may not be representative of atmospheric dust trans-
- 10 ported over long distances. Thus, more ice nucleation studies on airborne, transported dust also from deserts other than the Sahara are crucial to quantify the ability of atmospheric dust to nucleate ice. Furthermore, if airborne dust is generally found to be less ice nucleation-active than surface-collected dust and does not show ice nucleation activity at temperatures above 263 K, it cannot explain first ice formation in clouds with top temperatures warmer than 263 K. For that other INP such as biological particles or different mechanisms such as seeder - feeder processes would need to be investigated. In our study the
- 15 ice nucleation activity of only one sample (Etosha) was not explainable by the known ice nucleation activity of its mineral components. The role of adsorbed organic material for the ice nucleation activity of the dust samples will be investigated in part 2 of this paper series.

The applicability of the parameterization by Niemand et al. (2012) to describe an average ice nucleation behavior of desert dust was confirmed by a global set of dust samples. However, the variation between the different samples in temperature was

20 up to 10 K. To more adequately describe immersion freezing by desert dust in the atmosphere, mineralogy sensitive emission and transport schemes would be desirable. We suggest, K-feldspar for temperatures above 250 K and additionally at lower temperatures Na-plagioclase feldspars and quartz emissions and transport should be quantified. Since this is complex and computationally expensive to implement, more studies quantifying the ice nucleation ability of dust as it is found in the atmosphere may circumvent this complexity.

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Author contributions. YB collected the Tenerife and Israel samples, initiated, planned and led the measurements, performed and analyzed the XRD measurements, analyzed the INP and aerosol data and wrote the manuscript, AW, JA and FR conducted the IMCA measurements, AW analyzed the IMCA data and collected the Australia, Mojave and Great Basin sample, AD performed the FRIDGE sample collection and analysis, HB supervised the FRIDGE data analysis and contributed to the manuscript, MP performed and analyzed the XRD measurements,

30 BS, ZAK and UL supervised the project and contributed to the manuscript.

Acknowledgements. The various dust samples in this paper have been collected by a number of people who the authors are very thankful to: Maria Kanakidou and her team (Peloponnese, Crete), Felix Lüönd (Atacama), Paolo D'Odorico and Christopher Hoyle (Etosha), Lukas Kaufmann, Konrad Kandler and Lothar Schütz (Taklamakan), Monika Kohn (Dubai), Joel Corbin (Morocco), Sergio Rodríguez (Tenerife) and un-

known Egyptian researchers (Egypt). Furthermore, we thank the rest of campaign members: Annika Kube, Larissa Lacher and Fabian Mahrt, as well as Hannes Wydler for technical support. Y. Boose is funded by the Swiss National Science Foundation (grant 200020 150169/1). The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-797 2013) under grant agreement n^o 603445 (BACCHUS). AD and HB gratefully acknowledge support by Deutsche Forschungsgemeinschaft (DFG) under the Research Unit FOR 1525 (INUIT).

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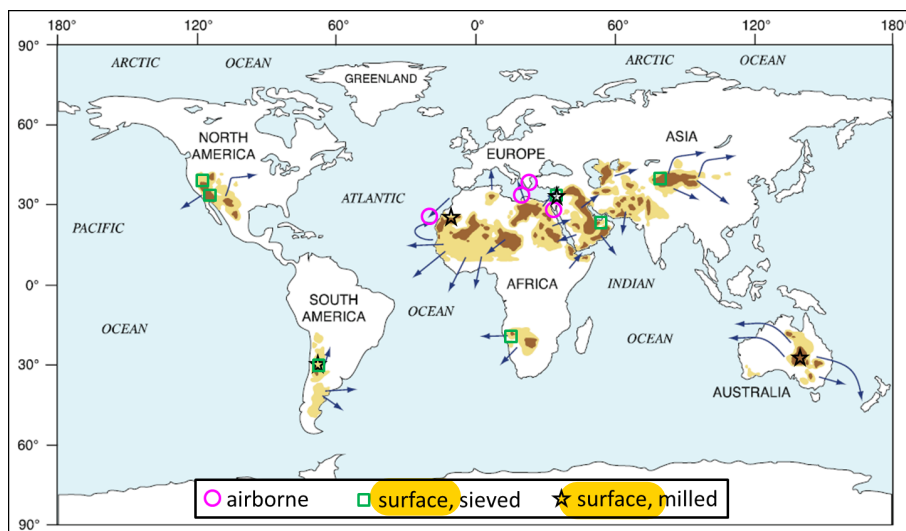


Figure 1. Collection sites of the dust samples. Green squares/black stars indicate sieved/milled samples which were collected directly from the surface, pink circles indicate samples that were collected either directly from the air or by deposition after transport from the Sahara. See text for details on the collection methods and treatment after collection. The map was adapted from Knippertz and Stuut (2014) and is based on data from Total Ozone Mapping Spectrometer (TOMS) satellite data of the absorbing aerosol index (*AAI*). Dark brown color indicates 21 - 31 days of *AAI* > 0.7, corresponding with significant amounts of dust or smoke. Yellow indicates 7 - 21 days of *AAI* > 0.7. Arrows show typical dust transport pathways in the atmosphere.

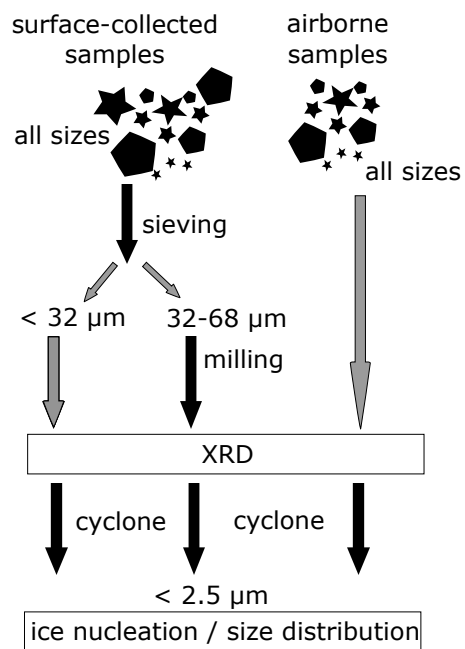


Figure 2. Schematic of size fractions used for XRD and ice nucleation.

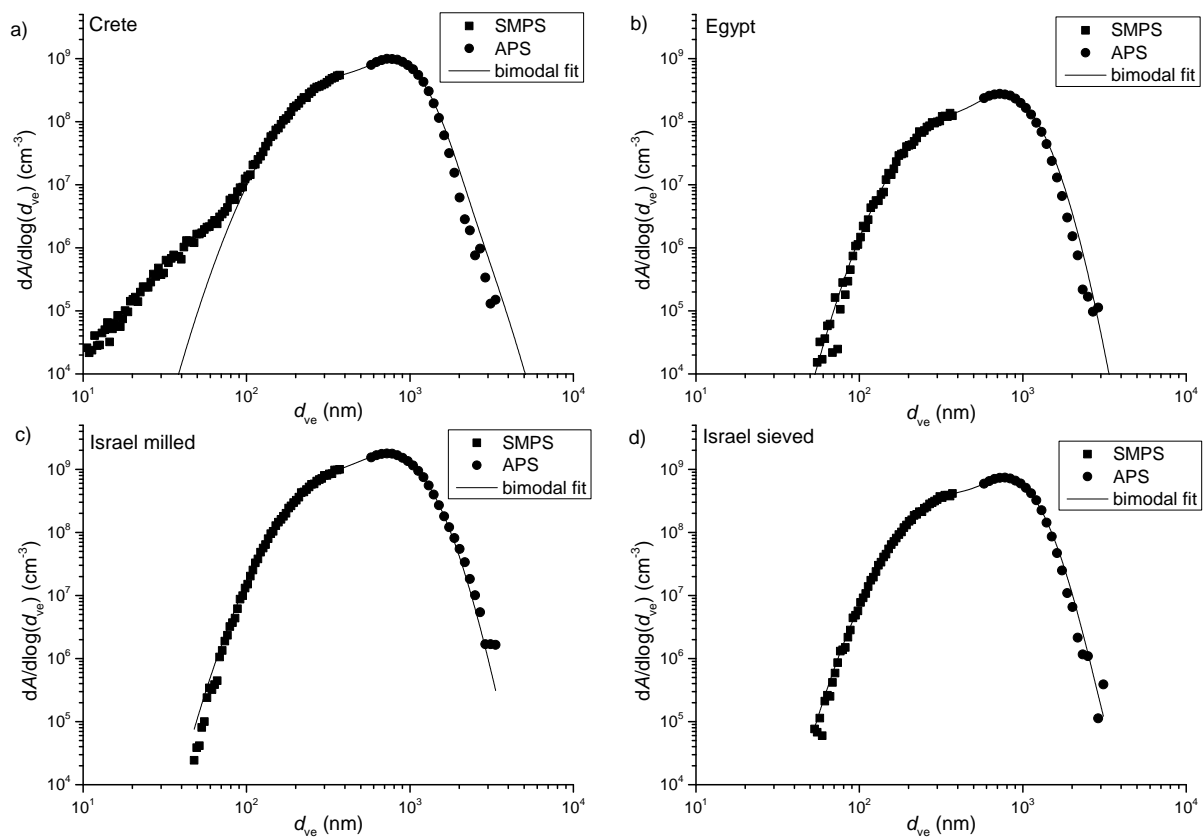


Figure 3. Sample surface area distribution of four of the dust samples with bimodal fits.

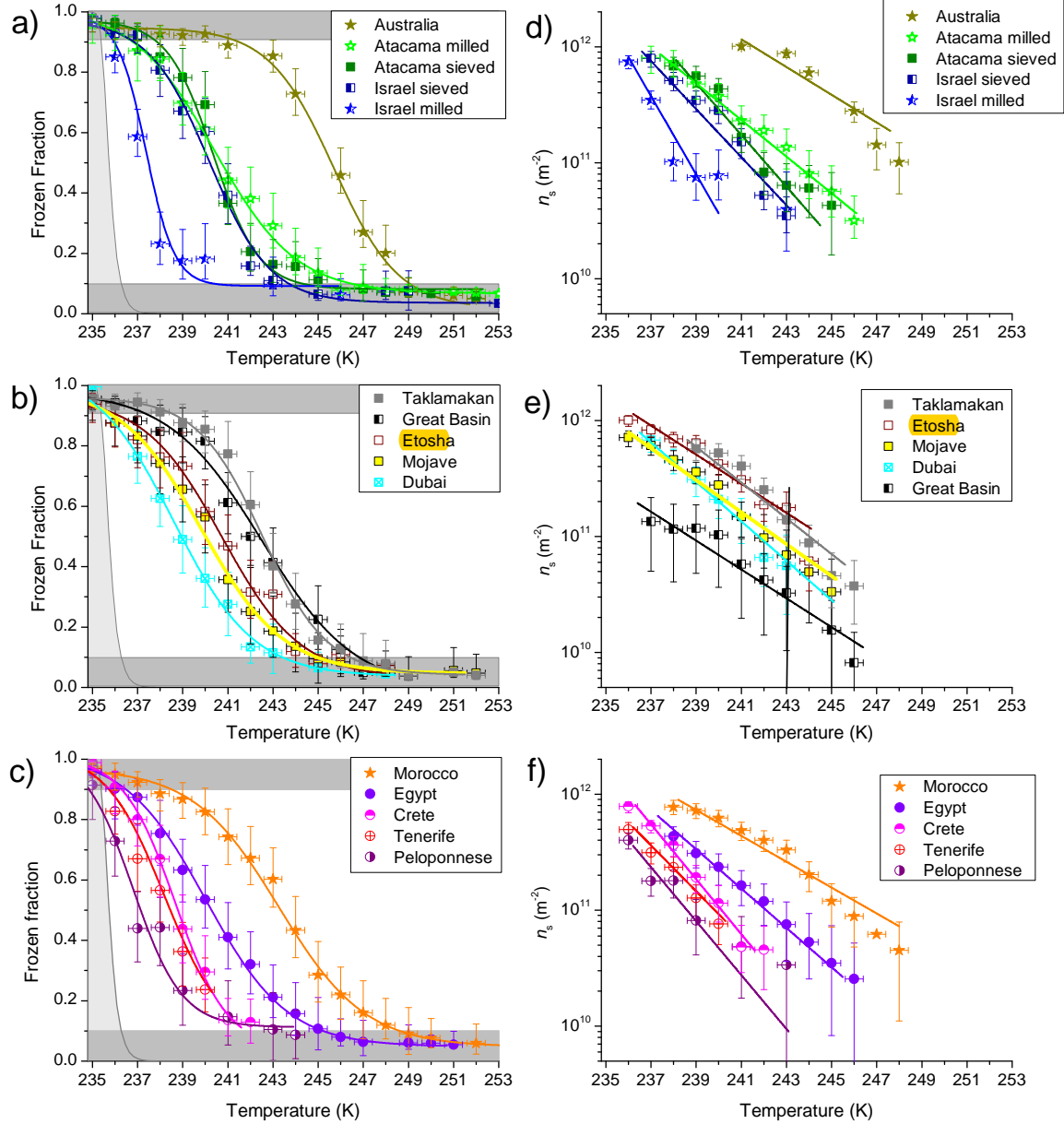


Figure 4. Frozen fraction of non-Saharan samples (panels a and b) and c) samples originating in the Sahara. Data were binned into 1 K-intervals. Lines are best sigmoidal fits. Squares: surface-collected and sieved, stars: surface-collected and milled and circles: airborne samples. The light gray area is the homogeneous freezing regime derived from classical nucleation theory (Hoyle et al., 2011; Ickes et al., 2015) and the two dark gray rectangles show the upper and lower detection limits of IODE. Ice-active surface site density of non-Saharan (panels d and e) and f) Saharan samples. Lines are best exponential fits to Eq.6. The fit parameters are given in Table 4.

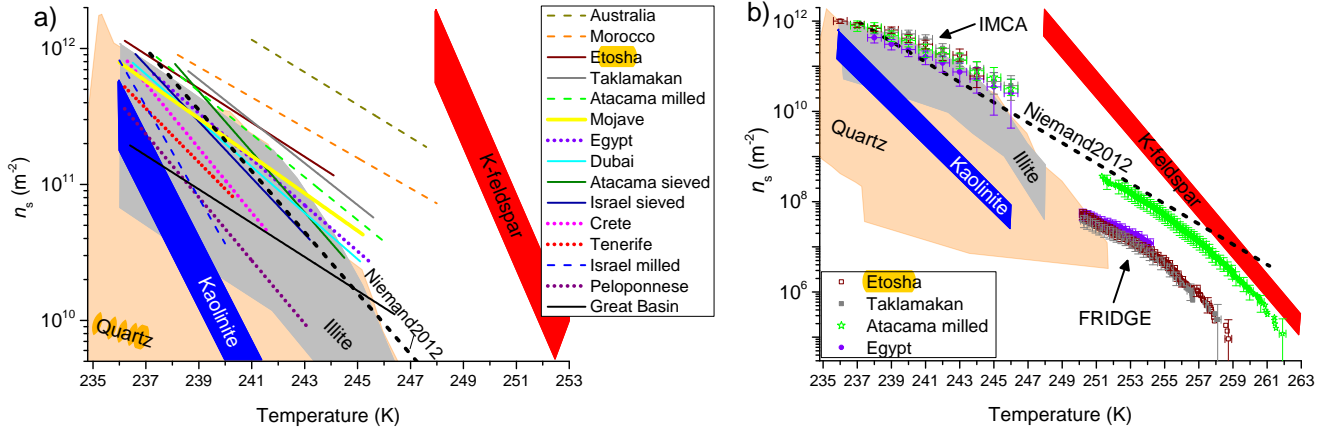


Figure 5. a) Ice-active surface site density fits for all dust samples. The fit parameters are given in Table 4. Solid lines indicate surface-collected and sieved samples, dashed lines surface-collected and milled samples and dotted lines are airborne samples. b) Full temperature range measurements taken by IMCA and FRIDGE. Colors and markers are the same as in Fig. 4. IMCA data are binned into 1 K-intervals. Error bars are drawn for every 10^{th} data point. A parameterizations for desert dust from Niemand et al. (2012) is shown as thick dashed line. Parameterizations for kaolinite (Murray et al., 2011), illite (Broadley et al., 2012) and K-feldspar (Atkinson et al., 2013) as well as the range of data for quartz (Atkinson et al., 2013; Zolles et al., 2015) are given as areas representing the range between $n_{s,\text{BET}}$, as provided in the literature, and the corresponding $n_{s,\text{geo}}$. See text for details on the calculations of $n_{s,\text{geo}}$.

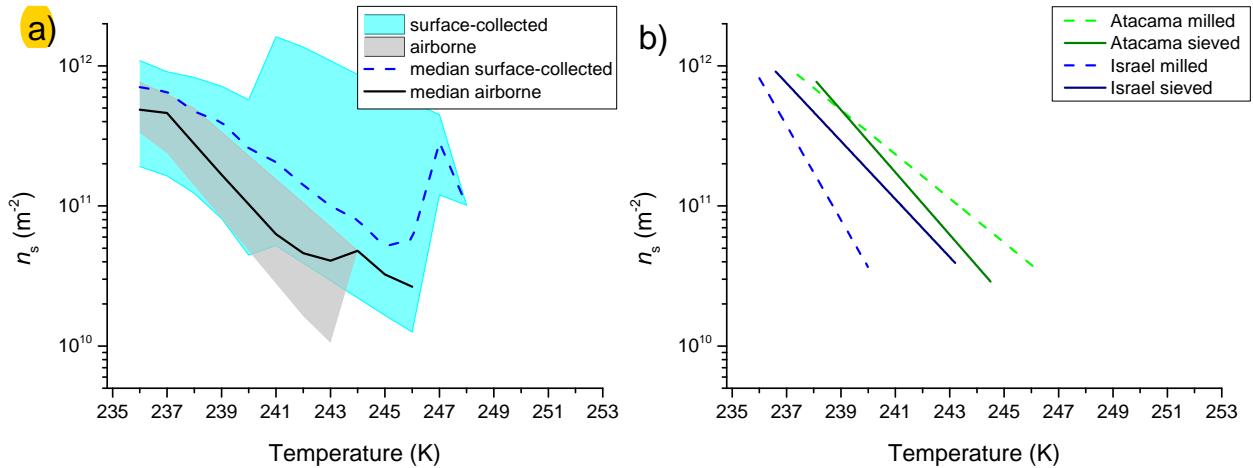


Figure 6. a) Median and minimum to maximum n_s -range of airborne and surface-collected samples. b) Comparison of ice-active surface site density of milled and sieved samples.

Table 1. Overview of the dust size distribution parameters: the mean particle surface area per particle $\overline{A_{ve,w}}$ with relative error $\delta(\overline{A_{ve,w}})$ and the corresponding diameter of a particle with this surface area: $\overline{d_{ve,w}}$ with the relative error $\delta(\overline{d_{ve,w}})$.

Sample number	collection site	type	$\overline{A_{ve,w}} (\mu\text{m}^2)$	$\delta(\overline{A_{ve,w}})$	$\overline{d_{ve,w}} (\text{nm})$	$\delta(\overline{d_{ve,w}})$
1	Atacama	sieved	2.79	0.17	940	0.08
2	Atacama	milled	2.56	0.24	897	0.11
3	Australia	milled	2.14	0.09	824	0.05
4	Crete	airborne	3.04	0.08	983	0.04
5	Dubai	sieved	2.18	0.18	830	0.09
6	Egypt	airborne	3.26	0.12	1017	0.06
7	Etosha	sieved	2.08	0.07	813	0.03
8	Great Basin	sieved	16.4	0.64	2133	0.39
9	Israel	sieved	3.32	0.14	1024	0.07
10	Israel	milled	2.57	0.12	904	0.06
11	Mojave	sieved	2.99	0.14	973	0.07
12	Morocco	milled	2.81	0.13	960	0.07
13	Peloponnese	airborne	3.27	0.06	1020	0.03
14	Taklamakan	sieved	3.69	0.19	1079	0.09
15	Tenerife	airborne	3.55	0.12	1061	0.06

Table 2. Mineralogical composition in wt% and uncertainty from the Rietveld refinement (see text for details). Where microcline and orthoclase are present in the same sample, their individual fraction could not be distinguished reliably. Nevertheless, the best Rietveld fit results are given for orthoclase and microcline individually in these cases. The Etosha sample was taken from Kaufmann et al. (2016) who do not provide a Rietveld fit uncertainty from AutoQuan but estimate a 15 % accuracy.

Mineral Type	Atacama sieved	Atacama milled	Australia milled	Cyprus airborne	Dubai sieved	Egypt airborne	Etosha sieved	Great Basin sieved
Ankerite							23	
Biotite		2.8±0.6			1.0±0.5			
Calcite				25.0±0.6	37.2±0.6	29.2±1.2	29	12.9±0.4
Chlorite				3.8±0.6	14.0±1.2	8.2 ±1.3		2.1 ±0.3
Cristobalite	12.7±1.9	14.0±1.7						
Dolomite				3.1±0.7	6.8 ±0.5	8.1 ±1.3	27	1.9±0.3
Gypsum				3.7±0.7		5.5±0.9		2.8±0.3
Halite				1.0±0.2		4.4±0.5		2.1±0.1
Hematite	4.0±0.5	3.2±0.4	0.6±0.1	0.9±0.2	1.4±0.2			0.9±0.2
Hornblende	1.3±0.7	1.8±0.6		1.5±0.4	1.8±0.5			1.0±0.5
Illite	10.0±1.0							
Kaolinite				12.4±1.0		10.5±1.5		17.7±0.9
Microcline			3.9±0.5					30.1±0.8
Muscovite	4.2±1.0	2.4±0.6			4.1±0.5	7.6±1.3	10	4.0±0.5
Orthoclase	11.8±0.9	22.3±0.9	4.2±0.5	5.1±0.6	2.4±0.4	3.5±1.1		
Palygorskite				4.5±0.5	3.4±0.5			
Na-plagioclase	39.3±1.6	43.2±1.4		7.2±0.4	9.5±0.4			3.7±0.3
Smectite							1	
Quartz	16.7±0.6	10.4±0.4	91.3±0.5	23.0±0.5	13.3±0.3	23.0±1.1	1	20.1±0.5
others					5.1±0.4		7	0.7±0.3

Table 3. Mineralogical composition in wt% and uncertainty from the Rietveld refinement using AutoQuan continued. Where microcline and orthoclase are present in the same sample, their individual fraction could not be distinguished.

Mineral Type	Israel sieved	Israel milled	Mojave sieved	Morocco milled	Peloponnese airborne	Taklamakan sieved	Tenerife airborne
Biotite							
Calcite	67.2±1.2	81.0±1.0	13.0±0.5	6.0±0.3	33.0±0.6	14.6±0.4	8.1±0.5
Chlorite			8.5±1.4	5.9±1.0	2.7±9.5	7.1 ±0.9	3.3 ±0.6
Cristobalite							
Dolomite/Ankerite	8.0±0.4	1.3±0.2	10.6±0.7	1.4±0.6	4.6±0.5	4.6±0.5	
Gypsum	1.2±0.2					1.8±0.5	3.2±0.5
Halite						0.9±0.2	0.6±0.1
Hematite	0.5±0.1		1.0±0.3	2.7±0.5	0.6±0.2		0.6±0.2
Hornblende			1.3±0.6		1.5±0.5	5.4±0.5	
Illite	4.2±1.6	0.3±0.2	17.4±1.4	3.0±0.7	12.5±1.0		14.2±1.1
Kaolinite	0.8±0.6	0.3±0.3			7.8±0.7		24.3±1.5
Microcline	1.7±0.4	1.3±0.4		3.8±1.0			6.0±0.7
Muscovite		1.1±0.5	11.25±0.8	1.8±0.3	4.8±0.8	8.0±0.6	11.0±0.8
Orthoclase			5.7±0.5	2.2±0.6	4.0±0.5	5.3±0.6	
Palygorskite	2.2±0.4	1.6±0.4			5.3±0.8		4.8±0.6
Na-plagioclase	2.3±0.5	0.7±0.3	16.3±0.7	8.8±0.4	5.0±0.4	19.3±0.8	4.8±0.5
Smectite	4.5±0.6	6.4±1.2					
Quartz	7.3±0.3	6.1±0.2	14.7±0.5	63.8±1.2	17.9±0.4	33.1±0.7	15.7±0.6
others			0.2±0.1		0.5±0.1		

Table 4. Overview of the dust n_s fit parameters a and b , the resulting R^2 and the number of data points in each fit, N .

Sample number	collection site	type	a (K^{-1})	b	R^2	N
1	Atacama	sieved	0.513	9.39	0.91	36
2	Atacama	milled	0.363	14.50	0.96	50
3	Australia	milled	0.274	18.93	0.89	16
4	Crete	airborne	0.545	7.32	0.98	30
5	Dubai	sieved	0.391	13.04	0.96	35
6	Egypt	airborne	0.390	13.22	0.96	41
7	Etosha	sieved	0.289	17.09	0.93	33
8	Great Basin	sieved	0.286	15.47	0.93	35
9	Israel	sieved	0.477	10.11	0.91	39
10	Israel	milled	0.777	-1.43	0.95	13
11	Mojave	sieved	0.317	15.62	0.96	46
12	Morocco	milled	0.257	18.55	0.95	45
13	Peloponnese	airborne	0.535	6.84	0.95	17
14	Taklamakan	sieved	0.355	15.00	0.93	21
15	Tenerife	airborne	0.455	10.16	0.97	14

Table 5. Overview of the Pearson correlation coefficients of the sum of selected mineral fractions and n_s at different temperatures. The names of the included sample numbers can be found in Tables 1 and 4. At 253 K only four samples were measured. At $T \leq 245$ K only samples with FF between 0.1 and 0.9 were included for the correlations. The Etosha sample (7) was only included in the correlation with calcite because it does not contain feldspars, illite and kaolinite and only traces of quartz. An asterix indicates that the correlation was significant at the 0.05 level.

n_s at	253 K	245 K	243 K	240 K	238 K
number of samples	3 (4)	7	11 (12)	13 (14)	13 (14)
samples included	2,6,(7),14	2,3,6,8,11,12,14	1,2,3,5,6,(7),8,9,11,12,13,14	1,2,4,5,6,(7),8,9,10,11,12,13,14,15	
K-feldspar	0.97	-0.43	-0.13	0.04	-0.15
feldspars	0.87	-0.32	-0.13	0.37	0.30
quartz	-0.96	0.89*	0.91*	0.52	0.45
illite		-0.18	-0.34	-0.14	-0.16
kaolinite	-0.35	-0.66	-0.47	-0.53	-0.56*
feldspars + quartz	0.66	0.80*	0.78*	0.65*	0.54
feldspars + quartz+ illite	0.66	0.81*	0.73*	0.61*	0.50
feldspars+quartz+kaolinite	0.74	0.67	0.70*	0.47	0.35
feldspars+quartz+illite+kaolinite	0.74	0.70	0.65*	0.42	0.30
calcite	-0.81	-0.60	-0.49	-0.45	-0.35

Table 6. Overview of the Pearson correlation coefficients of the sum of ice-active minerals and n_s at different temperatures of the samples where the mineralogy is representative for the size fraction smaller than $2.5 \mu\text{m}$. The names of the included sample numbers can be found in Tables 1 and 4. Only samples with FF between 0.1 and 0.9 were included for the correlations. The Etosha sample (7) was only included in the correlation with calcite because it does not contain feldspars, illite and kaolinite and only traces of quartz. An asterix indicates if the correlation was significant at the 0.05 level.

n_s at	243 K	240 K	238 K
number of samples	4 (5)	6 (7)	6 (7)
samples included	1,2,3,(7),13	1,2,4,(7),10,13,15	
K-feldspar	-0.22	0.99*	0.94*
all feldspars	-0.44	0.99*	0.94*
quartz	0.99	-0.23	-0.10
illite	-0.57	-0.41	-0.51
kaolinite	-0.57	-0.37	-0.28
feldspars + quartz	0.80	0.96*	0.94*
feldspars + quartz+ illite	0.84	0.88	0.83
feldspars+quartz+kaolinite	0.83	0.82	0.84
feldspars+quartz+illite+kaolinite	0.88	0.67	0.66
calcite	-0.61	-0.41	-0.44

Heterogeneous ice nucleation on dust particles sourced from 9 deserts worldwide - Part 1: Immersion freezing

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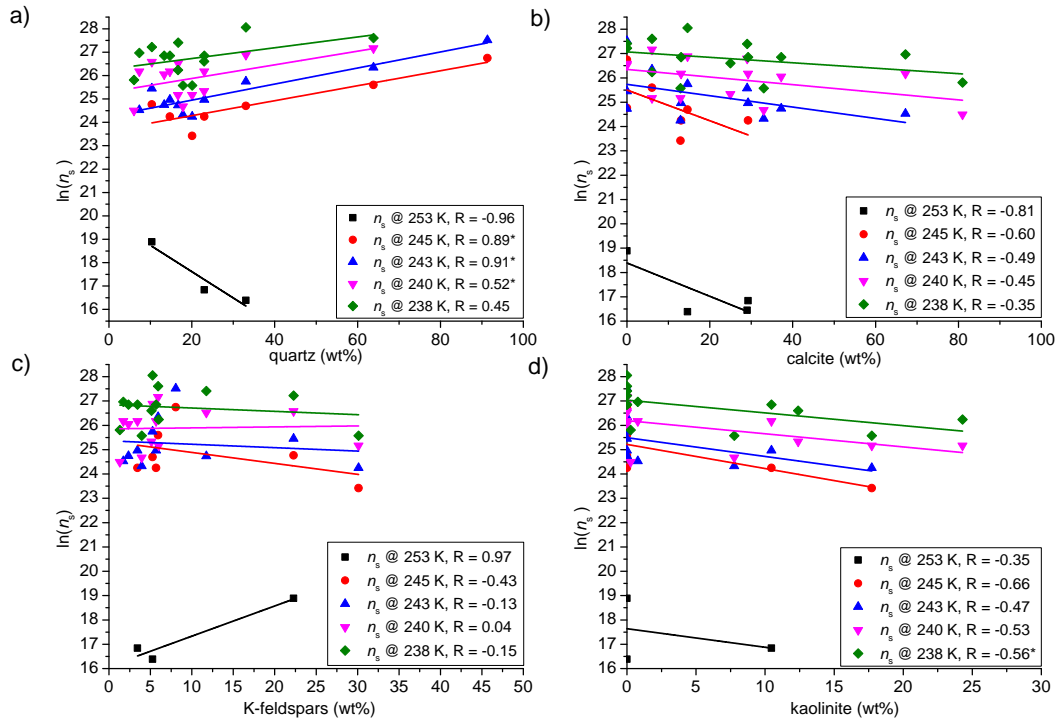


Figure 1. Correlation of n_s at five selected temperatures with four different minerals. An asterix indicates a significant correlation at the 0.05 level.

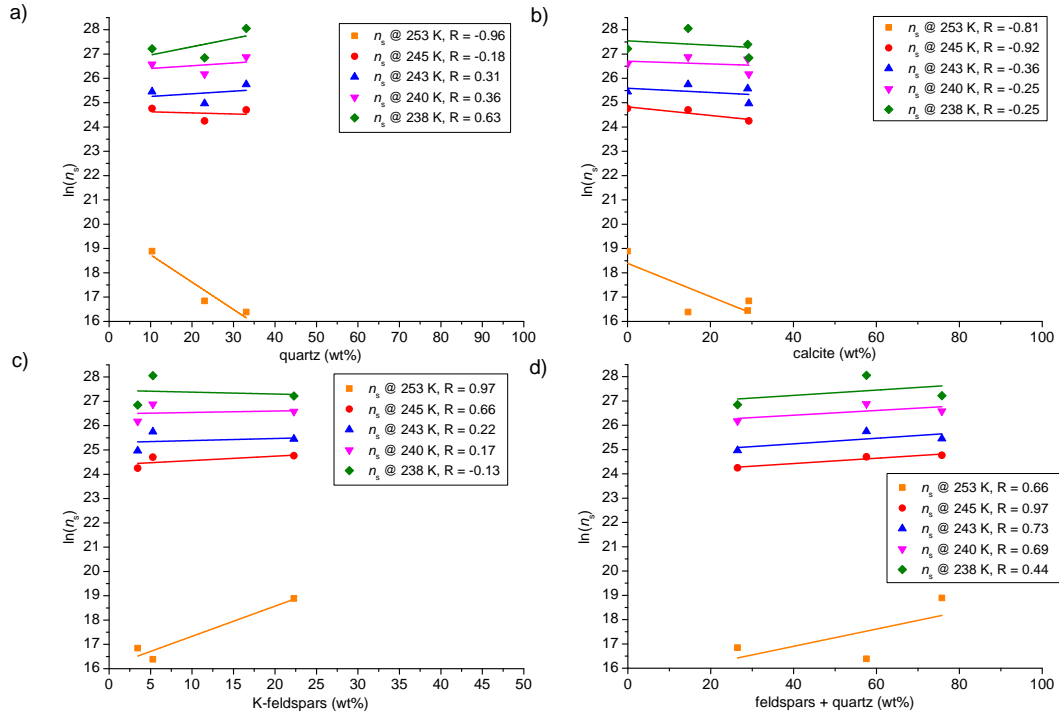


Figure 2. Correlation of n_s at five selected temperatures with four different minerals for the Atacama milled, Egypt, Etosha and Taklamakan sample.

Table 1. GPS coordinates of sample collection sites.

Sample Number	Collection site	type	latitude	longitude
1	Atacama	sieved	-22.03	-67.88
2	Atacama	milled	-22.03	-67.88
3	Australia	milled	-25.32	131.63
4	Crete	airborne	35.34	25.67
5	Dubai	sieved	24.83	55.66
6	Egypt	airborne	28.93	33.21
7	Etosha	sieved	18.01	16.01
8	Great Basin	sieved	37.16	-116.49
9	Israel	sieved	30.84	34.79
10	Israel	milled	30.84	34.79
11	Mojave	sieved	36.71	-117.17
12	Morocco	milled	31.21	-3.99
13	Peloponnese	airborne	37.97	23.78
14	Taklamakan	sieved	39.78	88.39
15	Tenerife	airborne	28.31	-16.50