We thank Reviewer 1 for their very constructive comments. We reproduce reviewer comments in blue in the following. Amended versions of the paper are given in *italics* for new sections and red text for the original text.

General comments:

The present manuscript is a follow up paper to "Heterogeneous ice nucleation on dust particles sourced from nine deserts worldwide – part 1: Immersion freezing" (Boose et al, 2016). In part 2 (the present paper), ice nucleation efficiency of minerals in deposition nucleation and condensation freezing modes is studied, as well as the effect of coatings (biological and volatile/semi volatile organic material). The paper is generally well written, and it complements part one nicely. However, in some way it is difficult to follow the paper as it at times rely on the reader to remember details of part 1. Generally, the authors are asked to check that the paper is consistent with the partner paper in the use of sample names, e.g. "Tenerife" in part 1, and "Izaña" in part 2, as well as minerals (e.g. specification of Feldspar and K-Feldspar). Additionally, there is little information on why some samples are selected for further analysis and others not, e.g. XRD of one sample before and after heating, Raman mapping of two desert samples and no airborne sample, the difference in number of samples in table 2, and why is Izaña2014_2 selected and not the other Izaña samples? In their results, the mineral fraction from feldspars and quartz correlate with the ice nucleation surface site density (ns), in both deposition and condensation mode, similar to what was found for immersion freezing in part 1. Some organic material coating the particles altered the ns, seen by comparing untreated and heated samples. In one sample, the ns is higher in the heated sample which is devoted to evaporation of volatile organic material. In this sample, also the minerology changed (gypsum to anhydrite) between the pre- and heated sample. A similar result was found in Grawe et al. (2018), but in this case it is devoted to an overestimation of ns because of large needle shaped particles that could cross the size selecting step. The authors are therefor asked to address the possibility of needle shaped particles (see more details below) and if necessary change their conclusions.

We thank the reviewer for these helpful comments and have addressed them below.

We have changed the naming of the Izaña201x_x samples into Tenerife201x_x and have numbered the 2014 samples from 1 to 3 to match part 1 of the paper:

Izaña2013_2 ➔ Tenerife2013
Izaña2014_2 ➔ Tenerife2014_1
Izaña2014_3 ➔ Tenerife2014_2
Izaña2014_5 ➔ Tenerife2014_3

We have also clarified the specification of components in the Feldspar and K-Feldspar group (see below).

Specific comments:

Page 4 "2.1 Dust sample origins and processing": How were the samples stored for up to 8 years. Will the storage change the samples (e.g. loss of volatile compounds, change in composition due to water uptake, changes in biological material on the surface)?

We have added the following part on sample storage and potential effects:

Pg.4, ln. 31: *Before arriving to the laboratory, samples were stored in various ways: Samples collected from the surface were typically stored for several weeks in PET bottles or other plastic containers. Airborne samples were stored in polypropylene tubes and sealed with paraffin wax tape. In the laboratory, all samples were stored in the dark at room temperature in polypropylene tubes after pre-processing (sieving/milling, see below). While changes in the ice nucleating ability due to water uptake, loss of volatile material or growth of biological material which may occur during storage cannot be excluded, they are assumed to be minor because the samples were collected and stored under dry conditions, hardly exposed to air and kept at a lower temperature than at which they were collected.*

Page 10 in the subchapter 3.2 "Ice nucleation and heat labile material": Three samples are discussed extensively from page 10 onwards, Etosha, Australia and Izaña 2014_2. It would be easier for the readers to have a summary of why these three samples are further investigated and discussed, compared to the rest.

We have added a sentence on

Pg. 10, ln. 28: *We performed IR-ATR spectroscopy on the Etosha and Tenerife2014_1 to investigate the nature of the material responsible for the respective decrease and increase in n_s with heating. Furthermore, we chose the Australia sample as representative for most other cases, where the n_s stayed the same. Figure 5 shows the IR-ATR spectra of the three samples before and after heating.*

And further on

Pg. 11, ln. 5: *Raman mapping was performed on the Etosha, Tenerife2014_1 and Australia samples. Due to strong fluorescence, however, the Tenerife2014_1 spectra did not yield any information and are thus not presented here. The Raman maps for the Etosha and Australia samples are shown in Fig. 6.*

We learn on page 12 (line 13) that there is a change in the mineralogical composition between untreated and heated samples. Please add the XRD results of heated and unheated samples, either to the paper or in a supplement. Large uncertainty is associated with comparing particle composition and bulk chemical analysis, which the readers also are made aware of in the paper. I would like to draw the authors attention to an article where the ice nucleation efficiency of coal fly ash particles were investigated by Grawe et al. (2018). In this case, needle shaped particles could explain the higher ns of one sample where anhydrite changed to gypsum after suspension. Many of the needles were larger than 300 nm (up to ~5 μm), but could - due to the fact that the dynamic shape factor of the needles differ significantly

We have added the XRD results of the unheated and heated Tenerife2014_1 sample (Figure 7) and refer to it on pg.13, ln. 7: *XRD analysis of the unheated and heated Tenerife2014_1 sample show the conversion of gypsum to anhydrite (Fig. 7).*

Furthermore, we have investigated the suggestion by the reviewer that needles may form when gypsum is transformed to anhydrite. We have compared SEM images of the Tenerife2014_1 sample before and after heating (now shown in Fig. 8 and in the supplementary). However, apart from one image (which we show in Fig. 8) we don't find any needles in the heated or unheated samples. Therefore, we don't think that the shape factor plays a role in our case. However, we now refer to the Grawe et al. 2018 study for the immersion mode ice nucleation activity of anhydrite. We use these data to discuss that anhydrite is more ice nucleation active than gypsum, which might be an explanation of the observed increase in n_s, which we find for the Tenerife2014_1 sample. However, because gypsum accounts only for 1 wt% and also needle formation is so limited, it seems unlikely to be the only factor. Therefore, we keep our other hypothesis of aliphatic compounds which is supported by the IR-ATR spectra and TGA measurements.

We have added and rephrased the following paragraph on pg. 13, ln.7:

XRD analysis of the unheated and heated Tenerife2014_1 sample show the conversion of gypsum to anhydrite (Fig. 7). Gypsum has a low ice nucleation ability, similar to the clay minerals kaolinite and illite (Zimmermann et al., 2008). Grawe et al. (2018) found anhydrite to have a higher ice nucleation activity than quartz in the immersion mode at temperatures below 243 K when dry generated but a much lower n_s when particles were generated from an aqueous solution. Anhydrite transforms back to gypsum when exposed to a relative humidity higher than 97% at room temperature (Bracconi et al., 2010). However, this process occurs on the order of hours to days, in line with the observed differences in n_s between wet and dry generated particles in Grawe et al. (2018). Potentially, the transformation to anhydrite during heating explains the higher n_s of the heated Tenerife2014_1 sample compared to the unheated one at subsaturated conditions. In this case, a partial conversion of anhydrite back to gypsum during RH conditions above water saturation might explain the unchanged n_s of the unheated and heated Tenerife2014_1 sample above water saturation. It should be kept in mind that the bulk mineralogy as determined by XRD is not necessarily representative for the particle surface where ice nucleation takes place. As needle formation has been observed in the transformation of gypsum to anhydrite (Azimi and Papangelakis, 2011; Grawe et al., 2016), we use the occurrence of needles in our sample as an indication that the gypsum - anhydrite transformation took place on the surface of particles and thus might be responsible for the change in ice nucleation behavior of the sample. In SEM images of the unheated Tenerife2014_1 sample (Fig. 8a) hardly any needles are visible. A small number of needles is observed at the center of the image of the heated sample (Fig. 8b) while no needles are found in other SEM images of

the heated sample (see supplementary material). The apparently limited needle formation and the fact that only about 1 wt% gypsum is contained in the sample, suggests that gypsum transformation under heat treatment should only have small effect on the ice nucleation behavior of the Tenerife2014_1 sample. However, given that at maximum only about 10 % of the particles act as INPs in case of the Tenerife2014_1 sample, the gypsum-anhydrite transformation might be non-negligible. Additionally, we suggest that the increase in n_s found under subsaturated RH_w conditions for the Tenerife2014_1 sample is caused by the volatilization of aliphatic compounds containing matter, as indicated by the IR-ATR and TGA measurements, which inhibited the active sites of the mineral dust itself.

Furthermore, we have amended our Conclusions (pg. 14, ln. 12):

Three potential explanations are found, two of them related to changes in the mineralogy: While it cannot be excluded that the increase in n_s was caused by a change in lattice spacing due to interlayer water release, it seems more likely that gypsum transforming to anhydrite made the sample more ice nucleation active. The Tenerife2014_1 sample is the only gypsum-containing sample that was investigated after heating, thus it remains an open question if and how much anhydrite contributed to the increase in n_s. Another reason for the increase could be that the ice nucleation active sites of the unheated sample were blocked by volatile organic material.

Technical comments:

Title: Change '9' to 'nine' to be consistent with the partner paper.

Done

'Ice nucleating particles' without hyphen, like in partner paper and in Vali et al. (2015).

Done

Figure 1: The black color of the CALIMA2014 sample symbols covers all the other samples. Please change this to make it easier for the readers to see all results. Please remind the reader that CALIMA is the same sample location as Izaña in the figure legend.

We have re-sorted the layers of Fig. 1 such that the CALIMA results are in the background. Furthermore, we added in the caption of Fig. 1: *"which took place at the Izaña observatory"*

Figure 2: Please add to the legend text explaining the astrix (as in table 2). Why is the Etosha sample not present in this figure?

We have added in the caption of Fig. 2 the following sentence:

The asterix in the legend indicates that the correlation is significant at the 0.05 level.

And on Pg. 9, ln. 2: *The Etosha sample was excluded from the correlation as it does not contain any significant amount of these minerals.*

Figure 3: Please remind the reader which samples are airborne, milled and sieved in the figure legend. Why is the Atacama sample called milled and not the Australia and Morocco sample? Why does the heated sample from Morocco only have an upper limit?

We added in the caption of Fig. 3: *Square symbols indicate surface-collected samples, stars milled samples, and circles indicate airborne samples.*

The Atacama sample is called milled and not the Australia and Morocco samples because there is also an Atacama sieved sample while there aren't any other Australia or Morocco samples.

The lower error bars of the Morocco sample were switched off unnoticed. The same figure with the error bars included is now plotted.

Furthermore, we also changed the markers in Fig. 2, the same way as they are in Fig. 3.

Figure 5: In the text, the samples are discussed in the following order (ref. P10, L5-14) Australia, Etosha and Izaña 2014_2. The two first show no change between unheated and heated, and in the last sample a change is discussed. It would be more logical for the reader if the locations appear in the same order as the text.

We have reordered Fig. 5 such that a) Australia, b) Etosha and c) Tenerife2014_2.

Figure 6: The figure contains a lot of information, but the grey maps (1) add no important information as the images are taken at relatively low magnification so the particles can't really be seen. Also, please remove: "see text for details".

We have deleted the grey maps in Fig. 6 and removed "see text for details" in the caption.

Table 2: Please define the K-feldspar and feldspars groups in the figure legend. ˇ

Please explain the readers why there are different numbers of samples.

We have added to the caption of Table 2 the following sentence:

K-feldspar comprises microcline and orthoclase, while feldspar refers to the sum of microcline, orthoclase and plagioclase. The number of samples included in each correlation varies because the n_s of the Mojave, Peloponnese and Tenerife2014_2 samples was below the detection limit at 242 K, and the size distribution measurements of the Tenerife2014_1 sample were corrupted for the RH-scan at 238 K.

Introduction:

Page 2, line 21: Please add a comma after the South Pole.

Done

Page 2, line 24: The term "potassium feldspars" is used sometimes, and "K-feldspars" other times. Please be consistent.

We have changed potassium feldspar to *K-feldspar*.

Page 3, line 31: Please specify the minerals in the K-feldspar fraction.

We have added: *, i.e. the fraction of microcline plus orthoclase,* behind K-feldspar fraction.

Page 3, line 33: Please specify the minerals in the feldspar fraction.

We have added: *(microcline, orthoclase and plagioclase)* behind feldspar fraction.

Methods:

Page 4, line 23: Please add country (Crete and Peloponnese, Greece) and then use the same structure as before, e.g. "… (Crete and Peloponnese, Greece), and the 10th of May 2010 (Aburdees, Egypt)."

Done

Page 5, line 16: "… mobility diameter between 12.2 – 615 nm…" Is the decimal place significant?

We agree that the decimal place is not of interest in this context and leave it out.

Page 6, line 25: Change 'tank' to 'sample container'

We decided to leave the word 'tank' here because this is how we describe the huge chamber where the aerosol is dispersed it, earlier in the manuscript and also in earlier publications. We feel that 'sample container' gives the impression of a much smaller volume.

Results and discussion:

Page 8: line 26 & 27: Please add p-value.

Done

Page 9, line 4: Please explain why these samples are selected.

We have changed

Pg. 9, ln. 4: Figure 3 shows the ns at 240 K and 242 K of the native, i.e. unheated, and the heated Australia, Atacama milled, Izaña2014_2, Peloponnese, Etosha, and Morocco samples.

to:

Pg. 9, ln 23: *In this section, the role of heat labile material on the surface of dust particles is investigated. A representative subset of the samples was selected to reduce the number of experiments necessary. The Australia and Morocco sample were selected because of their exceptional high n_s, the Etosha sample, because its mineralogy did not explain the observed n_s, the Atacama milled sample because we expected a higher n_s from its mineralogy, and finally the Tenerife2014_1 and Peloponnese samples as representatives for two airborne samples from different locations. Figure 3 shows the n_s at 240 K and 242 K of the unheated and the heated samples.*

Page 10, line 6: Please remind the reader that the spectra are from bulk material. E.g. "… related to the dominant minerals (in bulk) in the samples".

We have changed this sentence to (Pg.10, Ln.31): *to the dominant minerals in the (bulk) samples*

Page 11, line 7 & 8: "The minerals contained in the Etosha sample… " Please remind the reader which minerals so they don't have to look it up in the partner paper.

We have added *(i.e. ankerite, calcite, dolomite, and muscovite)* behind 'Etosha sample' (now p. 12, ln.1)

P 11, line 9: Sentence too long.

We have split the sentence. Now Pg. 12, ln. 2: *In case of ankerite the ice nucleation ability is unknown. Based on its similarity with dolomite, a carbonate known not to be ice nucleation active, it is assumed that ankerite is also not active.*

Page 11, line 10: In this line you abruptly move from the discussion of minerals to organic material.

We have added on Pg.12, ln.3: *Thus, one of the suggested candidates with the strong Raman signal at 3180 cm^{-1} is likely responsible for the ice nucleation activity of the Etosha sample.*

Page 11, line 33: Remove 'the' to During daytime,…

Done

References:

Azimi, G., and Papangelakis, V. G.: Mechanism and kinetics of gypsum–anhydrite transformation in aqueous electrolyte solutions, Hydrometallurgy, 108, 122-129, 10.1016/j.hydromet.2011.03.007, 2011.
Grawe, S., Augustin-Bauditz, S., Clemen, H. C., Ebert, M., Eriksen Hammer, S., Lubitz, J., Reicher, N., Rudich, Y., Schneider, J., Staacke, R., Stratmann, F., Welti, A., and Wex, H.: Coal fly ash: linking immersion freezing behavior and physicochemical particle properties, Atmos. Chem. Phys., 18, 13903-13923, 10.5194/acp-18-13903-2018, 2018.
Vali, G., DeMott, P. J., Möhler, O., and Whale, T. F.: Technical Note: A proposal for ice nucleation terminology, Atmos. Chem. Phys., 15, 10263-10270, 10.5194/acp-15-10263-2015, 2015.

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

Boose et al. reports measurements of the effectiveness with which a range of natural dust samples from around the world to nucleate ice from supersaturated water vapour. Various analytical techniques were used to determine the composition of the samples and to attempt to establish what components are responsible for observed ice nucleation, leading to the conclusion that quartz and feldspar content is responsible for the ice nucleation observed in most samples. In one sample organic substances were found to be largely responsible while in another removal of organics actually enhanced ice nucleation effectiveness. The conclusions of the paper are interesting and relevant to the scope of ACP, highlighting the substantial complexity in ice nucleation by natural samples. The paper is mostly well written, sensibly structured, and is entirely suitable for publication in ACP, after a few minor corrections

Minor comments

I have a few issues with the identification of feldspar phases via powder XRD in this work. Alkali feldspar structure is a complex topic and it is not clear to me that powder diffraction is adequate to certain about which polymorph is present in dust samples of the type characterised here. Indeed in part 1 of this study the authors state 'Where microcline and orthoclase are present in the same sample, their individual fraction could not be distinguished reliably' in the caption to the relevant table. It is not clear to me what has changed in the present study.

The analysis of XRD used in the present study is the same as used in part 1 (Boose et al. 2016c). Nothing has changed and the same uncertainty applies here as well.

The difference between orthoclase and microcline is essentially the degree of order of the aluminosilicate framework. There is not necessarily a hard line between orthoclase and microcline. Parsons et al (American Mineralogist (2015) 100 (5-6), 1277-1303) and references therein discuss some of the relevant issues. Additionally the differences between even very pure samples of the two minerals in powder XRD are subtle. It must be more difficult to be certain of phase when mixed dusts with very low feldspar contents are under investigation. In summary, if the statements in the paper regarding the relative amounts of orthoclase and microcline are to be kept a much better description of the powder XRD procedure, and justification the differentiation between orthoclase and microcline is needed. I do not think this is particularly key to the paper, because, as the authors say, there is not any difference between the feldspars as characterised anyway. I would suggest treating the topic as it was treated in part 1 of this study.

Relatedly, Pg 8 line 12 states that microcline is the more active K-feldspar polymorph without citation. I think this statement should be changed, or its origin cited and discussed. The superior ice nucleating ability of microcline seems to be assumed throughout the paper. I would note that Whale et al. (Phys. Chem. Chem. Phys., (2017), 19, 31186) which used pure feldspars '...found no correlation between ice-nucleating efficiency and the crystal structures or the chemical compositions...' of ice nucleation active feldspars, albeit in rather different conditions.

We thank the reviewer for these valuable comments. We have decided to take out the sentences which suggest microcline being more active than orthoclase. We had based this statement on earlier studies by Augustin-Bauditz et al. (2014), GRL (doi: 10.1002/2014GL06131) and Harrison et al. (2016), ACP (doi: 10.5194/acp-16-10927-2016) but admit that the study by Whale et al. (2017) proves this to not hold in general, which we had overlooked.

We have made the following changes to the manuscript:

Pg.2, ln.27: Amongst the K-feldspars, microcline has a remarkable ice nucleation ability at temperatures up to 271 K (Harrison et al., 2016). However, Kaufmann et al. (2016) found microcline only in one out of eight dust samples collected in potential atmospheric dust source regions in South America, Asia and Africa and microcline was only present in one out of four airborne Saharan dust samples studied by Boose et al. (2016c).

Was changed to:

Pg. 2, ln.27: *While Kaufmann et al. (2016) found K-feldspar only in one out of eight dust samples collected in potential atmospheric dust source regions in South America, Asia and Africa, we observed K-feldspar to be present in all but one sample from a collection of 21 samples from deserts around the world (Boose et al., 2016c).*

Pg.8, ln.9: Microcline was found in four out of five investigated Izaña samples (4-5 wt%) and orthoclase (4-5 wt%) is present in one Izaña and the other three Saharan samples. Comparing the bulk mineralogy to the surface-dependent ice nucleation ability has the caveat to introduce uncertainty. Within this uncertainty there is no detectable effect from the presence of the more ice nucleation active microcline K-feldspar over orthoclase for the airborne samples at the studied temperatures.

was changed to:

Pg. 8, ln.21: *Differentiating between microcline and orthoclase and comparing the bulk mineralogy to the surface-dependent ice nucleation ability, introduces uncertainty. Within this uncertainty, there is no detectable effect from the presence of microcline versus orthoclase in the airborne samples at the studied temperatures. This is in line with the findings by Whale et al. (2017) that there is no correlation between ice nucleating ability and the level of ordering in the aluminosilicate framework, which determines if orthoclase (less ordered) or microcline (more ordered) is present.*

And we deleted the following from the initial manuscript:

Pg. 12, ln. 30: Furthermore, we observed that the ice nucleation activity of airborne Saharan dust at these temperatures is not higher when microcline is present in the samples compared to when orthoclase is present at typical amounts of 4-5%. If one assumes that both feldspars are equally active at these low temperatures, this result is to be expected.

Naming of samples is not entirely consistent through the manuscript I think, this should be checked.

We changed "native" to "unheated" on originally Pg. 9, ln 4 and Pg. 12, ln12

Furthermore, we have changed the naming of the Izaña201x_x samples into Tenerife201x_x and have numbered the 2014 samples from 1 to 3 to be consistent with part 1 of this study:

Izaña2013_2 ➜ Tenerife2013
Izaña2014_2 ➜ Tenerife2014_1
Izaña2014_3 ➜ Tenerife2014_2
Izaña2014_5 ➜ Tenerife2014_3

Specific comments
Abstract line 7 to 9- sentence starting 'in this study,....' does not read well.

We have changed the sentence to:
Pg.1, ln.7: *In this study, the influence of semi-volatile organic compounds and the presence of crystal water on the ice nucleation behavior of desert aerosol is investigated.*

Abstract line 9- between 238 and 242K
Changed

Abstract line 15 reads poorly, missing comma after 'diminished'?
Comma was added after 'diminished'

Pg 2 Line 2- delete 'already'
Done

Pg 2 Line 25- ACP version of Paramonov et al. is available
Reference was changed to ACP version

Pg 3 line 32- clumsy wording, probably delete 'showing'
We replaced 'showing' with 'found'. The sentence now reads:
Pg.3, ln.31: *At T ≤ 245 K the best correlation of the ice nucleation activity was found for the bulk quartz plus feldspar content in the dust samples while the fraction of clays was negatively correlated with the ice nucleation activity.*

Pg 3 line 10- typo 'selected'
Corrected

Pb 3 line 33- clumsy sentence structure
Pg 3 line 35- 'over' not the right work I think.
The respective sentence

Quartz alone has been found to show various immersion mode ice nucleation activities in laboratory studies, ranging from being active at temperatures comparable to microcline (Zolles et al., 2015), over being active below feldspar temperatures but above those of clay (Atkinson et al., 2013), to showing ice nucleation activity at temperatures comparable or lower than those of clays (Kaufmann et al., 2016).
has been replaced by:

Pg.3, ln.34: *Quartz alone has been found to show various immersion mode ice nucleation activities in laboratory studies. Zolles et al. (2015) found quartz being active at temperatures comparable to microcline, while Atkinson et al. (2013) measured ice nucleation activity below feldspar temperatures but above those of clay. Kaufmann et al. (2016), on the other hand, only observed ice nucleation activity at temperatures comparable to or lower than those of clays.*

Pg 3 line 33 onwards- I note that there is interesting work on the topic of ice nucleation by quartz under review in ACPD at current (https://www.atmos-chem-physdiscuss.net/acp-2018-1020/), which may shed some light on the complexities of ice nucleation by various silicas.
We have added the following sentence on p. 4, ln. 2:

These differences in ice nucleation ability can be related to the history of the quartz samples and different ways of pre-processing them (Zolles et al., 2015).Milling quartz samples leads to a break-up of Si-O-Si bridges on the surface, leading to the formation of Si-OH and Si-O-OH in the presence of water vapor, which increases the ice nucleation activity of the quartz particles (Kumar et al., 2018b).

Further, we discuss our results now in the light of the study by Kumar et al. (2018b) in the Conclusions.
Pg. 12, ln.27: It remains unknown why laboratory studies show various ice nucleation activities of pure quartz particles (Atkinson et al., 2013; Zolles et al., 2015; Kaufmann et al., 2016), relating to the question of how ice nucleation occurs on dust in general and on quartz in particular.
Was changed to:

Pg. 14, ln. 2: *According to a recent study by Kumar et al. (2018b), the variation in quartz ice nucleation ability found in laboratory studies (Atkinson et al., 2013; Zolles et al., 2015; Kaufmann et al., 2016) and the superior ice nucleation ability of the quartz-rich samples from Australia and Morocco in this study and its partner paper, may be explained by the pre-processing of the samples. Milling of quartz samples, as done in our study, increases the ice nucleation ability of quartz by creating Si-O• and Si• radical sites which can then react with water vapor (Kumar et al., 2018b). However, milling may not be the only reason for formation of the silanol (Si-OH) groups on the surface of quartz, because exposure to water molecules in ambient humidity could also result in passively converting surface siloxane groups (Si-O-Si) to silanol groups (Boehm, 1966; Wang et al., 2018). As such quartz samples may still exhibit high ice nucleation activity in the absence of milling due to the particles chemical history. Thus, it remains an open question, how much quartz contributes to the ice nucleation ability of (unmilled) atmospheric dust.*

Pg 4 line 7- while RH is increased
Changed

Pg 8 line 15- Some justification for using the conditions stated might aid the reader.
The original sentence:
This comparison showed that the immersion mode ice nucleation activity at T ≤ 245 K correlates best

with the quartz and quartz+feldspar fractions of the dust samples, while at T = 253 K it correlates best with the K-feldspar fraction alone (Boose et al., 2016c).

was changed to:

Pg. 8, ln.27: *This comparison showed that the immersion mode ice nucleation activity correlates best with the K-feldspar fraction alone at T = 253 K, a temperature where only feldspar minerals are found to have significant ice nucleation activity (Atkinson et al. 2013). At T ≤ 245 K, the ice nucleation activity correlates best with the quartz and quartz + feldspar fractions of the dust samples (Boose et al., 2016c). At these lower temperatures, quartz and to a lower degree also clay minerals were found to nucleate ice efficiently (Atkinson et al. 2013).*

Pg 11 line 15- I'm not sure what is meant by the sentence 'However, it was not....'. I suggest clarifying this.

We have deleted the sentence. We just wanted to stress that ammonium sulfate alone is not responsible for ice nucleation of dust. However, this is likely obvious for the reader and the sentence rather confusing.

Pg 9 line 15- I am not sure what is meant by 'hardly' in this context? This sentence could be clearer.

We believe the reviewer is referring to pg. 9 ln. 17 of the initial manuscript. We have now changed this sentence from

However, the complexity of the dust samples in this study, which consist of several minerals and likely also various other components, cause the spikes to widen and hardly discrete steps to be observed.

to now pg. 10 ln. 5:

However, the complexity of the dust samples in this study, which consist of several minerals and likely also various other components, cause the spikes to widen thus reducing the possibility to observe discrete steps.

Pg 11 line 12- remove comma after 'both'

Done

Pg 12 line 6- brackets around '2006' after 'Laird'

Done

Pg 12 line 10- sentence starting 'Thus, according to our observations...' is clumsy

The respective sentence

Thus, according to our observations, the collapse of the smectite lattice should, if at all, only influence the Izaña2014_2 sample and then be related to an increase in ice nucleation ability.

was changed to:

Pg.13, ln.4: *Thus, the collapse of the smectite lattice should only influence the Tenerife2014_1 sample. In case it has an influence, this would be related to an increase in ice nucleation ability.*

Figure 2- It is not obvious what the * in 0.63* refers to without referring to final table.

We added a sentence in the caption of Fig. 2 for clarification:

The asterix in the legend indicates that the correlation is significant at the 0.05 level.

Heterogeneous ice nucleation on dust particles sourced from ~~9~~ nine deserts worldwide - Part 2: Deposition nucleation and condensation freezing

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Abstract. Mineral dust particles from deserts are amongst the most common ~~ice-nucleating~~ ice nucleating particles in the atmosphere. The mineralogy of desert dust differs depending on the source region and can further fractionate during the dust emission processes. Mineralogy to a large extent explains the ice nucleation behavior of desert aerosol, but not entirely. Apart from pure mineral dust, desert aerosol particles are often mixed with small amounts of biological material or particles exhibit a coating. Aging on the ground or during atmospheric transport can deactivate nucleation sites and thus strong ice-nucleating minerals may not exhibit their full potential. In the partner paper of this work, it was shown that mineralogy determines most but not all of the ice nucleation behavior in the immersion mode found for desert dust. In this study, the influence of semi-volatile organic compounds and the presence of crystal water on the ice nucleation behavior of desert aerosol ~~in addition to mineralogy~~ is investigated. This work focuses on the deposition and condensation ice nucleation modes at temperatures between 238 ~~to~~ and 242 K of 18 dust samples sources from 9 deserts worldwide. Chemical imaging of the particles' surface is used to determine the cause of the observed differences in ice nucleation. It is found that while the ice nucleation ability of the majority of the dust samples is dominated by their quartz and feldspar content, in one carbonaceous sample it is mostly caused by organic matter, potentially cellulose and/or proteins. On the other hand, the ice nucleation ability of an airborne Saharan sample is found to be diminished, likely by semi-volatile species covering ice nucleation active sites of the minerals. This study shows that in addition to mineralogy, other factors such as organics and crystal water content can alter the ice nucleation behavior of desert aerosol during atmospheric transport in various ways.

1   Introduction

The ice phase in clouds causes one of the largest uncertainties for understanding the role of clouds in the present climate and for projecting future climate (Boucher et al., 2013). While it is known that for the initial formation of ice in clouds warmer than 235 K certain aerosol particles, so-called ~~ice-nucleating~~ ice nucleating particles (INPs), are necessary, many aspects of

heterogeneous ice nucleation remain poorly understood (Coluzza et al., 2017; Kanji et al., 2017). Mineral dust is thought to be the most prevalent INP type in the atmosphere (Hande et al., 2015). Schaefer (1949) ~~already~~ found naturally occurring mineral dust particles to nucleate ice at temperatures $T < 258$ K. Cozic et al. (2008) and Kamphus et al. (2010) detected mineral dust in ice crystal residuals in mixed-phase clouds. In these clouds the most common ice-nucleating mechanisms are likely immer-

5   sion and contact freezing. Both mechanisms require a cloud droplet to form first and an INP to either initiate freezing from the inside of the droplet (immersion) or via contact with the surface of the droplet (contact freezing). Cziczo et al. (2013) observed mineral dust also in ice crystal residuals in cirrus clouds. When the relative humidity with respect to ice is high enough (e.g. $RH_i > 140$ % at 238 K), ice forms via homogeneous freezing of solution droplets without the help of an INP (Koop et al., 2000). At lower RH ice may form via immersion freezing on INPs in solution droplets (Zuberi et al., 2002) or via the deposi-

10   tion mode, where ice nucleation occurs on an INP directly from the vapor phase (Vali, 1985; Vali et al., 2015). Condensation freezing is understood as freezing occurring during the formation of a liquid phase, when water saturation is exceeded but before a droplet has formed. Recently, the differentiation between condensation and immersion freezing has been questioned (Marcolli, 2014; Vali et al., 2015). Furthermore, it has been suggested that freezing at water subsaturated ($RH_w < 100\%$) conditions, referred to as deposition nucleation, may in some cases be explained by condensation and subsequent freezing of

15   water in pores on the particles' surface (Pore Condensation and Freezing, PCF, Marcolli 2017).

Mineral dust is thought to have an influence on cloud microphysical processes on a global scale with global dust emission rate estimates of up to 5 Pg yr^{-1} (Engelstaedter et al. 2006 and references therein). DeMott et al. (2003) found increased concentrations of INPs in air masses over Florida which carried Saharan dust, while Creamean et al. (2013) observed precipitation in California to be influenced by dust from Asia and the Sahara. Over Europe, Chou et al. (2011) and Boose et al. (2016a) found

20   periods of Saharan dust advection to coincide with increased INP concentrations under mixed-phase cloud conditions. Even at the South Pole, Kumai (1976) identified about 60% of ice crystal residuals to be clay minerals.

For several decades, clay minerals were believed to be responsible for the ice activity of mineral dust, mainly due to their high mass fraction in airborne dust. Recently, ~~potassium feldspars~~ K-feldspars have been identified to nucleate ice at warmer temperatures or lower relative humidity than all other minerals, both in the immersion mode (Atkinson et al., 2013; Zolles

25   et al., 2015) as well as in the deposition and condensation modes (Yakobi-Hancock et al., 2013). Paramonov et al. (2018) found for three dust samples from Iceland, China and the Himalayas the ~~potassium feldspar~~ K-feldspar content to correlate well with the ice nucleation activity of dust at temperatures between 238 and 243 K. ~~Amongst the K-feldspars, microcline has a remarkable ice nucleation ability at temperatures up to 271 K (Harrison et al., 2016). However, Kaufmann et al. (2016) found microcline~~ While Kaufmann et al. (2016) found K-feldspar only in one out of eight dust samples collected in potential

30   atmospheric dust source regions in South America, Asia and Africa~~and microcline was only present in one out of four airborne Saharan dust samples studied by Boose et al. (2016c)~~, we observed K-feldspar to be present in all but one sample from a collection of 21 samples from deserts around the world (Boose et al., 2016c). Furthermore, feldspars are prone to chemical weathering processes in acids or water which may passivate certain active sites and decrease the feldspar's ice nucleation activity (Augustin-Bauditz et al., 2014; Wex et al., 2014; Harrison et al., 2016). The nature of these active sites is still under

35   debate. It is suspected that they are associated with high energy defects in the lattice structure such as steps, cracks and impuri-

ties (Fletcher, 1969; Marcolli et al., 2007) or crystal boundaries in twinned crystals (Harrison et al., 2016; Whale et al., 2017) (Harrison et al., 2016) where a (100) crystal plane is exposed to water or vapor (Kiselev et al., 2017). Whale et al. (2017) found that feldspars with perthitic microtexture, i.e. intergrowth of sodic alkali feldspar into a host of K-feldspar, have the highest ice nucleating ability. Berner and Holdren (1977) observed weathering to occur primarily at these excess energy sites on the

5 feldspar surface. During atmospheric transport, such chemical weathering processes or aging could alter the ice nucleation activity of feldspar particles compared to those on the ground or freshly cleaved crystals used in laboratory studies (Atkinson et al., 2013; Yakobi-Hancock et al., 2013; Harrison et al., 2016; Kiselev et al., 2017). By implementing parameterizations for marine organics and feldspar INPs into their global model, Vergara-Temprado et al. (2017) found indications that terrestrial INP concentrations could be dominated by feldspar. However, atmospheric aging effects were not taken into account. Thus,

10 feldspar has the potential to be the most important ice-nucleating mineral in the atmosphere but its atmospheric relevance is yet to be confirmed.

Atmospheric aging processes are challenging to observe in-situ, thus several laboratory studies have mimicked potential aging processes. These processes often modify the surface of dust particles and as such the ice nucleation ability of mineral dust. Zolles et al. (2015) could block and unblock surface ice nucleation sites with slected selected organic molecules. Sulfuric acid

15 coating leads to a reduction in the ice nucleation ability of mineral dust (Sullivan et al., 2010; Augustin-Bauditz et al., 2014), the exposure to low amounts of ozone increases it (Kanji et al., 2013) and coatings of organic aerosol make no difference to it in condensation mode (Koehler et al., 2010; Kanji et al., 2018). The presence of ammonium sulfate has been suggested to improve the ice nucleation ability of Saharan dust advected to Tenerife (Boose et al., 2016b). Recently, Kumar et al. (2018a) and Whale et al. (2018) confirmed that very dilute ammonium salt solutions (< 1 mol kg^{-1}) increase the ice nucleation temperature

20 of microcline by 3 to 4.5 K. While surface-collected dust particles from the Sahara were found to have negligible amounts of nitrate or sulfate, a high degree of mixing of nitrate and/or sulfate with mineral dust was observed after advection to Cape Verde, Tenerife or Ireland (Kandler et al., 2007; Dall'Osto et al., 2010).

Residues from ice-nucleating biological material such as fungal proteins or nanoscale pollenaceous INPs have been observed to adsorb to mineral dust while retaining their ice nucleation ability (Schnell, 1977; Conen et al., 2011; Augustin-Bauditz

25 et al., 2016; O'Sullivan et al., 2015, 2016). Even though desert soils contain typically < 1 % organic matter due to the low average annual precipitation (Troeh and Thompson, 2005), long-range transport of dust has been suggested to efficiently disperse bacteria on a global scale (Hara and Zhang, 2012). Enriched fluorescent particle concentrations, an indication for enriched biological material, in long-range transported Saharan dust were found by Kupiszewski et al. (2015) in ice crystal residuals from mixed-phase clouds in the Swiss Alps, and in condensation mode INPs at 241 K by Boose et al. (2016b) on the Canary

30 Islands. In contrast to biological material, secondary organic aerosol coatings have been observed to decrease the ice nucleation ability of dust particles in the laboratory in deposition mode (Möhler et al., 2008) but not in condensation mode (Koehler et al., 2010; Kanji et al., 2018).

In a partner paper to this work (Boose et al., 2016c) we investigated the immersion mode ice nucleation activity of airborne dust samples, which were collected after atmospheric transport or sampled from the surface in deserts. We showed that the

35 K-feldspar fraction of , i.e. the fraction of microcline plus orthoclase, of these dust samples correlates well with the ice-active

surface site density in the immersion mode at T = 253 K. At $T \leq 245$ K the best correlation of the ice nucleation activity was ~~showing~~ found for the bulk quartz plus feldspar (microcline, orthoclase and plagioclase) content in the dust samples while the fraction of clays was negatively correlated with the ice nucleation activity. Quartz alone has been found to show various immersion mode ice nucleation activities in laboratory studies~~, ranging from~~. Zolles et al. (2015) found quartz

5 being active at temperatures comparable to microcline~~(Zolles et al., 2015), over being active~~, while Atkinson et al. (2013) measured ice nucleation activity below feldspar temperatures but above those of clay~~(Atkinson et al., 2013), to showing~~. Kaufmann et al. (2016), on the other hand, only observed ice nucleation activity at temperatures comparable to or lower than those of clays~~(Kaufmann et al., 2016).~~. These differences in ice nucleation ability can be related to the history of the quartz samples and different ways of pre-processing them (Zolles et al., 2015). Milling quartz samples leads to a break-up of Si-O-Si

10 bridges on the surface, leading to the formation of Si-OH and Si-O-OH in the presence of water vapor, which increases the ice nucleation activity of the quartz particles (Kumar et al., 2018b). Quartz is the most abundant mineral on Earth and is widely spread in various soils. It is highly resistant to chemical and mechanical weathering (Goldich, 1938), the latter leading to its abundance increasing with particle size. But quartz is found to a lower degree also in smaller sized dust particles (e.g. 11% volume fraction of 1.6 μm sized particles over Morocco, Kandler et al. 2009).

15 The current paper focuses on the ice nucleation behavior at 238 to 242 K of airborne and surface collected dust samples. We investigate ice nucleation at a constant temperature while RH ~~conditions are~~ is increased from ice saturation to above water saturation. While the partner paper (Boose et al., 2016c) showed that mineralogy explains most but not all of the observed ice nucleation behavior of desert dust, this paper focuses on the role of compounds other than the pure minerals for ice nucleation. We use thermogravimetric analysis and chemical imaging methods to highlight the effect of other entities mixed with the dust,

20 such as organic material or soot, on the ice nucleation behavior. In addition to the samples studied in the partner paper (Boose et al., 2016c), three more airborne Saharan samples are investigated. Comparing the in total seven airborne Saharan samples to in-situ measurements in the Saharan Air Layer, we find low variability in the ice nucleation behavior of dust from different sources. Furthermore, we show that airborne samples containing orthoclase are similarly active at the studied temperatures as those containing microcline.

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2 Methods

2.1 Dust sample origins and processing

In this part of the series we present ice nucleation measurements of 18 dust samples. 7 airborne samples were collected after advection from the Sahara. 4 of the airborne samples were collected directly from the air in August 2013 and 2014 at the Izaña

30 observatory on Tenerife, Spain, using a custom-made large cyclone (Advanced Cyclone Systems, S.A.: flow rate: 200 m^{3}h^{-1}, D_{50} = 1.3 μm, the diameter at which the collection efficiency is 50%). The remaining three airborne samples were collected by deposition on solar panels or roofs in April 2014 (Crete ~~, Peloponnese~~and Peloponnese, Greece) and on 10th of May, 2010 ~~in~~ (Aburdees, Egypt). Nine samples were collected from the surface in the following deserts: (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. A map showing the locations is provided in Boose et al. (2016c). Before arriving to the

5 laboratory, samples were stored in various ways: Samples collected from the surface were typically stored for several weeks in PET bottles or other plastic containers. Airborne samples were stored in polypropylene tubes and sealed with paraffin wax tape. In the laboratory, all samples were stored in the dark at room temperature in polypropylene tubes after pre-processing (sieving/milling, see below). While changes in the ice nucleating ability due to water uptake, loss of volatile material or growth of biological material which may occur during storage cannot be excluded, they are assumed to be minor because the samples

10 were collected and stored under dry conditions, hardly exposed to air and kept at a lower temperature than at which they were collected. The Israel sample and the Etosha sample are from the same batch as those studied in Kaufmann et al. (2016). The surface-collected samples were sieved with a cascade of dry sieves (Retsch Vibratory Sieve Shaker AS 200) with 32 μm diameter being the smallest cut-off size. Most samples only contained a few weight percent in this size range. The Australia and Morocco samples were milled using a vibratory disc mill (Retsch, model RS1) as the fraction of particles in the sub-32 μm

15 size range was too low for ice nucleation experiments. Particles in the lowest available size bin (32 to 64 μm) of the Morocco sample were milled. The Australia sample was first sieved with a coarse, millimeter range sieve to separate any large material, and the remaining smaller fraction was milled. For the Israel and the Atacama dusts a sieved and a milled sample was included in the study. The Israel sample was first sieved and part of sub-32 μm fraction was milled while in case of the Atacama sample part of the initial, unsieved batch was milled.

20 To investigate if the ice nucleation activity of the samples is influenced by biological particles internally or externally mixed with the dust or by organic coatings on the dust particle surface, selected samples were heated to 300°C and stayed at this temperature for 10 h before the ice nucleation experiments. At this temperature proteinaceous material, such as bacterial and fungal INPs should be denatured (Pouleur et al., 1992) and the majority of organic material, such as glucose, is combusted and evaporated (Kristensen 1990 and references therein).

25 ## 2.2 Dust particle generation and size distribution

Dust particles were dry dispersed using a rotating brush generator (RBG, Palas, model RBG 1000) with N_2 (5.0) as carrier gas into a 2.78 m^3 stainless steel aerosol reservoir tank (Kanji et al., 2013) via a cyclone that confined the dust size distribution to below D_{50} = 2.5 μm. Total particle concentration was monitored using a condensation particle counter (CPC; TSI model 3772). The tank was filled with particles up to a concentration of 1200 cm^{-3}, which decreased steadily to about 300 cm^{-3}

30 over approximately 10 h. The tank was cleaned before an experiment by repeatedly evacuating and purging it with N_2 until the particle concentration decreased to 30 - 90 cm^{-3}.

The particle size distribution of all samples was measured with a scanning mobility particle sizer (SMPS; TSI; DMA model 3081, CPC model 3010) for mobility diameters (d_{m}) between ~~12.2~~12 - 615 nm and an aerodynamic particle sizer (APS; TSI; model 3321) for aerodynamic diameters (d_{aer}) between 0.5 - 20 μm. The mobility and aerodynamic diameters were converted

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to volume equivalent diameter (d_{ve}) by assuming a typical dust particle density of $\rho = 2.65$ g cm^{-3} (Hinds, 1999; Kandler et al., 2007; Hiranuma et al., 2015a) and optimizing the shape factor χ to receive the best overlap of two size distributions measured by the SMPS and APS. This yielded $\chi = 1.36$, which is in the range of earlier studies (Hinds, 1999; Alexander, 2015; Hiranuma et al., 2015a). Assuming spherical particles, the area size distribution was calculated and fitted with a bimodal

5 log-normal distribution. The mean particle surface area ($\overline{A_{ve,w}}$) was calculated from the resulting fit for each sample. Four size distributions and the fit parameters for all samples are provided in Boose et al. (2016c). During an experiment $\overline{A_{ve,w}}$ was reduced by between 6 to 24% due to a faster sedimentation of larger particles in the aerosol tank. The Great Basin sample was coarser than the other samples and settled out faster. Therefore two refills were necessary and $\overline{A_{ve,w}}$ varied by 64%.

10 ## 2.3 Mineralogical~~and~~, thermogravimetric and morphology analysis

The quantitative mineralogical composition of the bulk dust samples was investigated with the X-ray diffraction (XRD) Rietveld method (Rietveld, 1969) using a Bragg-Brentano diffractometer (Bruker AXS D8 Advance with CoKalpha-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

15 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). Due to the small amount of dust sample, it was not possible to do a mineralogical analysis of the identical size fraction as in the tank ($< 2.5~\mu$m). Instead, the entire size fraction of the airborne and the milled samples, and the sub-32 μm fraction of the sieved samples was used. The measured mineralogical composition is provided in Boose et al. (2016c) and that of the additional ~~Izaña~~ Tenerife samples

20 in Table 1. The ~~Izaña2014~~ Tenerife2014 ~~2~~ 1 sample was additionally measured by Powder XRD (Panalytical XPert Pro) in Bragg-Brentano geometry equipped with a Copper anode providing CuKa radiation. A diffractogram was recorded before and after heating the sample to 300°C for 10 h on a silicon sample carrier.

Thermogravimetric analysis (TGA) of six of the dust samples was conducted by gradually heating the dust samples from 40 to 300°C at 10 K/min and continuously recording the mass of the samples in a thermogravimetric analyzer (Model Pyris 1 TGA,

25 PerkinElmer). During the temperature scan, the samples were under a constant nitrogen flow of 20 ml/min.

The morphology of one samples was investigated using scanning electron microscopy (SEM, FEI Quanta 250 FEG, ThermoFisher Scientific).

2.4 Chemical imaging: ATR spectrometry and Raman mapping

30 Infrared-Attenuated Total Reflection (IR-ATR) spectroscopy was carried out on a FTIR (Bruker Vertex 80v) equipped with an ATR cell (Pike GladiATR, diamond ATR crystal). The beam path of the spectrometer and the optical parts of the ATR cell are under vacuum (1.65 mbar) to minimize the influence of water vapor and CO_2. The crystal where the sample is placed sits in a cell that is flushed with nitrogen gas before and through the measurement for the same reason. A liquid nitrogen cooled

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MCT detector is used for spectra acquisition. Spectra of the samples were recorded before and after a heat treatment. For the heat treatment the samples were placed for 10 h into a laboratory oven at 300°C. The spectral window was set between 700 and 4000 cm^{-1} with a resolution of 1 cm^{-1}. Spectra for the ~~Izaña2014_2~~Tenerife2014_1, Etosha and Australia samples were recorded this way. Raman images were recorded on a confocal Raman spectrometer (WiTec alpha300 RSA+) using a 488 nm

5   laser, 50x magnification, 600 lines mm^{-1} grating and a laser power of 4.7 mW. For Raman imaging the dust was impacted on a clean aluminium surface as described in Ofner et al. (2017) and subsequently mapped with the aid of a Piezo XY-stage. Raman mappings were carried out before and after the same heat treatment as for the IR-ATR measurements. The Etosha and Australia samples were mapped by this method.

2.5   Deposition and condensation nucleation experiments and data treatment

10   Ice nucleation experiments were conducted with the portable ice nucleation chamber, PINC (Chou et al., 2011; Boose et al., 2016a). Aerosol particles are sampled from the tank, dried and introduced into the chamber, where they are layered between two particle-free sheath air flows. Before an experiment, the two chamber walls are coated with a thin layer of ice. During an experiment a temperature gradient is applied between the walls, leading to diffusion of water vapor and heat. A linear gradient of temperature and the partial pressure of water vapor between the walls leads to supersaturation with respect to ice. At a

15   constant aerosol layer temperature, the relative humidity (RH) is raised at a constant rate until supersaturation with respect to water of a few percent (RH_w = 103-105%) is reached. If ice nucleation occurs under these conditions, ice crystals grow on the INPs and are detected in the lower part of the chamber by an optical particle counter. As the ice nucleation mechanisms cannot be identified visually in PINC we refer to the deposition mode at $RH_\mathrm{w} < 100\%$ and to condensation freezing at $RH_\mathrm{w} > 100\%$. We use these relative humidity-based thermodynamic regimes as an operational definition, which does not

20   exclude the possibility of PCF to occur at $RH_\mathrm{w} < 100\%$ (Marcolli, 2017). Condensation mode refers here to the conditions above water saturation where full droplet activation prior to freezing cannot be guaranteed.

In the deterministic concept (Langham and Mason, 1958) ice nucleation is assumed to take place at so-called ice nucleation active sites on the particle's surface (Vali, 1966). The probability of such a site to be present on a particle and thus of the particle to nucleate ice at a certain temperature scales with the particle's surface area (Archuleta et al., 2005; Connolly et al.,

25   2009; Welti et al., 2009). To account for this dependency and compare the ice nucleation ability of the different dust samples the ice-active surface site density n_s was calculated:

$$n_\mathrm{s} = -\frac{\ln(1-AF)}{\overline{A_\mathrm{ve,w}}} \approx \frac{INP}{N_\mathrm{tot}\overline{A_\mathrm{ve,w}}} \tag{1}$$

with the total particle concentration N_tot and the activated fraction AF given by INP/N_tot. The approximation is only valid for $AF < 0.1$ which is the case in this study. As aerosol particles larger than 1 μm were in the size range of the ice crystals and

30   could not be differentiated based on size in the optical particle counter spectra, the n_s was corrected by subtracting the average n_s at RH_i = 100 to 103%. At these low RH_i values no ice nucleation is expected, thus counts in the size range of ice crystals are assumed to be large dust particles.

The ice nucleation activity of the Australia, Atacama milled, Etosha, ~~Izaña2014_2~~Tenerife2014_1, Peloponnese and Morocco samples was additionally measured after they had been exposed to 300°C for 10 h. For these experiments the tank was not used. Instead, dust was dry dispersed using particle-free air from a sonicated flask via a cyclone with a cut-off of 2.5 μm and a diffusion dryer into PINC, a CPC, an APS, and a SMPS. The unheated samples were additionally measured with the same set-up to allow direct comparison. The n_s measured with the tank set-up in comparison to the sonicated flask set-up for the unheated samples varied between a factor of 1/3 to 3, which is a good agreement given the limitations of n_s as a comparison parameter (Hiranuma et al., 2015b, 2018). Possible reasons for the differences are the sonicated flask breaking up larger entities, thus leading to a different mineralogy per size bin than the rotating brush generator, or uncertainties stemming from the use of a different measurement set-up. This shows the limits of using n_s for such complex, polydisperse samples, which ideally should remove any size dependency. To reduce set-up dependent uncertainty, only results measured with the same measurement set-up are compared in the following discussion.

3 Results and Discussion

3.1 Ice nucleation in the deposition and condensation mode and dust mineralogy

Ice-active surface site density was determined for 18 dust samples of which 4 are from the Sahara and were collected after atmospheric transport at the Izaña observatory in Tenerife, and 3 after atmospheric transport in the Peloponnese, in Crete and the Sinai Peninsula in Egypt. Figure 1 shows RH-scans at three temperatures for these Saharan samples together with RH-scans measured online at the Izaña observatory during the CALIMA campaigns in August 2013 and 2014, when the observatory was located in the Saharan Air Layer. The data and description of the location and campaigns are given in Boose et al. (2016b). The online and offline measured n_s agree well. Most of the n_s curves of the different Saharan samples span an order of magnitude. In Fig.2 a scatter plot of $\ln(n_s)$ at RH_w = 102% against the quartz plus feldspar content of the dust samples is shown which is discussed in more details below. It reveals that the airborne Saharan samples are similar in n_s and their quartz plus feldspar fraction (20 - 30 wt%). This holds true for most other mineral components, as shown in Table 1. The biggest differences are found for smectite and calcite, the latter accounting for 25 to 33 wt% in the Crete, Egypt and Peloponnese samples but only for 4 to 7 wt% in the ~~Izaña~~ Tenerife samples. Smectite on the other hand was only found in the ~~Izaña~~ Tenerife samples (23 to 32 wt%) and not in dust from the other three locations. Smectite and calcite are both known to have a low ice nucleation activity (Atkinson et al., 2013; Kaufmann et al., 2016). Thus, the similar amount of one or the other mineral in all Saharan dust samples is in line with the observed similar n_s. ~~Microcline was found in four out of five investigated Izaña samples (4-5 wt%) and orthoclase (4-5 wt%) is present in one Izaña and the other three Saharan samples. Comparing the~~ Differentiating between microcline and orthoclase and comparing the bulk mineralogy to the surface-dependent ice nucleation ability~~has the caveat to introduce~~, introduces uncertainty. Within this uncertainty, there is no detectable effect from the presence of ~~the more ice nucleation active microcline K-feldspar over orthoclase for~~ microcline versus orthoclase in the airborne samples at the studied temperatures. This is in line with the findings by Whale et al. (2017) that there is no correlation between ice nucleating ability and the level of ordering in the aluminosilicate framework, which determines if orthoclase (less ordered) or microcline (more

ordered) is present.

To determine how well the dust mineralogy can overall predict the ice nucleation activity, the correlation of $\ln(n_s)$ with the fractions of the most common minerals in the dust samples was compared in the partner paper (Boose et al., 2016c). This comparison showed that the immersion mode ice nucleation activity ~~at~~ correlates best with the K-feldspar fraction alone at $T = 253$ K,

5   a temperature where only feldspar minerals are found to have significant ice nucleation activity (Atkinson et al., 2013). At $T \leq 245$ K, the ice nucleation activity correlates best with the quartz and quartz+feldspar fractions of the dust samples ~~, while at $T = 253$ K it correlates best with the K-feldspar fraction alone (Boose et al., 2016c).~~ (Boose et al., 2016c). At these lower temperatures, quartz and to a lower degree also clay minerals were found to nucleate ice efficiently (Atkinson et al., 2013). Before investigating the role of other compounds, here we do a similar correlation analysis of the $\ln(n_s)$ at $T = 238, 240$

10   and 242 K and $RH_w = 97\%$ and 102% with the fraction of various minerals contained in the dust samples. Figure 2 shows exemplarily a scatter plot of $\ln(n_s)$ at $RH_w = 102\%$ against the quartz plus feldspar content of the dust samples. The Etosha sample was excluded from the correlation as it does not contain any significant amount of these minerals. The surface-collected samples with a high ratio of quartz and feldspar tend to have a higher n_s than the airborne samples. This trend is similar at the three investigated temperatures. The resulting correlation coefficients for the investigated mineral fractions are provided in

15   Table 2. The findings by Boose et al. (2016c) for the immersion mode n_s are confirmed in the deposition and condensation mode: at all three tested temperatures, the highest correlation of n_s is found for the fraction of quartz, followed by the quartz + feldspar fraction. The correlation with quartz alone is dominated by the Australia sample, which consists of 91 wt% quartz and is by far the most ice nucleation active dust sample. The remaining samples, which consist of at most 64 wt% of quartz, correlate only weakly with quartz alone (e.g. R = 0.29, p=0.27, at $T = 238$ K and $RH_w = 102\%$) and better with quartz plus

20   feldspar (R = 0.41, p=0.08). Adding illite to the quartz + feldspar fraction leads to insignificant changes of the correlation coefficient while adding kaolinite reduces it. Calcite and kaolinite alone are always negatively correlated with n_s in both deposition and condensation mode. These observations are reasonable when compared to the findings of Atkinson et al. (2013), who found a higher n_s for quartz over clay minerals at $T > 236$ K but lower n_s for quartz than for feldspars for $T > 242$ K. Generally, the correlations are lower in this study compared to the immersion mode data from Boose et al. (2016c). A possible

25   reason for this is that the only partial activation of INPs at these measurement conditions in PINC due to an inhomogeneous RH-profile along the particle trajectories inside the chamber (Garimella et al., 2017) weakens the effect of differences in mineralogy. Another reason could be that surface coatings play a more prominent role at lower RH values because they are less diluted than in immersion mode. Correlating mineralogy, which is based on the bulk fraction, with the surface property n_s, leads to additional uncertainty, as described above. Effects by non-mineral substances such as coatings are discussed in the following.

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3.2 Ice nucleation and heat labile material

In this section, the role of heat labile material on the surface of dust particles is investigated. A representative subset of the samples was selected to reduce the number of experiments necessary. The Australia and Morocco sample were selected because of their exceptional high n_s, the Etosha sample, because its mineralogy did not explain the observed n_s, the Atacama milled

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sample because we expected a higher n_s from the mineralogy, and finally the Tenerife2014_1 and Peloponnese samples as representatives for two airborne samples from different locations. Figure 3 shows the n_s at 240 K and 242 K of the ~~native, i.e. unheated ,~~ unheated and the heated ~~Australia, Atacama milled, Izaña2014_2, Peloponnese, Etosha, and Morocco~~ samples. In case of the ~~Izaña2014_2~~ Tenerife2014_1 sample the heat treatment led to an increase of n_s at $RH_w < 100$ % while it had no effect above water saturation. In contrast, the maximum n_s of the Etosha sample decreased by one order of magnitude at 240 K after heating. At 242 K the n_s was below the detection limit as can be seen by a scattered flat n_s curve in Fig. 3b. The heating had a small decreasing effect on the n_s of the Peloponnese sample at all RH values and little to no significant effect on the n_s of the remaining samples. A change in ice nucleation ability due to the heating gives an indication on the nature of the active sites, i.e. if they are inherent to the minerals themselves or a semi-volatile coating material or due to biological particles, which are impacted by the heating. An RH dependency of the change in ice nucleation ability may suggest that the material which contains or coats the active sites is susceptible to dissolution.

We investigated these possible implications further by thermogravimetric analysis, IR-ATR and Raman spectroscopy of the samples. The relative mass loss under increasing temperature is shown in Fig. 4a and its first derivative in Fig. 4b. If pure samples of single minerals or organic species were studied, the TGA would show discrete steps in mass loss, indicated by spikes in the derivative plot. However, the complexity of the dust samples in this study, which consist of several minerals and likely also various other components, cause the spikes to widen and hardly discrete steps to be observed. For ~~examples~~example, Xi et al. (2004) showed that the mixture of a montmorillonite with varying concentrations of organic surfactant shifts the peak in the derivative mass between the higher temperature of the montmorillonite to the lower temperature of the surfactant, depending on the concentration of the surfactant. This makes it impossible to identify exactly which species are evaporated at which temperature. However, taking into account the temperature range, a qualitative analysis is possible.

The Morocco, Australia and Atacama milled samples, which all showed no change in n_s after heating, exhibit a small, gradual decrease in mass of at maximum 0.5% between 40°C and 300°C. In the case of the three samples whose n_s changed after heating, i.e. the Etosha, Peloponnese and ~~Izaña2014_2~~ Tenerife2014_1 samples, a larger mass loss is found. A first decrease in mass of about 1% (Etosha) to 2% (both airborne samples) is observed between 40°C and 110°C. The Etosha sample shows a second graduate mass release from 220°C onwards (1%). The two airborne samples Peloponnese and ~~Izaña2014_2~~ Tenerife2014_1 show small steps in mass release between 110°C and 225°C and 110°C and 170°C, respectively, and a continuous reduction in mass above these temperatures, reaching a total loss of 3% and 8% at 300°C, respectively.

The temperature ranges where the mass loss occurs can be related to different materials which were evaporated and potentially altered the ice nucleation behavior. The first decrease in mass at 40°C to 110°C is mostly due to the evaporation of adsorbed water on the surface of the dust particles or of volatile material such as volatile organics. At temperatures between 110°C and 300°C the mass loss is mainly related to decomposition of organic matter, e.g. amides, carboxylic and phenolic functional groups (Miyazawa et al., 2000) or the combustion of certain organic compounds such as cellulose (Stamm, 1956; Lipska and Parker, 1966). Kristensen (1990) studied various biogenic organic materials, such as cellulose, glucose, bacteria (Escherichia coli, bacillus subtilis), and humic and glutamic acid, which showed either a bimodal or trimodal pattern in the TGA derivative. They observed for all samples a first peak at 160-180°C which accounted for 10-42% of the mass loss and a second mass loss

peak between 340°C and 490°C. Most minerals present in the dust samples are stable at T $\leq$ 300°C apart from smectite and gypsum (Földvári, 2011), as further discussed below.

We performed IR-ATR spectroscopy on the Etosha and Tenerife2014_1 to investigate the nature of the material responsible for the respective decrease and increase in n_s with heating. Furthermore, we chose the Australia sample as representative for most other cases, where the n_s stayed the same. Figure 5 shows the IR-ATR spectra of the three samples before and after heating. The bands between wavenumber 700 to 1200 cm^{-1} are related to the dominant minerals in the (bulk) samples: quartz in case of the Australia sample; dolomite, calcite and ankerite in the case of Etosha; and kaolinite and smectite in case of the Tenerife2014_1 sample. Kaolinite also has signals at 3619, 3650 and 3685 cm^{-1} (Lafuente et al., 2015). No significant differences are observed between the unheated and the heated Australia and Etosha samples. The intensity differences in the mineral bands are likely related to single grains unrepresentatively amplifying the signal during sampling. The Tenerife2014_1 sample on the other hand shows clear differences before and after heating. A loss of intensity in the OH stretch region between 3500 and 3100 cm^{-1} is observed, which is too pronounced to be from adsorbed water only. Further intensity loss is observed in the C-H aliphatic region with decreasing bands between 3000 and 2850 cm^{-1}. This points to volatile organics being present on the unheated sample which were released during heating.

Raman mapping was performed on the Etosha, Tenerife2014_1 and Australia samples. Due to strong fluorescence, however, the Tenerife2014_1 spectra did not yield any information and are thus not presented here. The Raman maps for the Etosha and Australia samples are shown in Fig. 6. They reveal bands between 1200 and 1700 cm^{-1} with a distinctive pattern related to soot and carbonaceous material (Sadezky et al., 2005) being present on many particles in the Australia sample (Fig. 6a-2 and 6a-4) and on some in the Etosha sample (Fig. 6c-2 and 6c-4). The carbonaceous material is not affected by the heating (Fig. 6b and 6d). A cluster with a strong broad signal at 3180 cm^{-1} and a secondary band at around 1080 cm^{-1} is observed for the unheated Etosha sample, which is present on most particles (Fig. 6c-1 and 6c-3). After the heat treatment, no cluster is identified anymore containing the broad 3180 cm^{-1} band, yet the signal at 1080 cm^{-1} remains. This supports the interpretation that the band at 1080 cm^{-1} can be attributed to calcite. Furthermore, the band at 1080 cm^{-1} does not correlate with the 3180 cm^{-1} band, therefore they belong to two different compounds. The cluster analysis groups these signals for the unheated sample due to the spatial proximity of the materials on the dust. It is likely that on mineral dust grains with a high calcite content a compound was absorbed. During the heat treatment this absorbed compound disappeared and the calcite remained. Afterwards, the cluster analysis showed no group containing the 3180 cm^{-1} band. A filter (3180$\pm$175 cm^{-1}) was applied to search specifically for this signal. This revealed only very few particles carrying the related material after heating (Fig. 6d-1 and 6d-3).

Identification of the material which was released or decomposed during the heating was hampered by fluorescence inherent to the minerals in the samples and also possibly due to biological material if present in the unheated samples. The signal to noise/fluorescence ratio was optimized by impacting small amounts of the samples on a pure aluminum surface and by adjusting the laser power but the fluorescence could not be entirely suppressed. This, together with the complexity of the samples, inhibited an unambiguous identification of the species which were altered by the heating and may affect the ice nucleation ability. We suggest three possible candidates for the cluster with a strong Raman signal at 3180 cm^{-1} in the Etosha sample:

a) Amides typically show a Raman signal between 3300 and 3100 cm^{-1} (Socrates, 2001) as observed in the Etosha sample but distinct peaks are usually also observed for amides between 1700 and 1600 cm^{-1}, which are absent in the Etosha sample.

b) Pure ammonium sulfate has a broad band above 3000 cm^{-1} and a sharp peak at around 990 cm^{-1} (Bertram et al., 2011). While the broad band at 3180 cm^{-1} agrees well with the observed signal, a second band is found at 1080 cm^{-1} in the Etosha

5   sample. Ammonium sulfate has a band at 990 cm^{-1} which is significantly different from 1080 cm^{-1}. Thus, the signal can be attributed to the calcite which has a very prominent band at this position. In addition, the XRD measurements confirmed calcite to be present in the sample. c) Cellulose shows a broad band between 3575 and 3125 cm^{-1} and numerous bands between 1320 and 1030 cm^{-1} (Socrates, 2001). Additional bands at 1750 and 1725 cm^{-1}, 1635 and 1600 cm^{-1} and 1480 and 1435 cm^{-1} are not distinguishable in the Etosha Raman spectrum.

10 For the Etosha sample an effect of organic or other heat labile material on the ice nucleation behavior appears likely. The main minerals contained in the Etosha sample (i.e. ankerite, calcite, dolomite, and muscovite) are not known to be particularly ice nucleation active at the investigated temperatures. In case of ankerite the ice nucleation ability is unknown ~~but based~~. Based on its similarity with dolomite, a carbonate known not to be ice nucleation active, it is assumed that ankerite is also not active. Thus, one of the suggested candidates with the strong Raman signal at 3180 cm^{-1} is likely responsible for the ice nucleation

15 activity of the Etosha sample. Being part of proteins, amides are ubiquitous in nature. Similarly, cellulose is the most abundant organic compound on Earth (Kamide, 2005) amongst others as structural component of algae. Both ~~,~~ cellulose (Hiranuma et al., 2015b) and some proteins (Maki et al., 1974) have been identified to cause ice nucleation at the studied temperatures. Ammonium sulfate has been observed to correlate with higher INP concentration in Saharan dust (Boose et al., 2016b) and to increase the freezing onset temperature of microcline (Kumar et al., 2018a) and various other minerals (Whale et al., 2018)

20 by up to 3 K. ~~However, it was not found to be solely responsible for the ice nucleation ability of mineral dusts.~~ According to a study on the Ntwetwe Pan in Botswana by Thomas et al. (2014), the organic carbon concentration in a salt pan is about 1 wt% at the surface and consists of cyanobacteria and algae. We assume that similar values apply also for the Etosha pan. The Etosha sample was collected from the edge of the salt pan, a few hundred meters away from a fertile soil area containing the highest organic carbon content of the national park (Beugler-Bell and Buch, 1997). As wind erosion was identified in these

25 nearby fertile soils, aeolian transport potentially led to higher organic matter concentration at the edge of the pan compared to further to the center of the pan. Overall, this suggests that the Etosha sample's ice nucleation ability is almost entirely caused by organic matter, potentially cellulose or proteins which were mixed with or adsorbed onto the mineral dust on the ground explaining the almost complete suppression of ice nucleation of the heated samples.

In contrast to the Etosha sample, the ~~Izaña2014_2~~ Tenerife2014_1 sample consists of a number of minerals ice nucleation

30 active at the studied temperatures, e.g. orthoclase, plagioclase, and quartz (Table 1). The sample shows the largest mass loss in the TGA analysis. The rather steep step in the TGA loss curve at about 120°C suggests a certain species to be released at this temperature, probably containing aliphatic compounds as suggested by the IR-ATR measurements. The complexity of the airborne Saharan samples is indicated by García et al. (2017), who studied organic material in the Saharan Air Layer. They collected 42 PM2.5 and PM10 filters at the Izaña observatory in parallel to the ~~Izaña2013~~ Tenerife2013 sample collection

35 and the CALIMA2013 campaign in August 2013. Organic matter accounted for about 1.5 wt% of the aerosol composition

in the Saharan Air Layer and was determined to mainly consist of saccharides, related to organic material in soils, biogenic secondary organic aerosol particles resulting from isoprene and α-pinene oxidation, and organic compounds from natural and anthropogenic sources such as vegetation and engine emissions. During ~~the~~ daytime, the boundary layer reaches the altitude of the Izaña observatory and organic matter can originate from local sources. During nighttime the observatory is located in the free troposphere and aerosol sources are distant. Anthropogenic and natural emissions can originate from the North African coast or be advected from Europe (Rodríguez et al., 2011; García et al., 2017). As the dust collection took place over several days and nights, an influence of organic matter from local sources cannot be excluded.

Another explanation for the reduction in mass at temperatures below 300°C is the release of free water molecules from the crystal lattice as indicated also in the IR-ATR spectra between 3600 and 3100 cm^{-1}. In some cases, this affects the crystal lattice: Smectite, a swelling mineral, collapses under decreasing water vapor pressure as experienced during the heating. This decreases the interlayer spacing ~~(for an overview of the effect of layer charge on smectite swelling see Laird 2006)~~(for an overview of the effect of layer charge on smectite swelling see Laird (2006)). It is unknown if the change in crystal lattice has an effect on the ice nucleation ability of the otherwise only weakly ice nucleation active smectite (Pinti et al., 2012; Kaufmann et al., 2016). An effect cannot be excluded as lattice match with ice is believed to be one of the factors promoting ice nucleation (Pruppacher and Klett, 1997). In the studied samples, smectite was present in the ~~Izaña2014_2~~ Tenerife2014_1 sample (23 wt%) and traces were found in the Etosha sample (1 wt%). Thus, ~~according to our observations,~~ the collapse of the smectite lattice should ~~, if at all,~~ only influence the ~~Izaña2014_2 sampleand then~~ Tenerife2014_1 sample. In case it has an influence, this would be related to an increase in ice nucleation ability.~~Furthermore,~~

XRD analysis of the ~~native and heated Izaña2014_2 sample showed the decomposition~~ unheated and heated Tenerife2014_1 sample show the conversion of gypsum to anhydrite ~~. Gypsum has been found to show an intermediate~~ (Fig. 7). Gypsum has a low ice nucleation ability, similar to the clay minerals kaolinite and illite (Zimmermann et al., 2008). Grawe et al. (2018) found anhydrite to have a higher ice nucleation activity than quartz in the immersion mode at temperatures below 243 K when dry generated but a much lower n_s when particles were generated from an aqueous solution. Anhydrite transforms back to gypsum when exposed to a relative humidity higher than 97% at room temperature (Bracconi et al., 2010). ~~The ice nucleation ability of anhydrite at lower RH is not known~~However, this process occurs on the order of hours to days, in line with the observed differences in n_s between wet and dry generated particles in Grawe et al. (2018). Potentially, the transformation to anhydrite during heating explains the higher n_s of the heated Tenerife2014_1 sample compared to the unheated one at subsaturated conditions. In this case, a partial conversion of anhydrite back to gypsum during RH conditions above water saturation might explain the unchanged n_s of the unheated and heated Tenerife2014_1 sample above water saturation. It should be kept in mind that the bulk mineralogy as determined by XRD is not necessarily representative for the ~~particles'~~ particle surface where ice nucleation takes place. As needle formation has been observed in the transformation of gypsum to anhydrite (Azimi and Papangelakis, 2011; Grawe et al., 2016), we use the occurrence of needles in our sample as an indication that the gypsum - anhydrite transformation took place on the surface of particles and thus might be responsible for the change in ice nucleation behavior of the sample. In SEM images of the unheated Tenerife2014_1 sample (Fig. 8a) hardly any needles are visible. A small number of needles is observed at the center of the image of the heated sample (Fig. 8b) while no needles are

found in other SEM images of the heated sample (see the supplementary material). The apparently limited needle formation and the fact that only about 1 wt% gypsum is contained in the sample, ~~the effect of gypsum decomposition~~ suggests that gypsum transformation under heat treatment ~~is not deemed to be important for~~ should only have a small effect on the ice nucleation behavior of the ~~Izaña2014_2 sample. Instead,~~ Tenerife2014_1 sample. However, given that at maximum only

5 about 10 % of the particles act as INPs in case of the Tenerife2014_1 sample, the gypsum-anhydrite transformation might be non-negligible. Additionally, we suggest that the increase in n_s found under subsaturated RH_w conditions for the ~~Izaña2014_2~~ Tenerife2014_1 sample is caused by the volatilization of aliphatic compounds containing matter, as indicated by the IR-ATR and TGA measurements, which inhibited the active sites of the mineral dust itself.

10 **4 Conclusions**

In this study we showed that the fractions of quartz and the sum of quartz and feldspars in desert dust samples correlate better than all other mineral fractions with the ice nucleation active surface site density of the dust in deposition and condensation mode at temperatures between 238 K and 242 K. This is in line with the observations for the immersion mode presented in part 1 (Boose et al., 2016c) of this study. The high abundance of quartz in soils worldwide, its resis-

15 tance to chemical weathering processes and its presence in particles of all sizes make it a potentially widely spread atmospheric INP type. ~~It remains unknown why laboratory studies show various ice nucleation activities of pure quartz particles (Atkinson et al., 2013; Zolles et al., 2015; Kaufmann et al., 2016), relating to the question of how ice nucleation occurs on dust in general and on quartz in particular. Furthermore, we observed that the~~ According to a recent study by Kumar et al. (2018b), the variation in quartz ice nucleation ability found in laboratory studies (Atkinson et al., 2013; Zolles et al., 2015; Kaufmann et al., 2016)

20 and the superior ice nucleation ability of the quartz-rich samples from Australia and Morocco in this study and its partner paper, may be explained by the pre-processing of the samples. Milling of quartz samples, as done in our study, increases the ice nucleation ability of quartz by creating Si-O• and Si• radical sites which can then react with water vapor (Kumar et al., 2018b). However, milling may not be the only reason for formation of the silanol (Si-OH) groups on the surface of quartz, because exposure to water molecules in ambient humidity could also result in passively converting surface siloxane groups (Si-O-Si)

25 to silanol groups (Boehm, 1966; Wang et al., 2018). As such quartz samples may still exhibit high ice nucleation activity ~~of airborne Saharan dust at these temperatures is not higher when microcline is present in the samples compared to when orthoclase is present at typical amounts of 4-5%. If one assumes that both feldspars are equally active at these low temperatures, this result is to be expected.~~ in the absence of milling due to the particles chemical history. Thus, it remains an open question, how much quartz contributes to the ice nucleation ability of (unmilled) atmospheric dust. Apart from mineralogy, the ice nu-

30 cleation activity of desert dust is found to be influenced by organic material mixed with the dust. In a carbonaceous sample from the Etosha salt pan, where less than 1 wt% quartz and no feldspar were present, the ice-active surface site density is found to be almost entirely due to organic matter, likely cellulose or proteins, which are mixed with the dust. On the other hand, the deposition mode ice nucleation activity of an airborne Saharan dust sample was found to increase after heating. Three potential

explanations are found, two of them related to changes in the mineralogy: While it cannot be excluded that ~~this~~ the increase in n_s was caused by a change in lattice spacing due to interlayer water release, it seems ~~most likely that the~~ more likely that gypsum transforming to anhydrite made the sample more ice nucleation active~~sites~~. The Tenerife2014_1 sample is the only gypsum-containing sample that was investigated after heating, thus it remains an open question if and how much anhydrite

5   contributed to the increase in n_s. Another reason for the increase could be that the ice nucleation active sites of the unheated sample were blocked by volatile organic material. The volatilization of the aliphatic compounds during the heating recovered these active sites. This is further supported by the observation that no difference was found for the same sample in the condensation freezing mode, indicating that the water condensing on the surface may also recover the active sites. As this change in ice-active surface site density was not observed for a second airborne Saharan dust sample, it suggests that different aging

10   processes or mixing of Saharan dust with organic material during atmospheric transport can influence the dust's ice nucleation ability in both directions.

Author contributions. YB collected the Tenerife and Israel samples, conceived, and lead the measurement campaign, performed the ice nucleation measurements and analysis, performed and analyzed the XRD measurements, analyzed the TGA measurements and wrote the manuscript, PB performed and analyzed the SEM, IR-ATR and Raman measurements and contributed to the manuscript, JO contributed

15   to the Raman measurements, HG supervised the IR-ATR and Raman measurements and analysis and contributed to the manuscript, MP performed and analyzed the XRD measurements, ZAK performed the TGA measurements, BS, ZAK and UL supervised the project and contributed to the manuscript. All authors contributed to the interpretation of data.

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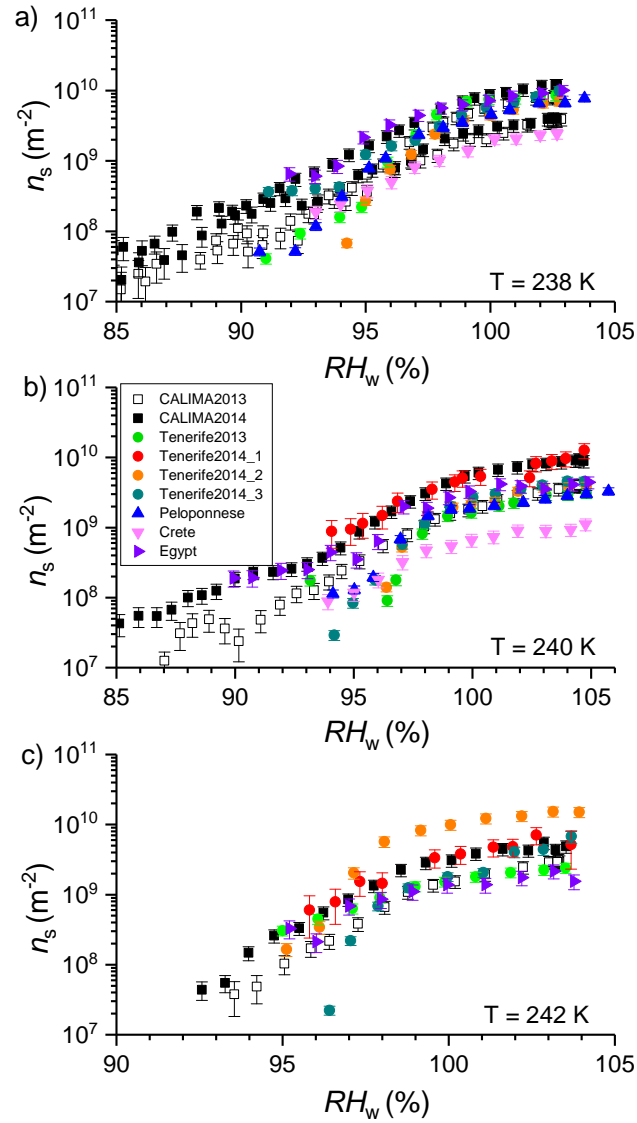
Figure 1. Ice-active surface site density at a) 238 K, b) 240 K and c) 242 K of samples collected airborne at the Izaña observatory on Tenerife in 2013/2014 (circles), in Egypt, Crete and Peloponnese (triangles) and measured in-situ during the CALIMA 2013 and 2014 campaigns (open and filled squares) which took place at the Izaña observatory.
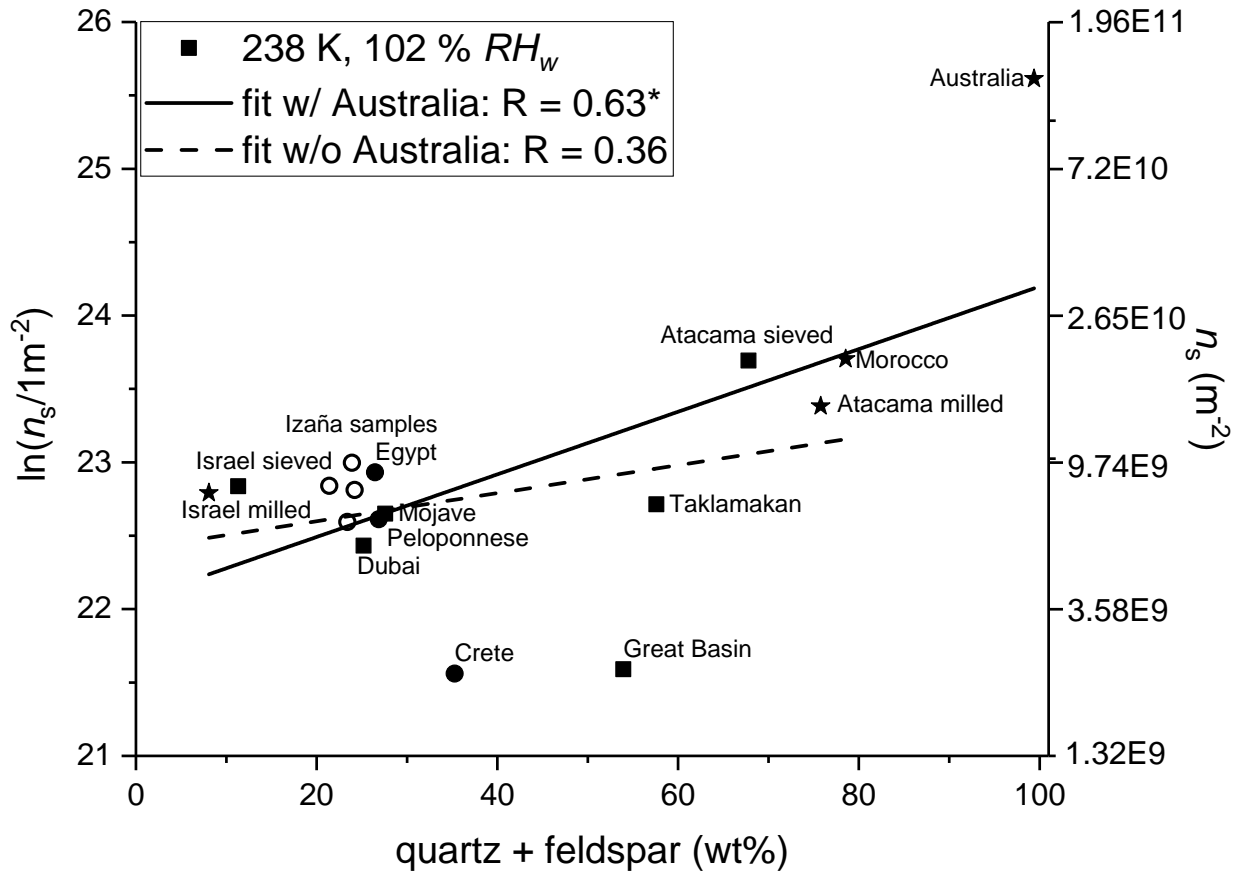
Figure 2. Natural log of the ice-active surface site density as a function of the sum of quartz and feldspar content of the samples. Square symbols indicate surface-collected samples, stars milled samples, and circles indicate airborne samples. For ~~lucidity~~clarity, the ~~Izaña~~ Tenerife samples are not named individually and instead shown as open circles. The asterix in the legend indicates that the correlation is significant at the 0.05 level.
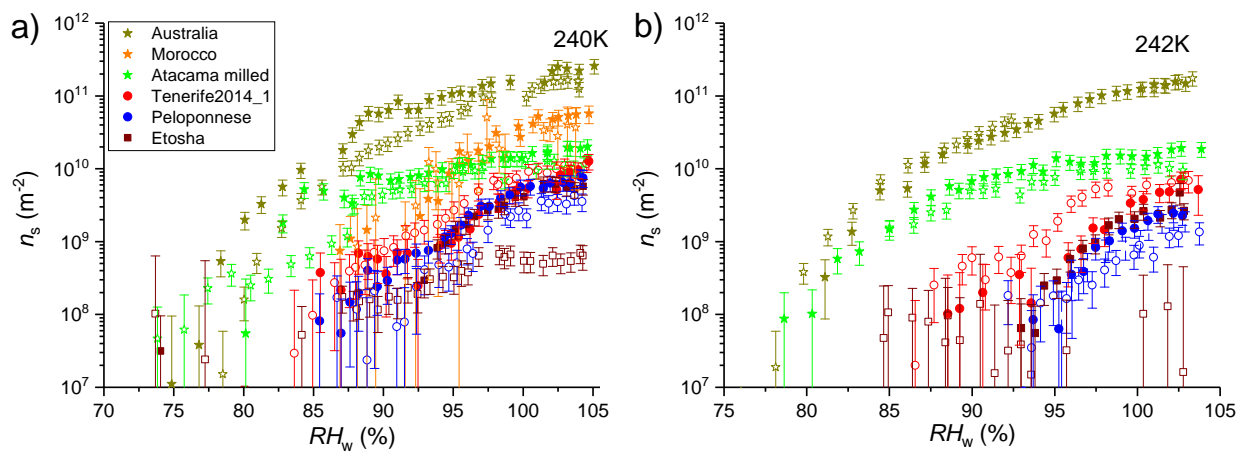
Figure 3. Ice-active surface site density at a) 240 K and b) 242 K of samples before (filled symbols) and after (open symbols) heat treatment. Error bars include the Poisson error of the INP measurements and the maximum variation of $\overline{A_{ve,w}}$. Square symbols indicate surface-collected samples, stars milled samples, and circles indicate airborne samples.
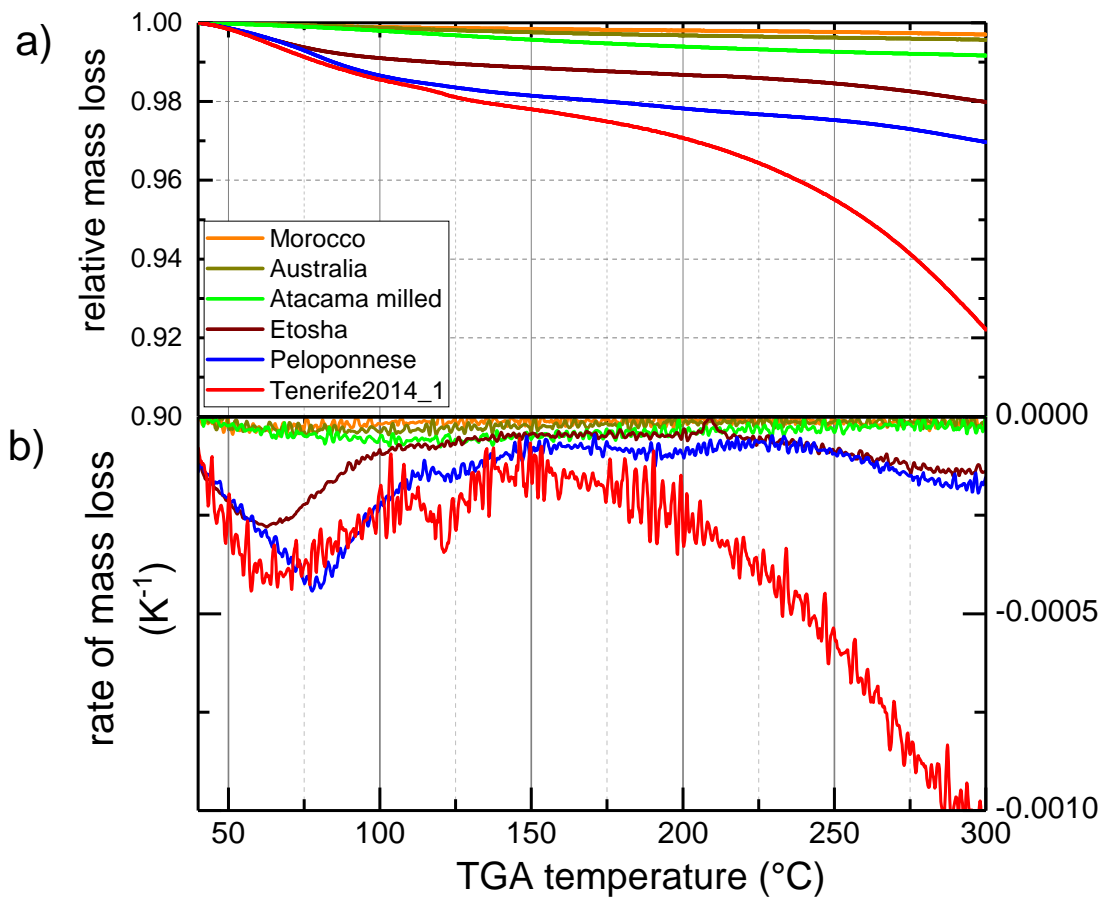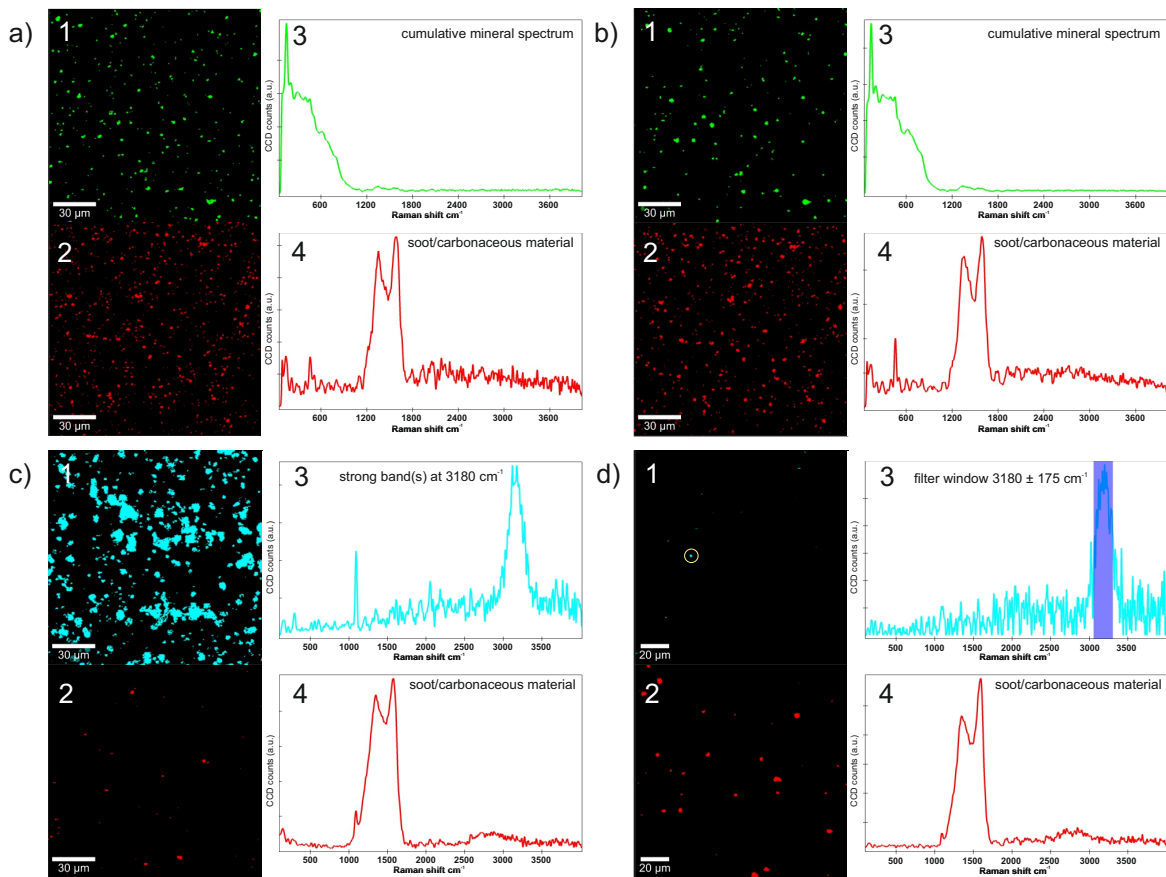
**Figure 4.** Relative mass loss (a) and its derivative (b) under heating of the different dust samples.
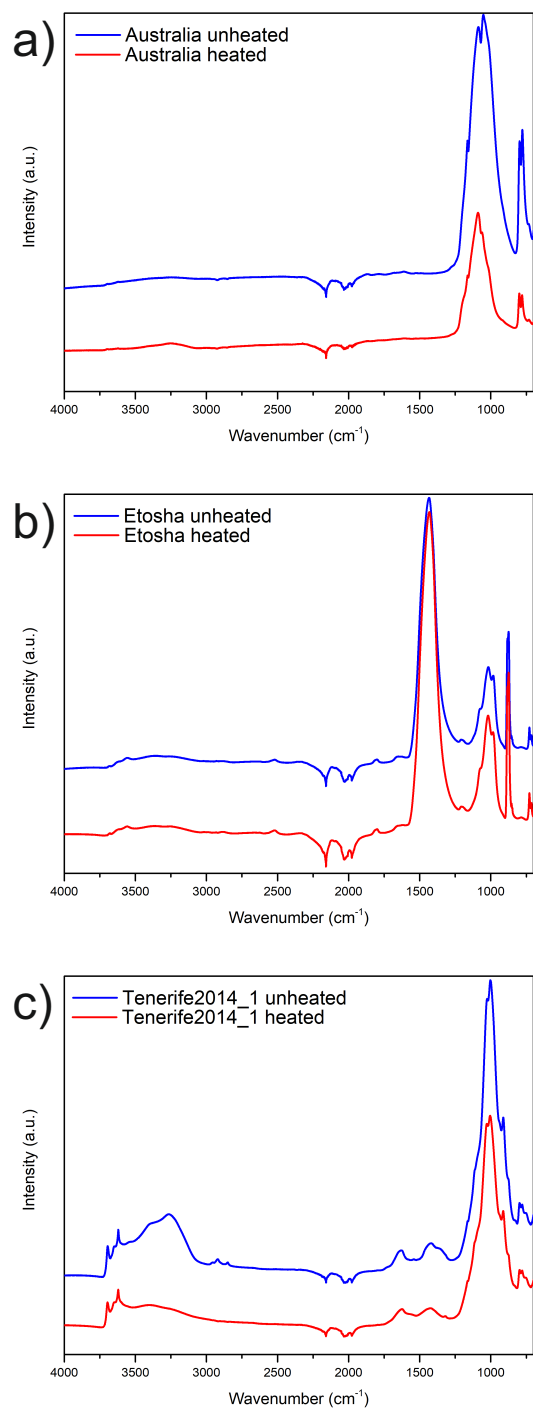
Figure 5. Attenuated Total Reflectance Infrared (ATR-IR) spectra for the a) Australia, b) Etosha, and c) ~~Izaña2014~~Tenerife2014 ~~2~~1 samples before (blue) and after heating (red).

Figure 6. Raman mapping results for the Australia (a and b) and the Etosha sample (c and d). ~~The grey maps (~~1) ~~show the location of all dust particles with the red square indicating where the Raman maps were taken.~~ and 2) ~~and 3)~~ of each panel show the location of particles from clusters with spectra similar to those shown in 4 3) and 5 4). In d2 d1) the particle is encircled for which the filter (d4 d3) found a spectrum. ~~See text for details.~~
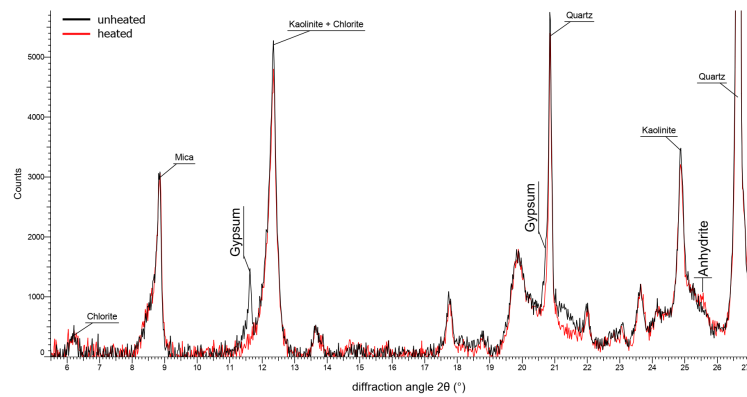
Figure 7. XRD diffractogram of unheated and heated Tenerife2014_1 sample. Vertical text indicates changes in peak height which were used to identify the decrease in gypsum and increase in anhydrite with heating. Horizontal text indicates peaks associated with other minerals in the sample.
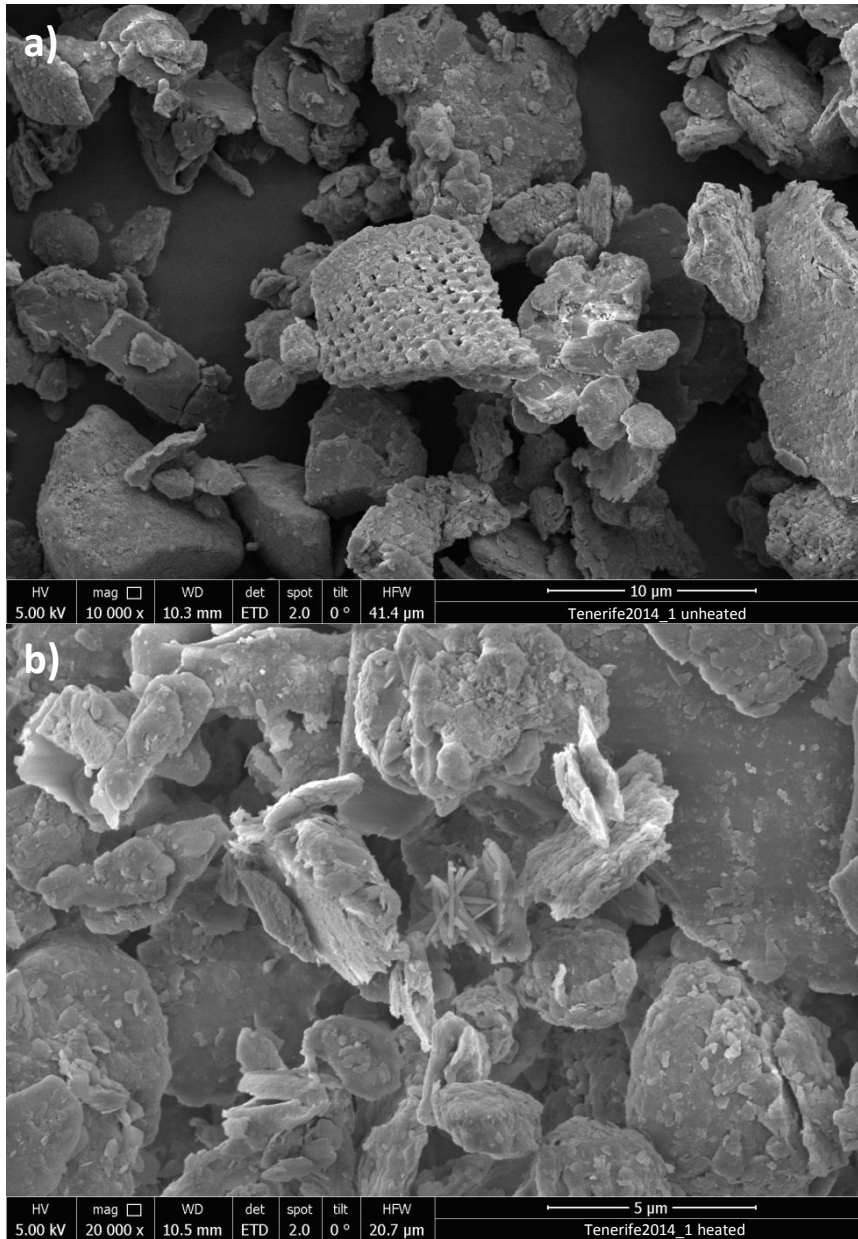
Figure 8. Scanning electron microscopy images of the a) unheated and b) heated Tenerife2014_1 sample. Note the different scales in the two images.

Table 1. Mineralogical composition in wt% of airborne Saharan dust samples. Crete, Egypt, ~~Izaña2013_2~~ Tenerife2013 (Tenerife in Part 1), and Peloponnese as in Boose et al. (2016c). Results were rounded to the nearest integer from the original Rietveld fit results, thus total composition ≠ 100 wt% may occur.

Mineral	Crete	Egypt	~~Izaña2013_2~~ Tenerife2013	~~Izaña2014~~ Tenerife2014_1	Tenerife2014_2	~~Izaña2014~~ Tenerife2014_3	~~Izaña20~~
Calcite	25	29	7	4	6	6	
Chlorite	4	8	2	3	2	1	
Dolomite	3	8	2	2		2	
Gypsum	4	6	2	1	3	2	
Halite	1	4			2	1	
Hematite	1		1	2	1	1	
Illite			6	16	7	9	
Kaolinite	12	11	16	18	13	14	
Microcline			4		5	5	
Muscovite	9	8	7	7	7	8	
Orthoclase	5	4		4			
Palygorskite	5		2	2	3	3	
Plagioclase	7		4	8	6	5	
Smectite			32	23	32	30	
Quartz	23	23	14	12	13	14	

Table 2. Overview of the Pearson correlation coefficients of the sum of selected mineral fractions and $\ln(n_s)$ at different temperatures. An asterix indicates that the correlation was significant at the 0.05 level. K-feldspar comprises microcline and orthoclase, while feldspar refers to the sum of microcline, orthoclase and plagioclase. The number of samples included in each correlation varies because the n_s of the Mojave, Peloponnese and Tenerife2014_2 samples was below the detection limit at 242 K, and the size distribution measurements of the Tenerife2014_1 sample were corrupted for the RH-scan at 238 K.

T	238 K	240 K	242 K	238 K	240 K	242 K
RH_w	97 %	97 %	97 %	102 %	102 %	102 %
number of samples	18	19	16	18	19	16
K-feldspar	0.02	0.03	-0.06	-0.08	-0.07	-0.13
~~feldspars~~ feldspar	0.15	0.08	0.05	0.05	-0.09	-0.17
quartz	0.63*	0.52*	0.47	0.71*	0.74*	0.71*
illite	-0.14	-0.15	0.11	-0.01	-0.04	0.13
kaolinite	-0.66*	-0.56*	-0.41	-0.51*	-0.35	-0.19
feldspars + quartz	0.64*	0.5*	0.44	0.63*	0.56*	0.49
feldspars + quartz+ illite	0.63*	0.49*	0.47	0.65*	0.58*	0.53*
feldspars+quartz+kaolinite	0.51*	0.40	0.35	0.54*	0.51*	0.48
feldspars+quartz+illite+kaolinite	0.50*	0.38	0.37	0.55*	0.51*	0.51
calcite	-0.12	0.05	-0.22	-0.31	-0.26	-0.32