

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 mineralogy 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  $n_s$  of one sample where anhydrite changed to gypsum after suspension. Many of the needles were larger than 300 nm (up to  $\sim 5 \mu\text{m}$ ), but could - due to the fact that the dynamic shape factor of the needles differ significantly

from unity - cross the size selection step in the DMA. Needles can be formed in both directions, from anhydrite to gypsum and gypsum to anhydrite. An example of the formation of anhydrite needles from gypsum is seen in Azimi and Papangelakis (2011). Can this also be the case of the one Izaña sample? The loss of the OH peak could also be explained by gypsum converting to anhydrite. If this is the case in your study then please change the conclusion. If not, then the discussion should cover why this volatile organic coating only applies to one sample. Isn't this expected from the other airborne samples too, at least the other Izaña samples?

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 (Braconni 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 astrich (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. ✓

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  $n_s$  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<sup>-1</sup> 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.