

We thank Reviewer 2 for his/her constructive comments. We reproduce the reviewer's comments in *blue* and our responses in black.

*P2 L38: DeMott 2013a (a needs to come first)*

We introduced DeMott 2013a at this position to follow the order. We added also Stephens et al. (1990) (Stephens, G. L., Tsay, S.-C., Jr., P. W. S., and Flatau, P. J.: The relevance of the microphysical and radiative properties of cirrus clouds to climate and climatic feedback, *J. Atmos. Sci.*, 47, 1742-1754, doi:10.1175/1520-0469(1990)047<1742:trotma>2.0.co;2, 1990). (line 38)

*P2 L67-68: This statement seems misleading - Harrison et al. (2016) points out that the fresh sanidine can be as active as microcline.*

We have removed the reference “Harrison et al. (2016)” from the concerned statement. The statement “Microcline has been reported to be IN active at higher temperatures than orthoclase and sanidine” is supported by Kaufmann et al. (2016). (lines 70-71)

*P2 L70-72: I suggest the authors to provide some additional information regarding the active site “assumption” (there is no direct observation of it in immersion freezing) and prescribe how it may be responsible for heterogeneous freezing in more detail here. Such information may benefit some statements in this manuscript (e.g., P9 L296-299; P14 L489) to sound less ambiguous.*

Active sites, nucleation sites, or, just sites have become a very common concept in the discussion of ice nucleation in the atmosphere. In Vali et al. (2015), a site is defined as a “preferred location for ice nucleation on an INP, or equivalent”. Although sites responsible for immersion freezing cannot be directly observed, their existence is plausible considering refreeze experiments, which show statistically relevant differences between the freezing temperatures of samples taken from the same stock suspension when they are subjected to repeated freezing cycles (Vali, 2014; Kaufmann et al., 2017). Such differences cannot be explained assuming that a uniform surface common to all particles of a sample is responsible for freezing. An active site needs to be large enough to accommodate a critical ice embryo. Applying classical nucleation theory, Kaufmann et al. (2017) determined active sites with areas of 15 – 50 nm<sup>2</sup> to be responsible for ice nucleation on mineral dusts. In the revised manuscript, we explain the concept of active sites in the introduction starting on line 49: “Statistical analysis of freezing experiments indicates that heterogeneous ice nucleation is induced by active sites present on a foreign body termed as ice-nucleating particle (INP). Active sites are preferred

locations for ice nucleation with minimum areas in the order of 10 – 50 nm<sup>2</sup> based on estimates using classical nucleation theory (Vali, 2014; Vali et al., 2015; Kaufmann et al., 2017). (lines 49-52)

*P3 L74: “. . .included in the current IN parameterizations.”?*

We improve the formulation by writing: “needs to be taken into account”.

*P4 L115: The authors may want to introduce more of theoretical description of the water activity based immersion freezing approach (see Knopf et al., 2018 and references therein; doi: 10.1021/acsearthspacechem.7b00120) here first for the readers, who are not familiar with it.*

More discussion on *water activity based immersion freezing approach* has been added in the “Introduction”. Lines 86-89: “Describing the kinetic (non-equilibrium) IN process as a simple function of a thermodynamic (equilibrium) quantity  $\Delta a_w$  is tempting because of its simplicity. Therefore, the applicability of “*water-activity criterion*” proposed by Koop et al. (2000) for homogeneous IN to heterogeneous IN temperatures of various types of INPs in immersion mode has been probed by several studies in the past.” And lines 105-107: “Several other studies that have applied this approach to describe heterogeneous IN include Zobrist et al. (2006), Knopf et al. (2011) and Archuleta et al. (2005) (see Knopf et al. (2018) for a detailed review on this topic).”

*P4 L130-132: The authors may briefly discuss the reproductively of onset temperatures, such as  $T_{het}$ ,  $T_{hom}$  and  $T_{melt}$ , by DSC for the samples used in this study. This additional information may be beneficial to the readers, who are not familiar with the DSC technique.*

We experimentally determine the reproducibility by repeating all experiments at least once. We give the experimental variability that includes emulsion preparation and DSC measurements in the figure captions by stating e.g. for Fig. 3: “Symbols are the mean of at least two separate emulsion freezing experiments. Three symbols carry error bars to show representative experimental variations (min-to-max) in  $T_{het}$  and  $a_w$ .”

We add this information also to the methodology section 2.2 of the revised manuscript: “Average precisions in  $T_{het}$  are  $\pm 0.15$  K with maximum deviations not exceeding 0.8 K.  $T_{hom}$ , and  $T_{melt}$  are precise within  $\pm 0.1$  K. Absolute uncertainties in  $F_{het}$ , are on average  $\pm 0.02$  and do not exceed  $\pm 0.1$ .” (lines 165-167)

*P4 L144-P5 L150: Please clarify if the samples were re-sonicated or re-homogenized prior to each time trial DSC analysis. The presence/absence of any additional physical sample modifications should be stated.*

The suspensions were sonicated each time before preparing emulsion. This information is now

mentioned in the revised manuscript on lines 172-173: “Each suspension was sonicated for 5 min before preparing the emulsions in order to re-suspend the particles that have settled over time and avoid particle aggregation.”

*P5 L164-167: How does this BET specific surface value compare to the other values from previous microcline IN studies? Did the authors observe any deviation between BET and the geometric surface-to-mass ratio (i.e., the ratio of the total surface area concentration to the total mass concentration estimated by SMPS/APS)? If so, what is its atmospheric implication?*

Atkinson et al., (2013) report a BET surface area of 3.2 m<sup>2</sup>/g for their K-feldspar, a microcline, while the BET area of our microcline is 1.9 m<sup>2</sup>/g. These surface areas are similar to the ones of quartz (0.5 – 5.5 m<sup>2</sup>/g, Zolles et al., 2015), but lower than surface areas of kaolinites (10 - 25 m<sup>2</sup>/g, Pinti et al., 2012), and much lower than surface areas of illites (~100 m<sup>2</sup>/g, Pinti et al., 2012) and montmorillonites (30 – 84 m<sup>2</sup>/g, Pinti et al., 2012).

The specific surface area values evaluated from the laser diffraction particle analyser (LDPS) and SMPS/APS is 1.21 m<sup>2</sup>/g and 2.43 m<sup>2</sup>/g, respectively. From these minor differences we don't expect atmospheric implications.

*P5 L172-174: I like this statement showing negligible concentration dependency of the onset freezing T in DSC. Great job.*

We thank the reviewer for the appreciation.

*P6 L205: Clarify/elaborate what “an initial increase” meant here – e.g., an increase in  $T_{het}$  near  $a_w \sim 1.0$ .*

The intention was to highlight the increase in  $T_{het}$  near  $a_w \sim 1$ . The sentence has been modified to: “For all NH<sub>4</sub><sup>+</sup> solute cases in dilute concentrations viz. NH<sub>3</sub> (< 1 molal), (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (< 0.16 molal), NH<sub>4</sub>HSO<sub>4</sub> (< 0.18 molal), NH<sub>4</sub>NO<sub>3</sub> (< 0.67 molal) and NH<sub>4</sub>Cl (< 0.99 molal), there is an increase in  $T_{het}$  compared to  $T_{het}^{\Delta a_w^{het}}(a_w)$  near  $a_w \sim 1$ .” (lines 217-219)

*P8 L269-271 or P9 L320-321: The authors may extend this simulation-based discussion of ice-like ordering on the second bilayer, which seems to hold true for even nonmineral dust particles, by citing some more papers, such as Lupi et al. (2014, J. Am. Chem. Soc.) and Lupi and Molinero (2014, J. Phys. Chem. A).*

We thank the reviewer for the suggestion. The references have been added and discussed in the revised manuscript (lines 320-321) as “Using molecular dynamics simulations, Lupi et al. (2014)

and Lupi and Molinero (2014) have recently shown that even non-mineral graphitic surfaces can promote IN due to surface-induced ordered layering of interfacial water.”

*P9 L314: “. . . when compared with . . .”.*

Suggested change has been made.

*P10 L328-332: I suggest the authors to separate this sentence into at least two sentences – e.g., “. . . K<sup>+</sup> in the surface water. For instance, the comparison of . . .”.*

As suggested by the reviewer, the lines (328-332) have now been split into 3 shorter sentences as “The total absence of IN activity at higher K<sup>+</sup> concentrations indicates that the replacement of K<sup>+</sup> with H<sup>+</sup>/H<sub>3</sub>O<sup>+</sup> is essential for the IN activity of microcline. This suggests that the higher IN efficiency of K-feldspars compared with (Na, Ca)-feldspars does not stem from the beneficial effect of K<sup>+</sup> in the surface layer. For instance, the comparison of K<sub>2</sub>SO<sub>4</sub> with Na<sub>2</sub>SO<sub>4</sub> solutions with the same water activity shows that the presence of K<sup>+</sup> has even a more negative effect on  $F_{\text{het}}$  than Na<sup>+</sup>.” (lines 377-382)

*P10 L334-337: I suggest the authors to separate this sentence into two sentences – e.g., “. . .small structural fragments. This cations release presumably leads to. . . (Add proper references for this part if they are any)”.*

The suggested lines have been modified and split into 2 separate sentences as “Suspension of feldspars in water leads to the immediate release of surface cations within minutes (Nash and Marshall, 1957; Busenberg and Clemency, 1976; Smith, 1994; Peckhaus et al., 2016). Over a period of years, the continuous release of silica as silicic acid, hydrated alumina and small structural fragments leads to the slow disintegration of feldspar and to the buildup of new minerals (DeVore, 1957; Banfield and Eggleton, 1990).” (lines 384-387)

Two new references have been added to the second sentence, viz:

DeVore, G. W.: The surface chemistry of feldspars as an influence on their decomposition products, *Clays Clay Miner.*, 6, 26-41, doi:10.1346/CCMN.1957.0060104, 1957.

Banfield, J. F., and Eggleton, R. A.: Analytical transmission electron microscope studies of plagioclase, muscovite, and k-feldspar weathering, *Clays Clay Miner.*, 38, 77-89, doi:10.1346/CCMN.1990.0380111 1990.

*P10 L353-359: Please include the discussion of the recent study done by Abdelmonem et al. (2017, ACP, 7827-7837) regarding the effect of pH on IN.*

We refer to the study by Abdelmonem by stating: “The solution pH influences the surface charge of hydroxylated mineral surfaces. This again influences the ordering of water molecules at the water/mineral interface and the IN efficiency, as was recently shown by Abdelmonem et al. (2017). In case of feldspars, the pH of the solution is, in addition, an important parameter in determining the stability of the feldspar surface.” (lines 403-405)

*P11 L369-372: This observation regarding non-reversible IN ability is great. Good job.*

We thank the reviewer for the appreciation.

*P12 L411: “An exception includes. . .”.*

Suggested change has been made.

*Fig. 2: What does the minor heat flow peaks at  $T > 255$  K indicate? It seems not apparent in Fig. 4. What caused the observed difference?*

The minor heat flow peaks/spikes at  $T > 255$  K are heterogeneous freezing signals of particularly large single droplets in the tail of the droplet size distribution, which are not representative for the sample. Their presence is due to the coalescence of some smaller droplets probably while transferring the sample to the aluminum pan for DSC and is not reproducible. We mention them at the end of Secti. 2.2 of the revised manuscript. In addition, we add to the figure caption of Fig. 2: “Note that the spikes at  $T > 255$  K are due to the freezing of single particularly large emulsion droplets. They are not reproducible and therefore excluded from evaluation.”

*Fig. 3: Is there any way to overlay the results of previous ABIFM results for some reference mineral dusts in comparison to the authors’ results? If yes, please do. Adding some reference points may benefit the paper.*

We plot for comparison the heterogeneous freezing curve under the assumption that heterogeneous freezing can be predicted by a constant shift of the melting curve. This corresponds with the assumption of the activity based immersion freezing model (ABIFM) proposed by Knopf and Alpert (2013). INP that follow this assumption lie along this line. Such curves can e.g. be seen in Fig. 5 of Zobrist et al. (2008) and in Fig. 2 of Knopf and Alpert (2013). We consider that the figure would become too busy and confusing if we included results from other INPs. We mention in the discussion on line 267 of the revised manuscript: “Note that this derivation of the heterogeneous freezing temperatures on the basis of the solution water activity and the freezing temperature of the suspension in pure water is analogous to the one of ABIFM and results in the same prediction.” (lines 267-269)

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