

We thank Reviewer 2 for his/her thoughtful comments. We reproduce the reviewer's comments in black and our responses in blue. Line numbers refer to the revised, marked-up manuscript.

General comments: The extensive work by Klumpp et al. describes the heterogeneous ice nucleation properties of two mineral dust types, kaolinite and halloysite, that are chemically identical and have the same crystal structure, but differ in their morphologies. Comparison of their freezing properties before and after physical modification by milling showed that the morphology plays an important role affecting the chemistry as well. This study has an important contribution to the ice nucleation field of study and it improves our understanding of why a certain surface produce better ice nucleating sites compare to another. The manuscript is within the scope of ACP. The experiments were well designed, the results are well presented and well interpreted. The introduction is very thorough and focused. I recommend to publish the manuscript in ACP after the authors will address the following comments:

Major comments:

1. The authors suggest the notion of surface hydroxylated edges as ice nucleating sites, however, the current work did not provide a direct evidence for that. So, there is no mechanism which was found and I think this should be highlighted in the conclusion and discussed. Is there scientific way to establish this for example? A way to quantify that?

This is indeed a good question. Unfortunately, as long as direct experimental observation of the ice nucleation process is not feasible, we are left with circumstantial evidence to derive the role of the edges in ice nucleation on clay minerals. One major obstacle to establish a mechanism for ice nucleation is the unresolved chemical and topographic makeup of nucleation sites. These are typically defects in the regular mineral surface, which are too small and too few to be characterized experimentally.

To address this topic, we add the following text to the revised manuscript at the end of the discussion section on line 501:

“Yet, such comparative, experimental studies cannot elucidate the microscopic mechanism of heterogeneous ice nucleation. Specifically, they are unable to explain how topographical features and surface functional groups play together to boost the probability of ice nucleation above the one of bulk water at the same temperature. Traditionally, a direct templating effect is assumed to explain the IN activity of a surface. However, such a direct orientation of water molecules into an ice-like pattern seems unlikely given the irregular structure of the clay mineral edges. Rather, the requirement of a sufficient spatial extension of the nucleation site could point to a rearrangement of the liquid water structure to a higher degree of hydrogen bonding within a water volume of the size required to host the critical ice embryo. The role of the surface would then be to induce such a rearrangement by disrupting the prevalent liquid water structure at that temperature through hydrogen bonding to water molecules.”

2. What are the atmospheric implications? kaolin particles are common in the atmosphere and will atmospheric transport or cloud processing can affect its ice nucleating abilities in light of the results of this study?

This is again a very interesting question, which we address in the revised manuscript by inserting the following paragraph at the end of the discussion section starting from line 510:

“This study shows that freezing temperatures of kaolin particles are limited by platelet thickness, i.e. the number of layers stacked together in a particle. Thus, larger particles should be able to freeze water at higher temperatures than smaller ones. Indeed, bulk measurements with larger volumes show freezing temperatures up to or even above 260 K, potentially occurring on supermicron particles (Zimmermann et al., 2008; Pinti et al., 2012; Whale et al., 2015). Moreover, if immersion in water led to a partial delamination of the layers, a decrease in freezing temperature depending on the freezing mode could ensue. Indeed, there is experimental evidence that freezing temperatures are higher in contact and condensation mode, where dry particles induce freezing, than in immersion mode, where ice nucleation starts from wetted particles (Zimmermann et al., 2008; Lüönd et al., 2010; Welti et al., 2014; Whale et al., 2015; Nagare et al., 2016).”

3. In many cases along the manuscript the data presented without the uncertainties. Please make sure you report the uncertainties.

Following the reviewer(s) we add error bars/uncertainties when possible (Figs. 11 and 12). Please note the newly added section about the DVS method where we also mention the uncertainties (stop criterion: mass change rate ≤ 0.0005 % per minute) connected to the method. Given this precision we do not display error bars on data derived from DVS measurements.

4. There is no information about sample preparation and measurement process for surface area in the BET. Degassing was done? At which conditions? How many times each powder was measured?

Following the reviewer, we extended Section 3.3. Now it contains a detailed description of the DVS measurements.

Minor comments:

1. A figure describes kaolinite and halloysite structures can be included in the text or in the supplementary.

We added a figure that illustrates the kaolinite and halloysite structures as the new Fig. 1 and renumbered the other figures accordingly.

2. What is the source of difference between results of H₂O and N₂ surface area and pore size?

Surface adsorption of H₂O depends on the hydrophilicity of the surface. In the case of completely hydrophobic surfaces, there would be no adsorption of water vapour at all. The rather hydrophobic siloxane surface of kaolin minerals could lead to a low bias in surface area. Conversely, pores with diameters below 2 nm would fill with water below a water vapour saturation ratio of 0.35 and therefore interfere with the determination of surface area. Such pore space could arise at the rugged edges of kaolinite and halloysite, thus inducing a high bias in the surface area determined through water vapour adsorption. We consider therefore the agreement between H₂O and N₂ surface areas as astonishingly good. It should also be noted that DVS measurements take place at 25°C compared with -196°C for N₂-BET analysis, which could affect the total surface area, too.

3. Line #271: Please detail to which sample variability you refer to?

We reformulate to:

“The smaller differences between repetitions for the higher concentrated samples suggests that the larger portion of sample investigated at 1 wt % represents the average sample properties better than the five times smaller portion required at 0.2 wt %, which would imply composition or particle size inhomogeneity within the sample.

4. Line #275: Please explain what is the cause for the 1 K difference in the homogeneous freezing temperature between the different measurements.

Since the heterogeneous and homogeneous peaks overlap to different extent for every sample, the homogeneous onset cannot be determined to high accuracy. We mention the homogeneous freezing temperature in the text to provide the reader with a point of orientation within the DSC curves rather than to draw any conclusion from its value or spread.

Technical comments:

Line #86: Please provide a reference.

We added Murray et al. (2012), Boose et al. (2016) and Kaufmann et al. (2016)

Line #192: For uniformity, notice the use of backslash in temperature change rate here while in the rest of the text there is a use of superscript.

Changed to superscript

Fig 3: missing units to the y-axis for Thet.

Added

Fig 5: missing units to the y-axis for Thet.

Added

Fig 9. Missing bracket in the caption.

Added

Fig 10. Missing bracket in the caption.

Added

References

Lüönd, F., Stetzer, O., Welti, A., and Lohmann, U.: Experimental study on the ice nucleation ability of size-selected kaolinite particles in the immersion mode, *J. Geophys. Res. Atmos.*, 115, <https://doi.org/10.1029/2009JD012959>, 2010.

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Whale, T. F., Murray, B. J., O’Sullivan, D., Wilson, T. W., Umo, N. S., Baustian, K. J., Atkinson, J. D., Workneh, D. A., and Morris, G. J.: A technique for quantifying heterogeneous ice nucleation in microlitre supercooled water droplets, *Atmos. Meas. Tech.*, 8, 2437–2447, <https://doi.org/10.5194/amt-8-2437-2015>, 2015.

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