Author's response to Anonymous Referee #1

Below we provide in blue-colored font a point-by-point reply to each comment.

I would like to congratulate the authors on the development of a novel and useful instrument for linking topographic features on bulk systems to ice growth. The results are clearly presented and the manuscript is well written. Nevertheless, I have a few comments listed below.

We thank the referee for the kind words regarding our novel approach to studying ice growth, as well as the referee's insightful comments.

General comments:

The paper initially describes the technique as an instrument for elucidating atmospheric ice formation. However, the primary focus of the results are about ice growth and propagation on the feldspar mineral. Although this is an interesting observation and result, it is not very atmospherically relevant. As in the atmosphere, the aerosols acting as INPs are between approximately 50 and 10000 nm. Therefore, it is likely that individual droplets would not exist on the surface of the aerosol particle. Rather, the entire aerosol would be immersed in a cloud droplet above water saturation and the ice nucleation event would cause the entire droplet to freeze. This renders the step height analysis unnecessary for atmospheric ice formation. I think this should be more clearly presented in the manuscript.

We concur with the referee that our observations on extended feldspar surfaces cannot straightforwardly applied to atmospheric conditions. We agree that most aerosol particles are typically completely immersed in a cloud droplet already at very modest supersaturations. We address this issue by adding text in the manuscript to: (1) Clarify at the outset that and why we are looking at extended substrates, thus not raising the not-to-be-fulfilled expectation that we examine realistic aerosol particles. (2) Describe more precisely the atmospheric conditions for which we believe our results might be relevant. Specifically, we:

Changed the first sentence in the abstract to: "*We developed a method for examining ice formation on solid* <u>*substrates*</u> <u>*exposed to*</u> *cloud-like* <u>*atmospheres*</u>*.*"

Before the last sentence of the introduction we added: "*While studying aerosol particles collected from the atmosphere would provide a more direct connection to atmospheric conditions. The typically complex structure and chemistry of these particles often precludes identifying the individual nanoscale processes that are important. For this study, instead, we choose extended flat substrates of known composition on which the role of individual topographic features can be examined.*"

In first sentence of paragraph 2.1.1. changed "*To create cloud-like conditions*" to "*To create a cloud-like atmosphere*".

In the discussion and outlook section we added the following two statements:

"*This process can be viewed as an extension of the pore condensation and freezing mechanism (Christenson 2013; David et al. 2019; Fukuta 1966; Marcolli 2014; Pach and Verdaguer 2019) to higher humidity.*"

" Typically, most aerosol particles are completely immersed in a cloud droplet already at very modest supersaturations. As discussed in detail in (Friddle and Thürmer 2019a), the step-facilitated mechanism described above is expected to be relevant when a cavity-free feldspar particle, initially devoid of ice, is suspended in air colder than -20^{o}C that becomes slowly saturated. According to Fletcher's estimate (Fletcher 1962; Pruppacher and Klett 1997) that a humidity of RH_w> 130% is required for a measurable nucleation rate of water droplets with a contact angle of ≈ 45^o on a planar insoluble substrate. Hence condensation of supercooled water will be confined to step edges, where the water will freeze rapidly, thus initiating ice formation."

Nevertheless, the step height analysis is potentially an interesting and important result for the material science, biomedical and food preservation fields. Perhaps the authors should present the step height analysis in reference to those fields.

Following the referee's suggestion we added to following statement to the discussion and outlook section: "*In the discussed example of ice formation, the step-height analysis is used to corroborate the involvement of the liquid phase of water during the observed rapid formation and propagation of ice on feldspar, while the link between surface-step height and the ability of an isolated aerosol particle to initiate ice nucleation is neither direct nor obvious. Nevertheless, such step-height analysis might benefit future studies in fields of material science, like corrosion and aircraft icing (Gent, Dart, and Cansdale 2000; Kreder et al. 2016), where the behavior of the examined materials is affected by the abundance of surface steps."*

Although it is discussed that certain sites repeatedly nucleated ice while others lost that ability, it would be nice to show some examples of the types of sites that retained or lost their ice nucleating ability. For example, do they differ in geometry, location on the mineral surface etc.

We did not perform an exhaustive study on the sites that lose or gain the ability to nucleate ice. With our optically limited spatial resolution of the ice crystals we are unable to decisively make a statement on the local surface structure (sub 10 nm) where nucleation occurs.

Do the crystals that emerge from pits below water saturation or protrusions above water saturation have the same orientation as discussed in the Kiselev et al., (2017) study?

We did not observe the regularity in crystal orientation as reported in the Kiselev study. We added at the end of section 4: "Our data neither reveal nor rule out any preferred crystal orientation of the observed ice structures."

Minor Comments:
What is the resolution of the AFM? What is the tip width and how does this affect the mapping of the topographic features?

We did not characterize the radii of the AFM tips we used. Although the manufacturer specifies the tip radii is < 10 nm, typically over extended use situations the tip radius is approximately 20 nm, putting the theoretical lateral resolution at about 4nm, while the vertical resolution is atomic. That said, the data used in our mapping is constructed of individual scans of 512x512 pixels covering 100x100 μm^2. This limits the spatial resolution to the pixel size of 195 nm. We included the tip model and vendor in section 2.2.

What is the temperature uncertainty of the thermistor? Is there an impact of the temperature measurement occurring below the standoff stage rather than below the sample itself (see Fig. 1)?

The inherent error in the thermistor reading is negligible (less than 0.1 C) compared to the uncertainty introduced by the sensor placement below the sample. In the setup in for these experiments we do not use a sensor within the sample volume, however the flux of cold gas impinging the base of the sample plate is 20 times greater than the flux flowing over the top of the sample. Thus, only a small differential is expected between the sample base and sample volume temperatures. We revisited our temperature measurements and found a slight error in our original reporting of the temperature of the sample plate. Our measurements of the sample plate temperature were on average -29.5 ± 0.2 °C, where the error is the standard deviation of the readings over 9 runs. We take a conservative estimate to place the error at ± 0.5 °C. We have included this revised temperature and error throughout the paper, as well as adjusted the estimated AHin values accordingly.

What are the uncertainties in the iced step height analysis? Please add error bars to the Fig. 6. Is there a reason that the largest step heights have a lower iced fraction above 0.75 AHin or is this due to the uncertainty of calculating the iced fraction of a step. This result is in direct conflict with the statement that higher iced steps would retain ice longer than shorter steps (see discussion and outlook).

Uncertainty in histogram data is difficult to define without a priori knowledge of the distribution, and therefore the variance of a given bin. The noise observed in the curves for large humidities at large step heights arises from the random nature of ice coverage and limited data. The order of step icing, and in turn local dehydration, is random in each experiment. Therefore, in some runs a section of steps will be dehydrated, while in others those same steps will become iced. Since tall step heights are present in fewer numbers this random dehydration path can remove a noticeable portion of those steps from the overall counts of iced steps. We included the following sentence in the caption to figure 6, "Fluctuations in the ice fraction curves, particularly at high AHin and large steps, reflect the random dehydration of some larger step heights which are present in far fewer numbers than smaller step heights."

It is not stated how the humidity would be calibrated at other temperatures? Would the AHin be increased until water is observed and then this be used as 100 % RH in the cell?

The reviewer is correct, the humidity would have to be re-calibrated for a different temperature.

I understand that once droplets are formed, the humidity would drop in the chamber, but at the highest AHin used in the study ~200 % RH, do the droplets continue to grow/merge? As mentioned in the general comments, the experiments conducted above water saturation are investigating ice growth. Please make this clearer on page 5 line 11.

The actual humidity within the cell volume local to the viewing area is unknown and must be well below 200 % RH. As seen in the accompanying videos, in most areas the ice forms before the droplets are able to grow/merge to an appreciable size. We have changed this sentence to read, "Above saturation, we observe a very different pathway to ice formation." Where we removed "mode of" to distinguish from direct observation of ice nucleation.

<u>Detailed comments:</u>

Page 2 Line 5: Please add Pach and Verdaguer, (2019) We have now added this reference twice in the experimental results section 3.

Page 2 line 16: Remove "however" as this confuses the sentence and move the citations to the end of the sentence. Thank you for the suggestion, we have made this change.

Section 2.1.1 please reference Figure 1. Thank you, this is called out in the first sentence of section 2.1.1.

Section 2.1.1 on page 3 line 10 is not numbered correctly. Please change to 2.1.2 Thank you, we have corrected this.
Page 3 line 16: Capitalize "figure" Thank you, we have corrected this.

Page 3 line 24-26: This sentence seems unnecessary here especially as it is not explored in this study. Ether reformulate to state that in theory this would be an additional advantage or remove.

We reformulated this sentence to: "The *last point has the potential benefit of keeping the AFM tip near the same temperature as the sample surface, allowing, in principle, to image ice or the sample surface without raising their temperature (not explored here).*"

Page 5 line 3: Please add appropriate references for ice formation from capillary condensation such as: Campbell et al., (2017); Campbell and Christenson, (2018); David et al., (2019); Marcolli, (2014); Pach and Verdaguer, (2019)

Thank you, we have added the following appropriate references here: (Christenson 2013; David et al. 2019; Fukuta 1966; Marcolli 2014; Pach and Verdaguer 2019)

Page 6 line 5: numbering of section is off, change to 4.2. Thank you, we have corrected this.

Page 6 line 27: please change ice formation to ice growth We have made the change.

References:
Campbell, J. M. and Christenson, H. K.: Nucleation- and Emergence-Limited Growth of Ice from Pores, Phys. Rev. Lett., 120(16), 165701, doi:10.1103/PhysRevLett.120.165701, 2018.
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David, R. O., Marcolli, C., Fahrni, J., Qiu, Y., Sirkin, Y. A. P., Molinero, V., Mahrt, F., Brühwiler, D., Lohmann, U. and Kanji, Z. A.: Pore condensation and freezing is responsible for ice formation below water saturation for porous particles, Proc. Natl. Acad. Sci., 116(17), 8184–8189, doi:10.1073/pnas.1813647116, 2019.
Kiselev, A., Bachmann, F., Pedevilla, P., Cox, S. J., Michaelides, A., Gerthsen, D. and Leisner, T.: Active sites in heterogeneous ice nucleationâˇAˇ Tthe example of K-rich feldspars, Science, 355(6323), 367–371, doi:10.1126/science.aai8034, 2017.
Marcolli, C.: Deposition nucleation viewed as homogeneous or immersion freezing in pores and cavities, Atmos Chem Phys, 14(4), 2071–2104, doi:10.5194/acp-14-2071-2014, 2014.
Pach, E. and Verdaguer, A.: Pores Dominate Ice Nucleation on Feldspars, J. Phys. Chem. C, 123(34), 20998–21004, doi:10.1021/acs.jpcc.9b05845, 2019.