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

The preprint "Ice Nucleation by smectites: The role of the edges," is a well written account of freezing experiments of various smectites. In addition to investigating various mineralogies the authors have conducted experiments to examine the role of specific charge carriers (cations) and also how aging in air and water environments might change the ice nucleating potential of these minerals. The work is motivated by observations that various mineral dust particulates are noted to be potentially important atmospheric ice nucleators in certain temperature ranges. While overall, I think the manuscript is well written and certainly a quite deep dive into smectite assisted ice formation I do have a few comments and concerns related to the manuscript.

Moreover, as I have not previously evaluated an EGUsphere preprint in this regard I have spent some time trying to ascertain the appropriate way to contextualize the work. My understanding is that this preprint is aimed at ACP audiences. In this case I do think the authors would benefit by bringing their story full circle and reconnecting the work to the atmosphere in the discussion/conclusions. Absent this connection, much of the manuscript reads equally as well as an examination of mineral freezing, absent a strong atmospheric connection. Some questions that the authors might consider revisiting:

I. They mention previous work on illite, and this clay has been (in the context of the INUIT project) proposed as a potential freezing standard that could be used, for example, for instrument intercomparisons. Do the results presented here shed light on whether such a choice would be useful? For example, any standard might need to be stored for long periods of time with the hope that users one year would observe the same sample characteristics in another.

Illites have cation exchange capacity higher than that of kaolinite but lower than that of swelling smectites (Kahr and Madsen, 1995). Several layers of water adsorption have been reported for illites when exposed to high RH conditions (Schuttlefield et al., 2007; Baltrusaitis and Grassian, 2009). This can be put into context with storing samples over long time periods. Given the robustness of illite (as well as kaolinite) in terms of negligible ion exchange and interlayer swelling, it seems to be a good freezing standard. For example, the same illite NX sample tested via emulsion freezing experiments by Pinti et al. (2012) and Kaufmann et al. (2016), albeit with a time gap of few years, does not show any remarkable difference in heterogeneous freezing onset temperature.

II. How representative of atmospheric aerosol can one take these emulsion freezing experiments to be? One gets the feeling the 3-part Kumar series cited would need to be re-read in full to appreciate the details. What is the droplet size distribution? What are the biggest and smallest droplets? Why do not all the droplets freeze before homogeneous temperatures? In analogous droplet freezing or other assay experiments, even with quite rarified INP freezing most always proceeds to completion before homogeneous temperatures, and or at higher temperatures than pure water, "blank" experiments. Perhaps the authors could include a pure water, "blank" DSC thermogram for comparison?

For clarity, we have this discussion in the Methodology (Section 2.4.1). As suggested by the reviewer, we have updated Figure 1 and included a "pure water" DSC thermogram (orange curve) for comparison. "The median droplet diameter in the emulsion is ~2–3 µm in terms of number size distribution, but a broad distribution in terms of volume. Droplets with diameters of about 12 µm are considered to be relevant for the freezing onset in the DSC experiments (Marcolli et al., 2007; Kaufmann et al., 2016). The random spikes at temperatures warmer than the heterogeneous freezing onset are caused by the freezing of few large droplets (sometimes up to 300 µm present at the tail-end of the droplet size distribution) and are excluded from the evaluation. Their presence is likely due to the coalescence of some smaller droplets probably while transferring the sample to the aluminum pan for DSC and is not reproducible.

In case of emulsions with pure water only ("blank water"), the droplets start to freeze at 237±0.2 K (Figure 1). However, when we introduce dust particles, the number of particles in a single droplet is governed by the volume of the droplet. With increasing droplet volume, the probability of accommodating particles in that droplet increases. Hence, the freezing of larger droplets dominates the heterogeneous freezing signal. While, the homogeneous freezing signal results either from the freezing of smaller empty water droplets or droplets containing particles which are ice nucleation inactive. F_{het} reported in this study cannot be directly translated into absolute quantifiable parameters, rather it should be considered as a qualitative parameter to compare the efficacy of ice nucleation of different dust samples or to assess the changes in efficacy due to different treatments. We also use heterogeneous freezing onset to characterize the freezing temperature because it is a very well-defined parameter easily evaluated from the thermograms. A combination of T_{het} and F_{het} parameters provide a good measure of the overall ice nucleation abilities of the smectites."

Several droplet freezing setups or other assay experiments (e.g. Yun et al. (2020), Whale et al. (2018)) utilize droplets that are several orders of magnitude higher in volume and are in contact with a flat hydrophobic surface. Such few and large droplets freeze entirely due to a single ice nucleation event and represent the best, yet rare, ice nucleation active sites on a given surface. In comparison, the emulsion freezing experiments yield better statistics by utilizing large populations of small droplets in a single experiment. However, DSC does not register freezing event but the heat flow associated with the heat release during freezing.

The relationship between freezing events and heat flow has been shown in Marcolli et al. (2007). This imparts another challenge in directly comparing droplet assays and emulsion freezing experiments.

As mentioned previously, an emulsion primarily consists of droplets of diameter less than 12 μm, with varying numbers of dust particles. The assessment of particle surface area exposed in a single droplet is a challenge owing to the size distributions of both the droplets and the dust particles. Therefore, emulsions are not entirely representative of the aqueous cloud droplets (typically 5–50 μm in diameter). However, the supercooled temperature range that can be probed using emulsion freezing is of utmost relevance for mixed-phase cloud regime.

The thermogram measurements themselves are quite interesting but again here I am left wanting a bit more detail. There is reference to the "typical" case and more details to be found in the Kumar et al. 2018 paper. However, in examining Figure 1 of that publication I am left with several questions as it relates to the current study. The methods for peak determination, onset determination, and peak integration laid out in that earlier publication seem to rely a bit on well separated and distinct peaks. Quite often in the study submitted here that is not the case and peaks are more strongly convoluted or sometimes two peaks are not clearly evident. This raises the following questions:

I. Figure 1 of the earlier paper indicates that peak onset is determined using some type of asymptote? Has the same method be used here? Would not a 2nd derivative better reflect the inflection of slope that would indicate onset?

We define the freezing temperatures (T_{het} and T_{hom}) as the onset points of the freezing signals (i.e., intersection of the tangents at the greatest slope of the freezing signal (intersection of the tangents at the greatest slope of the freezing signal and the extrapolated baseline) as outlined in Figure 1 of Kumar et al. (2018) (also, Figure 2 of Klumpp et al. (2022b)). Indeed, a 2nd derivative would yield a proper inflection of slope. However, the uncertainties in T_{het} and T_{hom} observed via multiple freezing runs of any sample encompass that arising from inflection point variations in a narrow temperature range. For clarity, we added a Figure A in the Appendix A, which illustrates the peak onset and frozen volume fraction derivations.

II. When peaks are poorly separated, take many of the traces in Figure 2(b), how are the peaks deconvoluted for integration etc.? It seems that in this case a doublet fitting algorithm would be more suited to the data? What is outlined in the earlier paper seems a bit crude for the convoluted peaks observed here.

A vertical line drawn from the minimum intensity point between the homogeneous and heterogeneous freezing peak is taken as the separator between the areas under the heterogeneous and homogeneous freezing peaks. We consider this signal separation method as more robust than curve deconvolution considering the variability in curve shapes, though it is crude and comes with considerable uncertainties (Figure A in revised manuscript). Nevertheless, the combination of T_{het} and F_{het} gives a good overview of the discernable changes in ice nucleation ability due to ion exchange and aging conditions.

III. I understand that the peak normalization $F_{het}+F_{hom}$ implies that all droplets are frozen in all cases (or at least the same amount (volume) of ice is formed in every experiment). Is this also robustly observed? There is no small droplet curvature dependence, that suppresses freezing?

The total volume of water in each emulsion sample is not exactly the same. This is due to volume displacement by the added dust particles (which vary in size in each batch) in every aliquot of suspension taken to prepare an emulsion. The heat released during freezing is approximately proportional to the volume of water that freezes in the sample with a minor deviation from this proportionality arising from the temperature dependence of the freezing enthalpy (Marcolli et al., 2007). Therefore, the latent heat released during a freezing experiment varies from emulsion-to-emulsion. Hence, evaluating F_{het} as a normalized parameter (i.e. ratio of the heterogeneous freezing signal to the total freezing signal) helps to compare the general ice nucleation behavior of the samples across multiple emulsion tests.

IV. In Figure 1 a few of the traces (SWa-1, 5 wt%, SHCa-1, 5 wt%, Laponite) exhibit one peak only – is this then only homogeneous freezing, as is supposed for the Laponite? Others, e.g. SAu-1, 1 wt%, seem to show three peaks. What is happening in these cases?

Contrary to Laponite, the SWa-1 and SHCa-1 samples show heat signals that are not entirely flat baselines before reaching their homogeneous freezing signals. Hence, we report in Table 4 a heterogeneous freezing signal for SWa-1 and SHCa-1, albeit very faint and flat. The weak signals are difficult to visualize when DSC curves are stacked one on top of the other. For clarity, we have added markers to highlight the heterogeneous freezing onset points in Figure 1.

Indeed, SAu-1 and MX-80 show two distinct heterogeneous freezing signals, with T_{het} values of 247/240 K and 247/241 K, respectively. The dual signals suggest activation of different sets of ice nucleation active sites on such surfaces in two different temperature regimes. Though, we think that both types of sites belong to smectites' surface features, instead of impurities. Our reasoning for this is discussed in detail towards the end of Section 3.1.

We have clarified some of these aspects in point III above. To add to that, DSC does not register freezing events but the heat flow associated with the heat release during freezing. As previously mentioned, the relationship between freezing events and heat flow has been shown in Marcolli et al. (2007). The heat release is approximately proportional to the volume of water that froze heterogeneously or homogeneously and is represented by the integral of the peak over time (not temperature). Several droplet assay studies report the ice nucleation active site density (n_s), assuming the deterministic description for nucleation events, to compare ice nucleation behavior of variety of particles. This is rather convenient to translate droplet number frozen fractions to n_s, due to monodisperse distribution of droplets (Vali et al., 2015; Whale et al., 2018; Yun et al., 2020). On the other hand, it is a drawback of the DSC method that droplet number frozen fractions cannot be derived directly. We attempted to quantify this in Kaufmann et al. (2016), but significant uncertainties were observed which are associated with the dust particle size distribution, the droplet size distribution and frozen water volume fractions in cases with overlapping heterogeneous and homogeneous freezing signals. Therefore, we use water volume frozen fractions (F_{het}) as parameter to assess the changes in general efficacy of dust samples to nucleate ice. For example, any changes observed in F_{het} (in combination with T_{het}) for a sample are indicative of general effect of a treatment (ion exchange and/or adsorption, aging, surface dissolution, etc.) on its overall ice nucleation ability.

Indeed. We ran freezing experiments on two different STx-1b suspensions that had been aged for two years, and both showed a secondary freezing signal at 246 K. The origin of this signal is not clear. We speculate that new sites might have formed due to some aggregation of the delaminated layers over such long time period. We have addressed this in Section 4.5(viii).

As we mentioned previously, F_{het} reported in this study cannot be directly translated into absolute quantifiable parameters, rather it should be considered as a qualitative parameter to compare the efficacy of ice nucleation of different dust samples or to assess the changes in efficacy due to different treatments. We also use heterogeneous freezing onset to characterize the freezing temperature because it is a very well-defined parameter easily evaluated from the thermograms. The range of freezing temperature observed for various smectites are in agreement with previous studies carried out with similar dust loadings of water droplets (Welti et al., 2009; Atkinson et al., 2013). A combination of T_{het} and F_{het} parameters provide a good measure of the overall ice nucleation abilities of the smectites. As suggested by the reviewer, we add a discussion on atmospheric implications to Section 5:

"The portion of smectites in atmospheric mineral dust composition varies drastically based on origin, source and atmospheric transport (Murray et al., 2012; Boose et al., 2016; Kaufmann et al., 2016). Only few previous studies have investigated the IN abilities of smectites, yet, with different smectite samples investigated in different freezing modes, and with different sample aliquots (Hoose et al., 2008; Zimmermann et al., 2008; Welti et al., 2009; Pinti et al., 2012; Atkinson et al., 2013), which hampers the comparison of IN activity between the different studies. Nevertheless, freezing temperatures seem higher in studies where the experiments started from dry particles. When smectites immersed in water undergo delamination, a decreased IN activity in immersion mode is indeed expected compared with contact and condensation freezing, which occur while the samples are wetted. Therefore, the effective IN activity of smectites might be underestimated if immersion freezing results are also applied to condensation and contact freezing conditions.

Since ice nucleation active sites are typically very few surface features or defects, too small to be easily characterized experimentally, observation of the ice nucleation process on ice active sites is not feasible. In addition, ion exchange and interlayer swelling features of several smectites add another challenge in assessing the underlying ice nucleation mechanism and the identity of the ice active sites on such surfaces. However, their structural similarities to non-swelling clay minerals provide some indication to similarities in ice nucleation mechanisms. From this study, we suggest that IN ability of smectite particles is limited by platelet thickness. This is in agreement with Klumpp et al. (2022a) who elucidate the role of the edges in the IN ability of kaolin minerals."

Specific Suggestions by Page and Line Number (page, line):

- *(1,24) replace "the one" with 'that'*
  Done.
- *(Introduction) I would simply like to complement the authors on the very complete mineralogy both here and in the Methodology section.*
  We thank the reviewer for the appreciation.
- *(8,232) rephrase, 'is reported as a voltage'*
  Done.
- *(Figure 1) It seems this figure could be better utilized with at least freezing onset also indicated. Also, extracting one of these curves and illustrating the peak deconvolution would be useful.*
  We have revised the figure as suggested by the reviewer. Additional figure showing T_{het} and F_{het} evaluation is added in the Appendix A.
- *(Figure 2) The meaning of "...heterogeneous and homogeneous freezing curves sum up to the same value...." is very vague. The same expression is also used in other captions and also pertains to clearly defining the peak normalization as I have alluded to in point III above. I also recommend using the same terms in the figure and caption. I understand "no solute" and "pure water" to mean the same thing, but it would be better if the phrasing matched.*
  We have changed the expression to "All curves are normalized with respect to the total areas under the heterogeneous and homogeneous freezing curves." Terminology corrected in the captions for pure water cases (replaced with the name of the sample), as suggested by the reviewer.
- *(15,366) Although not strictly incorrect, verbing a noun like "evidences" is quite often an awkward wording. This verbing of evidence is done multiple times and I would suggest rephrasing.*
  Done.
- *(15,391) rephrase, '...no clear trend towards higher or towards lower.....'*
  Done.

A general comment on the "Ion Exchange" section. Have the authors considered how the evolution of the Debye layer and ordering of screening charges may also change water structuring at the interface? I feel that the cation and valency are address, but the near field interactions are not mentioned.

We have renamed Section 4.1 to "Exchangeable cations and ion adsorption" and added the following discussion.

"It has been previously established that feldspars can undergo cation exchange and adsorption when exposed to salt solutions (Nash and Marshall, 1957; Demir et al., 2001; Demir et al., 2003). Contrary to laboratory experiments, classical molecular dynamics (MD) simulations have not been able to capture ice nucleation on K-feldspar surfaces. Though (001), (010) and (100) surfaces of K-feldspar exposed to various salt solutions (including ammonium-containing solutions) show that sorbed ions affect interfacial water orientation, albeit unfavorable for ice nucleation (Kumar et al., 2021). MD simulations performed on basal surface of kaolinite exposed to various solutions revealed that the interfacial ions played minor part in inhibiting ice nucleation by blocking the regions of clear surface (Ren et al., 2020). On the other hand, our study shows that within measurement uncertainty, the IN ability of fresh STx-1b is not affected when cation concentrations are close to or even surpass the CEC limit where surface and interfacial ion concentrations might be high."

- *(16,402) rephrase, '...as made evident...' (see verbing comment above)*
  Done.
- *(16,416) rephrase, '...we investigate the relationship between IN activity and particle morphology.'*
  Done.
- *(Figure 3,422) 'sum to'*
  Done.
- *(Figure 3) Define CEC in main text and utilize here. Not generally appropriate to first define an acronym in a figure caption. SD appears to be used for one standard deviation, but also is not strictly defined. Using '1' would perhaps better communicate the intent if I understand correctly.*
  Done
- *(Figure 3,424) '...a few days...'*
  Done

Summation: Overall the submitted preprint is quite well written and presents a thorough suite of results related to smectite freezing. To make the manuscript suitable for publication in ACP I believe the above concerns should be addressed. Moreover,

the authors should return to the atmosphere in the discussion/conclusions to emphasize the points of connection. Finally, one of the most interesting results is related to edge nucleation being the limiting length scale in the nucleation activity of these materials. However, the evidence for this presented here, while well-reasoned, is not direct. Some indication of what kind of direct studies could follow or are planned/underway would add to conclusions. I think one will find in the freezing literature that not only edges, but steps and basal plane imperfections, like screw dislocations, can initiate freezing. The dimensionality of these may be quite different compared to the layer thickness, and therefore add anchor points that a simple 'edge' model would not have.

We have added the following discussion in Section 5 to address these aspects.

"Such aspects of ice nucleation at special sites, e.g. defects and edges, could potentially be explored via molecular simulations which offer the possibility of probing the small spatial dimensions and short timescales involved in ice nucleation. However, there is still either a lack of detailed atomic configuration for such features for some minerals (e.g. feldspars), or the features in question are currently difficult to generate in simulations and obtain meaningful conclusions (e.g. clays)."

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