Review of "Ice Nucleation by smectites: The role of the edges," by A. Kumar et al. 2022

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 inter-comparisons. 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.

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?

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?

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.

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 surpresses freezing?

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?

V. What physically do F_{het} and F_{hom} represent? I understand that these values are indicative of how likely it is that something freezes heterogeneously vs. homogeneously. However, given these represent normalized integrals of the heat, which I anticipate scales like volume/mass, does this mean a doubling of F is a 2^3 increase in heterogeneous freezing? It would be helpful for the authors to give this a meaning that is more easily physically interpreted.

VI. The 2 year trace in Figure 5 contains 2 filled red squares – what does this indicate? Two separate heterogeneous activations?

Point V also ties into the atmospheric applications of the DSC measurements. Is freezing fraction here somehow related to what one might expect for an activated fraction in the atmosphere? That is, beyond onset temperature, how can one translate some of these results at least qualitatively to discuss comparisons with ice nucleation in the atmospheric context. For example, it is understood that soot can nucleate ice, but that it often does so quite inefficiently, like 1 particle per million is an active INP.

Beyond these general questions, below I list some specific questions/comments that are perhaps better considered as the enter into the text.

Itemized Scientific and Editorial Comments:

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

• (1,24) replace "the one" with 'that'

• (Introduction) I would simply like to complement the authors on the very complete mineralogy both here and in the Methodology section.

• (8,232) rephrase, 'is reported as a voltage'

• (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.

• (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.

• (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.

• (15,391) rephrase, '...no clear trend towards higher or towards lower.....'

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.

• (16,402) rephrase, '...as made evident...' (see verbing comment above)

• (16,416) rephrase, '...we investigate the relationship between IN activity and particle morphology.'

• (Figure 3,422) 'sum to'

• (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 '1σ' would perhaps better communicate the intent if I understand correctly.

• (Figure 3,424) '...a few days...'

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.

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