

We thank Gabor Vali for his constructive comments. We reproduce his comments in *blue* and our responses in black.

Although it may be marginal to the specific topic of this paper, it seems worthwhile to pursue further points raised in my previous comment about how DSC results may be viewed with a sharper focus on the nucleation events which are to be studied. DSC data make important contributions to ice nucleation studies and the opportunity arose with this paper to discuss some aspects of those measurements with a view toward better exchange of information between different researchers.

Gabor Vali raises here important questions concerning the interpretation of freezing experiments performed with DSC. We consider these points as a general discussion of the potential of DSC to investigate ice nucleation and we will therefore formulate our responses accordingly.

The paper is consistent with the terminology it uses (as defined on lines 287-290 and in Fig. A) in accord with previous publications. To this reviewer, that terminology has some unfortunate aspects. Strictly speaking, there is no 'heterogeneous and homogeneous freezing' and it is not a good shorthand for indicating heterogeneous and homogeneous nucleation events. Similarly, 'freezing peak' is an awkward shorthand designation. It is understandable, when describing DSC data, that freezing is used in many contexts since that is the source of the detected signal. However, since the goal of the measurements is to diagnose and understand nucleation, that usage is distracting. Reference to freezing diverts attention and loses the sharpness that nucleation implies as a near-instantaneous process at a very specific location.

The distinction between ice nucleation and freezing is crucial in discussing our DSC results. During DSC experiments with emulsion samples, freezing of each droplet in the emulsion is initiated by a nucleation event. In contrast, the heat signal just informs us about the heat release during freezing, which is delayed with respect to ice nucleation and droplet freezing as discussed in Marcolli et al. (2007). Even if nucleation resulted in complete, instantaneous freezing, we would not be able to derive nucleation events from the DSC signal, because the delay in heat transfer is substantial. The analysis in Marcolli et al. (2007) indicates that in our DSC instrument, the heat release of each droplet follows an exponential decay law with a time constant of 11 s. Most importantly, the heat retention transiently increases the DSC sample temperature, resulting in a temporary deviation from the nominal cooling rate. Depending on the intensity of the heat release, nucleation might be almost complete when the heat signal peaks. Therefore, the onset is the best-defined temperature to reference a heat signal.

The foregoing point comes into focus with respect to T_{het} . I raised questions about the physical meaning of this parameter in my previous comment. The authors responded by saying that they do not mean it to be a threshold or onset of nucleation, as I referred to it, but a 'freezing onset temperature'. Since there is no freezing without nucleation this response eludes the real issue of the interpretation of what T_{het} stands for. Onset is not a good way to characterize the nucleating abilities of samples in general, because it arises from a small number of events highly dependent on particle concentration (loading) and chance. With T_{het} the meaning of onset is even more fuzzy as there are evident DSC signals beyond T_{het} indicating some nucleation activity of the sample at higher temperatures. So, while T_{het} is a convenient reference temperature, calling it something else than 'onset' temperature would avoid questions about its meaning. By determining T_{het} by extrapolation from the slope of the thermal signature, the problem of dependence on a small fraction of the nucleation events is avoided but the ambiguity of the physical meaning is not resolved.

Perhaps consideration has been already given to using the point of steepest slope of the thermal signal as the reference temperature. That temperature, say T_s corresponds to large numbers of nucleation events, albeit not necessarily a maximum, and it seems easier to relate to than to T_{het} . Neglecting droplet size

variations, or in cases where uniform droplets are used, T_s would correspond to a peak in the differential nucleus spectrum. The use of T_s would avoid awkward situations such as having T_{het} appear on a totally flat part of the curve displayed, e.g. SHCa-1. 5% in Fig. 1. which is probably due to the normalization of the curves to a uniform height making the first pulse inappreciable.

With T_{het} , we refer to the onset of the freezing peak recorded by DSC. The onset temperature of a DSC signal is an unambiguous parameter that we apply based on its general definition within the field of DSC. Using T_s as proposed by Gabor Vali would not change the appearance of the onset being on the flat part of the curve for e.g. SHCa-1. We have added DSC thermograms of SHCa-1, SWa1 and Laponite samples separately in Fig. 1(b) for better clarity.

T_{het} should not be identified with the onset of ice nucleation. The onset of ice nucleation, although frequently used in ice nucleation studies, is in fact an ill-defined parameter as it refers to specific setups that are characterized by a sample volume in which the INP number or mass are usually only varied within narrow limits. Because continuous flow diffusion chambers investigate a much lower number of INPs, the freezing onset of an INP type in these instruments is much lower than in a drop-freezing assay with microliter-sized sample aliquots. Owing to the small droplet size in emulsions, ice nucleation temperatures in these experiments are in a similar range as the ones in continuous-flow diffusion chambers and much lower than the ones in drop-freezing assays.

In emulsion freezing experiments, the INP surface or mass per droplet is subject to large uncertainties because of the polydispersity of the emulsion droplets as discussed in the appendix of Kaufmann et al. (2016). Because of the uncertainties in nucleation temperatures and amount of INPs per droplet, emulsion freezing experiments performed with DSC are not suited to derive INP spectra or ice-nucleation active site densities.

The other parameter used to characterize nucleation activity in a sample is F_{het} . This parameter is a measure of the mass loading of the sample and the size distribution of particles in the droplets with the nucleating material. Beyond comparisons, it provides little quantitative information on the nucleating ability of the material being tested.

We are well aware of this drawback. The strength of DSC is the capability to compare the ice-nucleation activity of different samples with reasonable expenditure of time. To build on the strength of our method, we focus in our DSC emulsion freezing experiments on the comparison of similar samples, like the comparison of the IN activity of different smectites in this study, or changes in ice-nucleation activity due to the addition of solutes. Comparison with ice nucleation data obtained with other techniques would require the transformation to INP spectra, which is not feasible with DSC emulsion freezing experiments as explained above. We think that microfluidic devices would be the instruments of choice to provide ice nucleation data that can be converted to INP spectra in the temperature range below 250 K.

In essence, the foregoing comments are aimed at shifting focus in the descriptions of the results on nucleation rather than the freezing that results from it. No specific recommendations are made here on how to achieve that. The authors and the editor may decide that this is not the time to reconsider how DSC data are presented.

We fully agree that a shift from freezing to ice nucleation would be desirable. Moreover, instead of ice nucleation onsets, full INP spectra or ice-nucleation active site densities should be reported. As explained above, this is not achievable with emulsions, which always lead to polydisperse droplet distributions. The method of choice to obtain monodisperse droplet populations of small enough size to avoid ice nucleation on impurities is in our opinion microfluidics.

On a more specific aspect of the paper, the arguments in Section 4.5 should perhaps consider more than size as influencing nucleating ability of a site. Ice nucleation literature abounds in discussions about the roles of unique sites (crystal steps, specific molecular arrangements, etc.) versus the general properties of a substrate surface. This paper considers the size necessary for embryo formation on the basis of CNT, thus implicitly assuming that average surface properties form the criteria for nucleation. It would increase the value of the paper if the authors included some discussion about the possible role of unique sites.

Our discussion of the IN activity of smectites concentrates on size because smectite platelets are so thin that size matters for nucleation sites. We agree that size is not the only criterion for a nucleation site. Section 4.5, titled “Connection between particle thickness and IN activity” concentrates specifically on size. Therefore, in this section, we neglect the other relevant prerequisites for ice nucleation. We implicitly acknowledge the relevance of other criteria when we write in the very first line of Section 4.5 that the platelet thickness is “a limiting factor” and not “the limiting factor”.

In Section 5, we mention the relevance of surface functionalization as another relevant criterion, as we write in the second paragraph: “Furthermore, as the edges are densely hydroxylated, they fulfill a prerequisite for ice nucleation. Hydroxylated aluminosilicate surfaces are a feature that clay minerals have in common with feldspars, whose IN activity also increases in the presence of ammonia and ammonium solutions. Thus, a sufficiently large area equipped with hydroxy groups that are available for hydrogen bonding to water molecules seems key for ice nucleation by aluminosilicates in general.”

Following the suggestion of Gabor Vali, we add to this: “Besides the precise location of hydroxyl functionalities within the IN active area, additional topographical properties of the edge surface might also influence the quality of the nucleation sites.”

References

Kaufmann, L., Marcolli, C., Hofer, J., Pinti, V., Hoyle, C. R., and Peter, T.: Ice nucleation efficiency of natural dust samples in the immersion mode, *Atmos. Chem. Phys.*, 16, 11177–11206, doi:10.5194/acp-16-11177-2016, 2016.

Marcolli, C., Gedamke, S., Peter, T., and Zobrist, B.: Efficiency of immersion mode ice nucleation on surrogates of mineral dust, *Atmos. Chem. Phys.*, 7, 5081–5091, doi:10.5194/acp-7-5081-2007, 2007.

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

I feel the authors have adequately addressed my concerns. However, I would still argue that the way the authors treat the DSC curve analysis is rather rough and perhaps more quantitative data could emerge if better curve fitting algorithms were employed. Although we have not made the same suggestions I see from the Vali response that he had similar ideas. Moreover, it seems in the response to his point that a peak in the differential spectrum of the DSC curve would correspond precisely with the location of the steepest slope and that might be another useful marker seemed to be a bit misinterpreted. This is not peak temperature, as the response seems to narrow in on. Finally because the shapes of the curves (i.e., the tails) will not always be the same for the het and hom cases I do not entirely buy the argument that the chosen method of integration would not be significantly outperformed by a doublet deconvolution, and thus perhaps yield more insight. All of the singly peaked DSC curves are quite symmetrical, why would we not expect the same of others? Thus knowing one tail should allow robust fitting of the other (the part convoluted with the other freezing behavior).

As we have explained in our responses to Gabor Vali, a curve fitting and deconvolution would not inform us about the nucleation events. Repeating here a part of the response we have given to Gabor Vali's comments, the heat signal just informs us about the heat release during freezing, which is delayed with respect to ice nucleation and droplet freezing as discussed in Marcolli et al. (2007). Even if nucleation resulted in complete, instantaneous freezing, we would not be able to derive nucleation events from the DSC signal, because the delay in heat transfer is substantial. The analysis in Marcolli et al. (2007) indicates that in our DSC instrument, the heat release of each droplet follows an exponential decay law with a time constant of 11 s. Most importantly, the heat retention transiently increases the DSC sample temperature, resulting in a temporary deviation from the nominal cooling rate. Depending on the intensity of the heat release, nucleation might be almost complete when the heat signal peaks. Therefore, the onset is the best-defined temperature to reference a heat signal.

Moreover, in emulsion freezing experiments, the INP surface or mass per droplet is subject to large uncertainties because of the polydispersity of the emulsion droplets as discussed in the appendix of Kaufmann et al. (2016). Because of the uncertainties in nucleation temperatures and number of INPs per droplet, emulsion freezing experiments performed with DSC are not suited to derive INP spectra or ice-nucleation active site densities. The method of choice to obtain monodisperse droplet populations of small enough size to avoid ice nucleation on impurities is in our opinion microfluidics.

This said, the author's larger point is that this information leads only to relative weighting and this is only one of a few barriers in the technique that prevent quantified nucleation information from emerging. Rather the point is more to give insight into what promotes freezing earlier versus later.

Itemized Scientific and Editorial Comments from the resubmitted tracked changes manuscript version:

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

- (11,293) should read....and are also shown in....*

Corrected.

- (11,294) Rigorously \sim means similar to, as in the same order of magnitude, whereas \approx means approximately. Here the later should be used given the range is less than 1 order of magnitude.*

Corrected.

- (11,300) should read....In the case of emulsions formed with pure water....*

Corrected.

• *(Figure 1, caption) should read.....For references purposes a DSC...for the samples.*

Corrected.

• *(22,487) The 2 sentences beginning, “Though (001),” and ending...“(Ren et al., 2020)” are difficult to read and include dangling clauses etc. I would suggest rephrasing to improve clarity.*

The sentence has been rephrased for clarity.

• *(30,673) should read....Only a few....*

Corrected.

• *(30,677) should read...started with dry particles*

Corrected.

• *(30,689) should read.....atomic configurations for*

Corrected.

• *(30,690) should read...in simulations to obtain....*

Corrected.

A general comment: at times the usage of “in immersion freezing mode” seems like it would better written ...in the immersion freezing mode.

Corrected at several places in the revised manuscript.

Although willing to review another edition of this manuscript, I do not see any acute need. I can recommend the manuscript for publication when these technical corrections are made and the editor is happy.

References

Kaufmann, L., Marcolli, C., Hofer, J., Pinti, V., Hoyle, C. R., and Peter, T.: Ice nucleation efficiency of natural dust samples in the immersion mode, *Atmos. Chem. Phys.*, 16, 11177–11206, doi:10.5194/acp-16-11177-2016, 2016.

Marcolli, C., Gedamke, S., Peter, T., and Zobrist, B.: Efficiency of immersion mode ice nucleation on surrogates of mineral dust, *Atmos. Chem. Phys.*, 7, 5081–5091, doi:10.5194/acp-7-5081-2007, 2007.