

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

This comment is not the usual full review of the paper under discussion. The minearology aspects and the conclusions of the paper are not questioned. Rather, this comment has a narrow focus on the question of how the DSC measurements described can be interpreted from the point of view of the singular approximation¹. Two points are addressed: (1) the use of the T_{het} parameter, and (2) the broader question of "surfaces versus sites" as the foci of attention in unraveling the factors governing heterogeneous ice nucleation². The first point is discussed, mainly, as a matter of clarification, but also as a manifestation of the focus of the paper on surfaces, thus emphasizing the importance of the discussion of the second point.

In the paper under discussion, results focus on the observed values of the temperature T_{het} , defined by extrapolation of the greatest negative slope of the thermogram to the abscissa. This characterization of the thermogram has been employed in several of the papers cited. It has the benefit of simplicity and allows comparisons of different results to be readily made.

In this paper, and several others using the DSC technique, T_{het} is referred to as the 'onset temperature' of nucleation for the sample being tested. The association of T_{het} with the 'onset' of activity is justified by the fact that T_{het} falls close to the where the thermogram begins to rise above zero. The strictly defined onset, i.e. the first detectable signal, is dependent on instrument sensitivity, emulsion drop sizes and sample concentration. The use of T_{het} as indicator of 'onset' sidesteps those variables and makes it a more robust parameter. However, T_{het} is dependent on the shape of the thermogram which, in addition to the nucleating ability of the sample, is influenced by the drop-size distribution in the emulsion, the size distribution of the suspended particles and perhaps other factors. For identical curves, one could write the simple relationship $T_{het} = T_{ms} + 1.5$, with T_{ms} as the temperature where the slope is steepest and the value of 1.5 is a rough reading from the curves in Fig. 2. In fact, in Fig. 1 the thermograms have quite varied shapes. In Fig. 2, the curves are remarkably similar, but even here, the 5×10^{-4} curve in panel (a) and the 5×10^{-2} and 5×10^{-6} curves in panel (b) do differ to an extent that can be noted by visual comparison of traces of the curves. The influences of these variation on T_{het} are small in Fig. 2 but seem more important for Fig. 5 and can't be judged for the other analyses.

In drop-freezing experiments (with individually observed drops) the onset temperature would be the first freezing event. Most researchers would put little weight on one event because of the uncertainties associated with it. Using the extrapolation notion, the cumulative spectra could be extrapolated to some value near the detection limit of an experiment, or to some selected reference value of $K(T) = x$. A problem that would arise would be what portion of the $K(T)$ curve to use for the extrapolation, just as the shape of the DSC curve influences the T_{het} point. To complete to comparison, the steepest part of the DSC curve would coincide with a peak in the differential spectrum, provided that variations of droplet sizes in the emulsion is neglected.

The practical issues related to the definition of an onset temperature were elaborated in the preceding paragraphs only to underscore that such a quantity is not a rigorous parameter and would have to be used with some caution.

We agree that it is important to keep in mind the limitations of T_{het} as a measure for ice nucleation (IN) activity. In this work and also in our previous studies, we use T_{het} in combination with F_{het} as a means to quantify and compare IN activities of different samples. Since this is not the full information provided by DSC thermograms, we display and discuss also the whole DSC curves in our studies.

Note, that we mean the whole freezing peak when we refer to a specific T_{het} . Therefore, we do not refer to T_{het} as the "onset temperature of nucleation" but as the "freezing onset temperature". With "freezing", we mean the process of ice nucleation and growth, which gives rise to the heat signal in the DSC. Due to the negligible heat release associated with nucleation, nucleation alone is invisible in DSC. The same is true for the freezing of a single micrometer-sized droplet. We use the freezing onset instead of the freezing peak temperature to characterize the position of the freezing peak because the location of the peak maximum is influenced by the total heat release (see Marcolli et al., 2007) and therefore is a less robust parameter than the onset temperature to reference a DSC peak. We have a detailed discussion in Section 2.4.1.

More important is to consider what an onset temperature, or the steep part of the thermogram, or a peak in the differential spectrum reveal about the sample. Here, one has to consider the totality of the information contained in the thermogram, or in the spectra, i.e. to recognize that nucleation is taking place over a range of temperatures due to nucleating sites of different effectiveness (characteristic temperatures). In this paper the temperature range over which freezing event occur in any given sample is between 3 K and 5 K. That is a relatively narrow range,

but comparable to the magnitudes of the differences observed due to surface treatments studied. The range of temperatures is very much dependent on droplet number and particle concentration. In most cases, by varying the concentration and/or by extending the sample size, the range of freezing temperatures can be broadened significantly. This variety of nucleating ability for particles of the same material or same source is the principal challenge and the fundamental interest in the study of heterogeneous ice nucleation.

The authors mention, and seem to agree with the importance of nucleating sites (line 53), yet no further emphasis on site variability is seen in the paper. They do not, as is done in other papers, link the assumption of a uniform surface to stochastic nucleation. They appear to consider that the shifts in the thermograms, as reflected in the shifts in T_{het} , are representative of the effects they wish to demonstrate and it is unnecessary to think about what differences among sites may occur on any given type of surface. That argument is perhaps overly simple.

The underlying assumption of our study is that freezing occurs on nucleation sites, which require a minimum size to host a critical ice embryo, and that this size determines the nucleation temperature. On a specific site, nucleation occurs with a certain probability that increases with decreasing temperature and can be described by classical nucleation theory as discussed in Kaufmann et al. (2017). As the width of the freezing signal in DSC is determined by heat release and not by the temperature distribution at which nucleation occurs, the signal cannot be directly related to nucleation. Moreover, as the heat signal per nucleation event depends on the droplet size, an exact knowledge of the droplet size distribution is required to extract nucleation temperatures from the signal. We undertook such a detailed analysis in Marcolli et al. (2007). In the subsequent studies we concentrated more on comparison of immersion freezing in the presence of solutes, for which DSC is well suited as it allows the measurement of different solutes and solute concentrations within an acceptable amount of time.

There is a basic disagreement between the approach that searches for physical and chemical characteristics of a surface and its nucleating ability, and the other approach that diagnoses nucleating sites even if the specific features of the site aren't determined. This is not the place to revisit the contrast and the potential overlaps of the two approaches. Briefly, the main advantage of the focus on the surface properties is that those properties can be determined with a large number of observational and theoretical tools. The main handicap for the focus on sites is that there is no direct way to examine the sites; indirect indications are deduced from the observed spectra and the influences of different factors; possible configurations of sites are inferred from molecular simulations.

Surface properties undoubtedly set the conditions for site formation; this may lead to some definition of the probability of site formation. However, the variety of sites that form (the range of freezing temperatures) irremediably raise the question of what factors come into play. One has to remember that the sites represent a minuscule fraction of the total surface area and that they differ from one another³. Thus, it seems necessary to think about how types of changes induced by treatments of the surface, as is done in this paper, lead to changes in site occurrence and character. There are attempts in that direction in the paper, but only average surface properties not local features are considered.

We fully agree. We are confronted with the fundamental problem that surface specific characterization methods lack the required resolution to resolve nucleation sites. Therefore, specific surface features need to be derived from average sample properties. The original idea behind this study was to investigate how IN activity depends on the exchangeable cations. To our surprise we found no such dependence, but we were astonished by the high variability of the heterogeneous freezing signal between smectite samples, which we tried to explain in the following.

The foregoing discussion doesn't contradict the authors' conclusion regarding edge surfaces of smectite plates as most likely nucleation sites. But, for example, ruling out basal surfaces (Section 4.2) mostly on the basis of molecular simulations of surface/water interactions may be softened if local features serving as sites are also considered. It is clear that the results described in the paper don't provide means of identifying what constitute nucleating sites; however, considerations of that problem may lead to the results making a more realistic addition to the accumulating knowledge about heterogeneous ice nucleation.

Our discussion of ice nucleation activity relies on the assumption that ice nucleation occurs on rare sites that provide suitable properties for ice embryo formation. On several occasions in the manuscript, we refer to nucleation sites, and in Sect. 4.5, we specify their approximate size as derived from classical nucleation theory and molecular simulations.

Minor points, with reference to line numbers:

313-318 The inclusion and exclusion of different samples as active and/or with peaks at 240 K is confusing and not in agreement with what is seen in Fig. 1. Also, what does 'around 240 K' mean?

We agree that the presence of a peak around 240 K as a common feature of the DSC curves does not become obvious at first glance. However, evaluation of the onset freezing temperatures reveals a T_{het} value between 239.9 and 241.2 K for all samples with the exception of Barasym and SHCa-1. We make this clearer in the revised manuscript by referring explicitly to Table 4, where we list T_{het} , and by exactly giving the freezing range in Section 3.1: “All IN active smectites with the exception of Barasym and the hectorite SHCa-1 exhibit a freezing peak with T_{het} around 240 K (exact range of 239.9–241.2 K, see Table 4).”

321-325 The temperatures of 240 K is called a standard freezing peak and those at 246.2 and 247.3 K as special peaks. These temperatures are onset values, according to Fig. 1, not peaks. This is confusing.

As explained above, we characterize freezing peaks by their onsets rather than the peak maxima because the onset is the more robust parameter than the peak maximum. With T_{het} , we refer to the full peak.

323 $T_{\text{het}} = 246.2$ isn't the value shown in Table 4.

Thank you for pointing this out. We have corrected the values in the revised manuscript.

~ 345, footnote in Table 4: what is meant by "highest uncertainty of SD" ?

We meant the largest uncertainty across all investigated samples. We have changed the footnote to “uncertainty does not exceed 0.5 K and 0.1 for T_{het} and F_{het} , respectively.”

1 The singular approximation focuses on the characteristic temperatures of nucleating sites and enumerates the frequency of different sites in terms of differential and cumulative spectra of characteristic temperatures.

2 This 'surfaces versus sites' phrasing of the issue harks back to Vali (2014, Atmos. Chem. Phys. 14, 5271- 5294; doi: 10.5194/acp-14-5271-2014).

3 For simplicity of discussion, the singular interpretation is applied in its simplest form. The randomness of embryo formation which leads to time-dependence and to scatter about the characteristic freezing temperature in the actual freezing event are ignored.