

## **Response to referees comments for “*Investigating the discrepancy between wet-suspension and dry-dispersion derived ice nucleation efficiency of mineral particles*” by C. Emersic et al.**

We thank the referees for their insightful comment. Here we reproduce them in black, followed by our response in red. In the main text of the manuscript any changes have also been highlighted.

### **Anonymous referee # 1**

#### **Major comments**

1) Hiranuma et al. ACPD, 2014, stated “Though the number of immersed particles can vary from droplet to droplet and the random placement of particles in the drop may be of an effect on the  $n_s$  values, the  $n_s$  spectra from suspension measurements are in general in reasonable agreement even over a wide range of wt% of illite NX samples. Thus, the influence of the random placement of particles in the drop and agglomeration on the  $n_s$  estimation for suspension measurements seems small.” This statement seems contradictory to the coagulation calculations in the current manuscript and conclusions reached in the current document. Please discuss.

We have investigated the effect of random placement of particles within drops in detail and did consider including this work in the current manuscript; there are differences when one considers the random placement vs bulk averaged placement of particles; however, we did not feel they were significant enough to explain the observations.

Here we reproduce some of our calculations on the random placement of particles to show the effect it has and argue that it does not explain the observed results.

We modelled the cumulative freezing curve one would expect in microlitre drops (Figure 1) and pico-litre drops (Figure 2) based on both bulk assumptions (which do not consider the statistical effects) and also statistical sampling, which considered the sizes of mineral particles one would expect in the drops and also the number of active sites one would expect on each of the mineral particles inside a drop. In the calculation one active site had to be present inside the drop, at a given temperature, for it to freeze. From this analysis we can plot out the theoretical cumulative freezing curve.

Looking at this analysis for micro litre drops (Figure 1) we see good agreement between bulk sampling and statistical sampling for both 0.8 wt% and 0.01 wt %; however, there is a slight difference at the highest frozen fractions, with the bulk method overestimating the frozen fraction at a given temperature slightly. This underestimation would result in an underestimation of  $n_s$  as calculated from the experiments, because the experiment would measure lower frozen fractions than expected from bulk arguments alone. However, it is a minor effect.

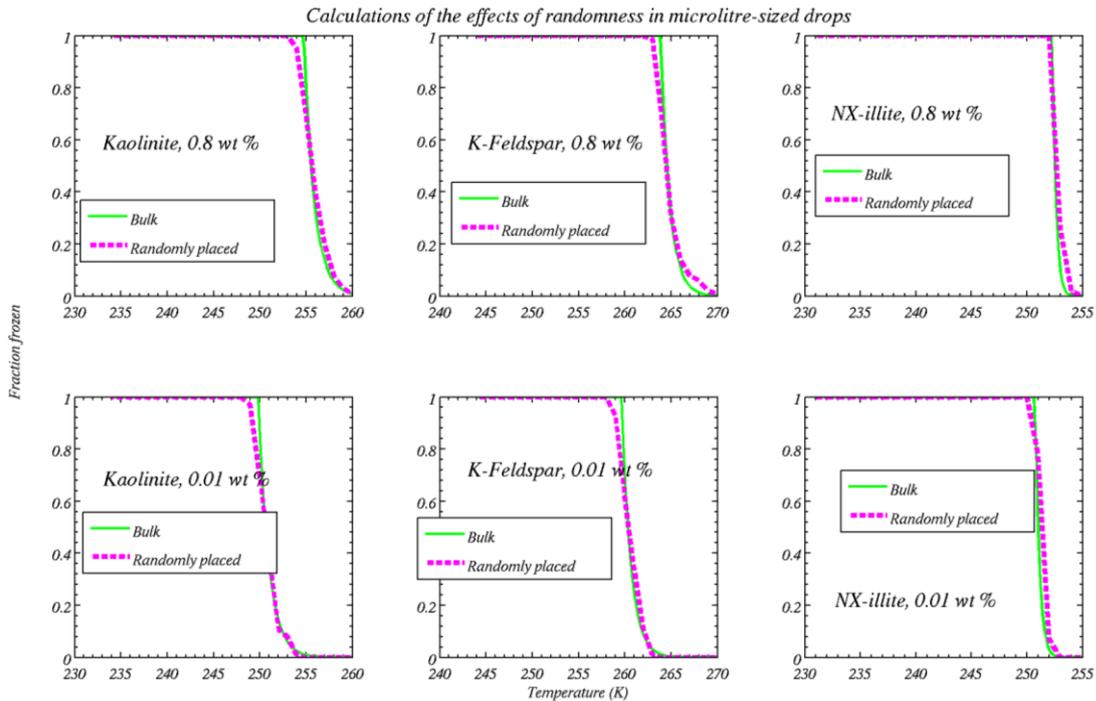


Figure 1. Modelled cumulative freezing curves in micro litre drops for Kaolinite, K-Feldspar and NX-illite. Green solid lines assume bulk averages for particle placement within drops and dashed magenta lines the random placement of particles within the drops. Top plots are for 0.8 wt% and bottom for 0.01 wt%. In general the agreement is very good; however, there are some small differences at the high frozen fractions, where the bulk consideration overestimates the frozen fraction.

In pico litre drops (Figure 2) this story changes slightly. The high wt % results (0.8 wt%) still show good agreement between bulk and random sampling; however, the low wt % (0.01 wt %) results show poorer agreement with not all drops freezing over the temperature range, in stark contrast to the bulk assumption. This is because it is possible to sample some drops that do not contain any mineral particles.

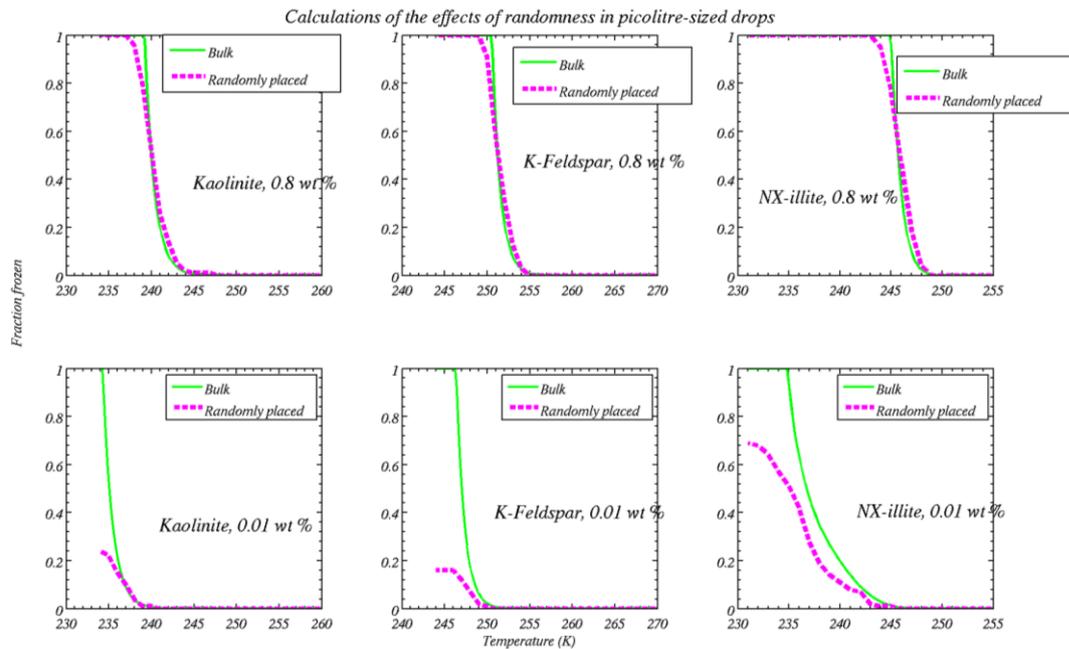


Figure 2. Modelled cumulative freezing curves in pico-litre drops for Kaolinite, K-Feldspar and NX-illite. Green solid lines assume bulk averages for particle placement within drops and dashed magenta lines the random placement of particles within the drops. The agreement is very good for wt % =0.8 (upper plots); however, the frozen fraction is significantly overestimated in the low wt % experiments (bottom plots). It should be noted that homogeneous freezing has not been calculated in these plots.

While this is interesting it likely does not affect our conclusions for two reasons:

- Only 0.8 wt % data are presented for the pico litre drops in Atkinson et al. (2013) on K-feldspar, so we have only compared with that data.
- The Kaolinite and NX-illite results for low wt % in pico litre will be masked by homogeneous freezing. That is homogeneous nucleation will freeze the drops anyway for temperatures less than about 238 K.

2) Were microliter samples with high concentrations of minerals used in the wet suspension experiments reported by Hiranuma et al. at temperatures of -28 C to -34 C?

The results presented in Hiranuma et al. for wet suspensions only go to temperatures as low as -24C so no they were not.

If microliter samples and high concentrations of minerals were used at these temperatures in the experiments reported by Hiranuma et al., then coagulation seems like an unlikely explanation for the difference between the dry dispersion and wet suspension experiments. Please discuss.

See above point.

3) It was not clear how the authors determined the ice particle concentrations reported in Table 1. For K-Feldspar at -21C the authors indicated with a footnote that

the CDP was used. For clarity, please indicate that CDP >18 microns was used (assuming this is correct). Also, does this mean the ice numbers from the 3V-CPI were used in all other cases or were 3V-CPI > 35 used in some of the other cases?

Yes thanks for pointing this out: we have made this clear in the revised manuscript.

4) In the text it was not clear how the authors determined the number of ice particles in the experiments and in some cases the decision sounded subjective. In some cases it sounded like they relied on ice particle concentrations from the 3V-CPI, but in other cases it sounded like they didn't rely on this result because the ice particles were somewhat rounded due to a lack of vapor growth. What criteria did they use to decide when to use and when not to use the ice measurements from the 3V-CPI. In addition in some cases it sounded like they used the data from the 3V-CPI > 35 microns to determine ice particle concentrations while in other cases it sounded like they did not since the 3V-CPI often over-sizes out of focus images of droplets (Connolly et al., 2007). What criteria did they use to decide when to use and when not to use the results from the 3V-CPI > 35 to determine ice particle concentrations? From my reading of this document it sounds like the results from the ice 3V-CPI should be used as a lower limit to the ice particle concentrations and the 3V-CPI > 35 microns should be used as an upper limit to the ice particle concentrations. Is this a valid statement?

It is correct that CPI is a lower estimate. The ice crystal concentrations determined from it are generally good when the sizes are greater than 40 microns. This is the case except at the lower temperatures when K-feldspar was used. Generally speaking when the particles are larger than around 40 microns we classify the images using automated software to discriminate ice crystals. When they are smaller it is more subjective, but we can be confident of a lower limit.

5) What is the uncertainty in the ice crystal concentrations determined for use in Equation 2? In table 1 the authors report an uncertainty from Poisson counting statistics, but what is the uncertainty from under counting with the 3V-CPI due to a lack of vapour growth and rounded ice particles and what is the uncertainty from over-sizing out of focus images of droplets with the 3V-CPI > 35 microns?

It depends on the size distribution. When particles are greater than around 40 microns we are fairly confident in the habit classification algorithm. If we are not sure, we have an unclassified category rather than risk erroneously classifying them as ice crystals. Because we are confident the remaining errors are due to Poisson counting errors.

6) In Figures 8 and 9 the authors should include the uncertainty in their results from the uncertainty in determining the ice crystal concentrations in their experiments (i.e. uncertainty from under counting with the 3V-CPI due to a lack of vapor growth and uncertainty from over-sizing out of focus images of droplets with the 3V-CPI > 35 microns).

Oversizing is not a problem for ice crystal classification. It is merely when the particles get large enough so that the classification algorithm works. We will make this clear in our manuscript.

Also, in Figure 9, have the authors included uncertainties in the parameterizations from Murray et al. 2011 (assuming uncertainties were given in the manuscript by Murray et al. 2011).

No, such errors were not included in the Murray et al (2011) manuscript.

7) Page 892, line 13-15, "However, the droplets lasted for a brief period (less than < 40 s)." Here the authors are referring to Figure 3, but in Figure 3 the black solid line suggests that the liquid droplets persist for at least 300 seconds. Please explain and give some explanation on how to interpret the black solid line in the bottom panels of figures 2-7.

Good spot! These are not actually drops, but the total from the CDP (cloud droplet probe), which includes aerosol particles, drops and ice crystals. Even though it is a droplet probe the CDP actually counts aerosol particles and ice particles. This is an oversight on our part and we will update the figures to reflect this.

8) Related to the comment above, on Page 893 the authors indicate that in Figure 5 the kaolinite particles nucleated ice in the absence of cloud droplets. I am not sure how the authors reach this conclusion since the presence of cloud droplets are indicated by the black solid line in the third panel of Figure 5.

See above. Our oversight and will be corrected.

9) In the dynamic light scattering experiments, why not do the experiments as a function of time to determine coagulation rates. This seems more relevant since coagulation rates would be more directly comparable with the coagulation calculations?

The investigation of coagulation vs time would be of high relevance to our study. However, within the time required for a single light scattering measurement, particles had already reached a stable diameter. To our knowledge, the only two ways to actually observe aggregation are:

- Either manually decrease the run time for single measurements: this has been tried and proved to produce results with too low signal to noise.
- Decrease the concentration of mineral particles: unfortunately, one would have to decrease the concentration to values lower than the technique can deal with. Under these conditions the instrument struggles to scale the correlation function properly, preventing the correct measurements of particle size.

Note that over much longer time scales ( $t > 15$  minutes) we often observed sedimentation of the particles and no measurements could be performed under these conditions.

10) It would be helpful to list the point of zero charge for the different surfaces of kaolinite.

OK, we will look into doing this.

11) Section 5.1.1 The discussion on colloidal forces in suspensions is useful and does suggest that it may be reasonable to neglect repulsive forces in the coagulation calculations. However, this section does not provide conclusive evidence that repulsive forces can be neglected. I also came to the same conclusion from Table 2.

We are not in a position to state this unequivocally, but are hoping to purchase an instrument that can measure this soon. The calculations are meant as a useful first step. If anything the calculations may over estimate the coagulation rates, but what we aimed to show is that it is not inconceivable that aggregation is playing an important role.

That said when one uses the ion concentrations presented in Hiranuma et al. for illite in water (their figure 3) we find that the forces between two particles become attractive over a much wider range of parameter space than our Figure 13 suggests (see Figure 3). At the ion concentrations shown in Hiranuma et al. one also finds that the zeta potentials of the clay minerals is close to  $\sim 10$  (mV) see Du et al. (2010) for an example, hence, Brownian coagulation is a reasonable assumption.

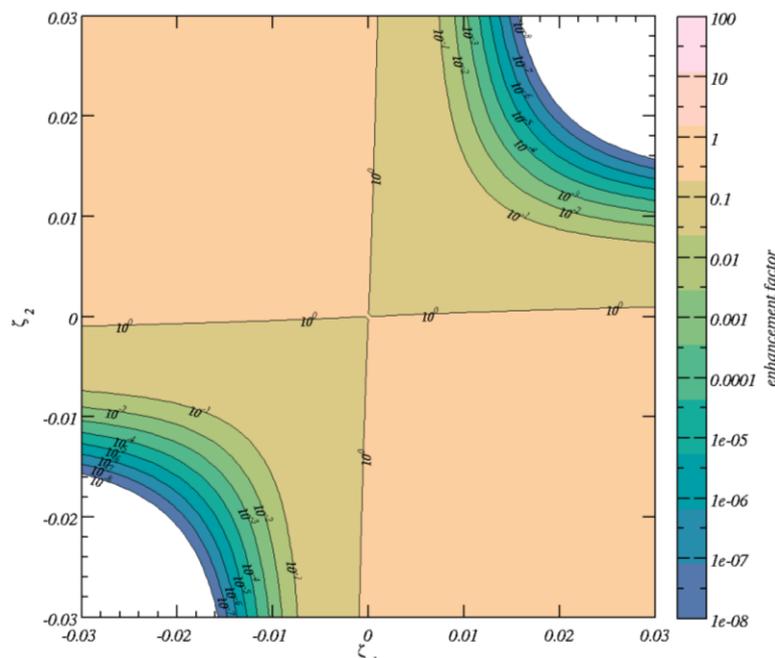


Figure 3. Enhancement over Brownian capture for two 0.1 radius micron particles with zeta potentials given on the x and y axes. Units for x and y axes are volts. This shows that a wider

range of zeta potentials can give rise to attractive forces between particles in comparison to the assumption of pure water.

It would be more convincing if the authors did a time dependent study using dynamic light scattering to show that the force of repulsion can be neglected

See above point about instrument limitations.

**Minor comments:**

1) Page 890, line 9-10, are there any particles > 5 nm in the filtered air.

None in the filtered air, but they are in the chamber air, see Figure 7 and Figure 8. We can not get them out of the background, but we have shown conclusively that they are not significant ice nuclei.

2) Figure 11 and 12. For the red solid lines there is a sudden drop at the earliest times, and then a straight line. Why is this line not an exponential curve? Please comment.

It is, but it very quickly gets limited due to lack of particles. i.e. the concentration is high, but the total number is too low for aggregation to continue and the particle concentration to drop exponentially.

3) In Figure 2, consider changing “droplets” in the annotation to “droplets (CDP)” to be consistent with the other annotations

Thanks. It needs to be changed to total from CDP anyhow, as noted above.

4) Figure 2. Please indicate that the dashed blue line corresponds to the right axis.

You are correct and we will make this clear.

5) It may be helpful to include a short description on each of the instruments used to measure droplet concentrations and ice crystal concentrations (i.e. PALAS WELAS 2000, CDP, SPEC 3V-CPI) since they are crucial to the interpretation of the data.

OK we will do this.

6) The figure caption indicates CDP > 20 microns, but the text refers to CDP > 18 microns. These two numbers should be the same to avoid confusion

Good spot, thanks and we will change this.

## Anonymous referee #2

### Major comments

The main concern for referee #2 was whether aggregation of the mineral particles could happen within droplets on a cold stage.

We don't see why it would not happen if the concentrations were high enough – why should it be significantly different to the bulk? That said following discussions we believe that aggregation is an important effect in all drop sizes, but most likely happens in the bulk suspension. Aggregation apparently happens in pico-litre drops in the clay minerals except at low concentrations, but it is not particularly evident in the Feldspar experiments. We believe this is due to the morphological differences between clays (platelets, which are more likely to bond strongly) and Feldspars. The Feldspars are more likely to form weaker aggregates in suspension, which may be disrupted when introduced into drops and aggregation may only be possible in the micro-litre drops as discussed in our manuscript.

They argue that statistical fluctuations of mineral particles within the drops is potentially a larger effect and cite Wright and Petters

We have looked at this somewhat too, with a numerical simulation (see our reply to the first comment of referee #1), but did not find it to be a significant effect, especially in microlitre drops. See Figure 1 and Figure 2.

They suggest the following sentences are too bold for the evidence presented:

-P888, L10-12 “, revealed the...”

-P888 L18-21 “revealed that...”

-P899 L22-26

-P902 L1-8

-P905 L8-10

There is the suggestion to tweak the structure to have section 4 separated into subsections.

We will do this.

### Minor comments

P 888 L6 & L 13: I suggest maintaining consistency of terms with a previous publication. The correct notation should be either ice-active surface site density (IASSD; Connolly et al., 2009) or ice nucleation active surface-site density (INAS density; Niemand et al., 2012). The same applies elsewhere, e.g., P889 L 13 & L 16, P 894 L12.

OK we will do this.

P889 L5-6: Hiranuma et al. discusses the potential effect of agglomerates and multiple nucleation modes besides chemical aging effect.

Correct, this will be stated.

P889 L11: Consider giving the description of Kaolinite (e.g., KGa-1b from Clay Mineral Society) here instead of Sect. 5.

We will do this.

P894 L3-4: So the surface area is scaled to the droplet number to calculate  $n_s$ ? If so, it is worth mentioning for clarity.

Yes, OK

P896 L8: Awkward sentence. I suggest rephrasing.

OK

P896 L15-16: The curves were manually fitted to the data.

We think you are suggesting we omit the phrase, "but fitted the data very well". We will do this.

P896 L19: Two lognormal modes according to Table 1?

Yes, will be stated.

P897 L1: 1-5% in mass? surface area?

In mass, it will be stated.

P897 L26: This sentence seems incomplete - do not do well what?

Should say "do not do well". Will change.

P898 L2: wet-suspension according to its first appearance.

Good, thanks.

P899 L7: between to?

Should be "two"

P900 L3 : I suggest using wt% to be consistent with what appears in figures. The same goes to other parts, e.g., P900 L 23.

Good, thanks.

P900 L4: M  $\Omega$  cm

Yes.

## Dr Benjamin Murray's comments

### General comments

Emersic et al. present a paper in which they compare chamber derived  $n_s$  values with parameterisations from the literature based on droplet freezing experiments. They present results for K-feldspar, kaolinite KGa-1b and nx-illite. The dust samples for these investigations were supplied by the authors of this comment as part of a collaboration between the groups at Manchester and Leeds in order to facilitate an inter-comparison of techniques.

At lower temperatures for each dataset they find good agreement between their chamber and the literature droplet freezing experiments, but at higher temperatures they report a larger  $n_s$  value for the chamber measurements. They go on to offer an explanation for this discrepancy.

While we are in agreement that a thorough inter-comparison of different methods to evaluate INP efficiencies is an important issue for the community, we do not see how this paper constructively adds to the effort and we do not recommend publication in ACP in its current form. In terms of the general topic, the **discrepancy between many ice nucleation instruments has already been reported and discussed** by Hiranuma et al. (2014) in a much more comprehensive inter-comparison article. The new and novel part of the paper is the discussion of aggregation in droplet freezing experiments.

The article mentioned above, Hiranuma et al. (2014) is more comprehensive from the point of view of more techniques were inter compared; however, it only investigated one sample, namely illite-NX, so from another perspective it is not as comprehensive; hence, we believe our results are an addition to current knowledge and note that this is stated by referees #1 and #2. In Hiranuma et al. aggregation was flagged as an important topic for further investigation in the full article, which is now published in ACP. Our paper validates the MICC results by comparing the illite-NX results with the previous literature (in our Figure 8) and adds more information on two extra mineral powders.

However, Emersic et al.'s explanation for smaller  $n_s$  values from droplet freezing experiments relies on the unsubstantiated assumption that aggregation of particulates substantially reduces the surface area of dust available for nucleation or that aggregated particles somehow fall out of the droplets. The authors have not taken into account a **significant body of literature which shows that coagulation does not substantially reduce the surface area of mineral dust** and that there is no dependency of  $n_s$  on mineral dust concentration.

The question of whether flocculated mineral particles offer less surface area than deflocculated mineral powders is a valid question to ask. Nevertheless regardless of whether flocculated minerals offer less surface area it should be recognised that

once colloidal particles reach sizes of 2-5 microns, which is what we are suggesting can happen, settling times are of the order of less than 20 minutes. Thus it is still possible to reduce the surface area available for nucleation. Aggregated platelets are shown from SEM images of the kaolinite sample (Figure 4) that has been in suspension and subsequently dried out. We see evidence of very large stacks of platelets and argue that there is the potential for a reduction in the surface area available.

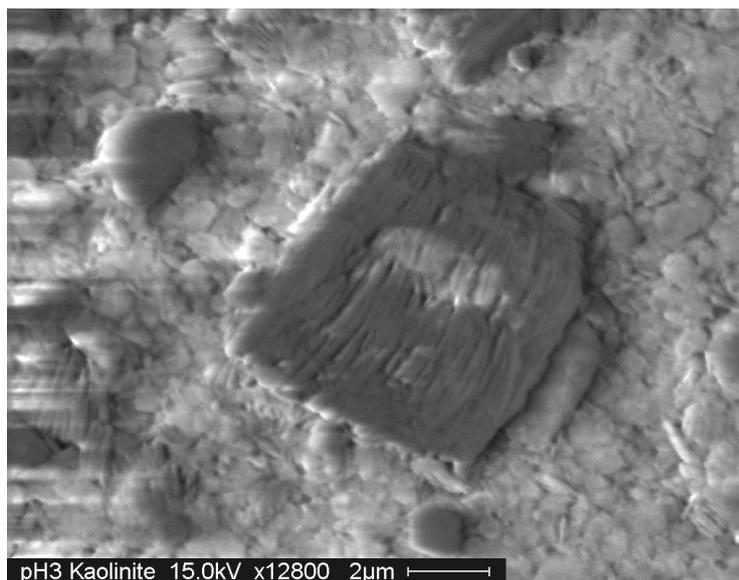
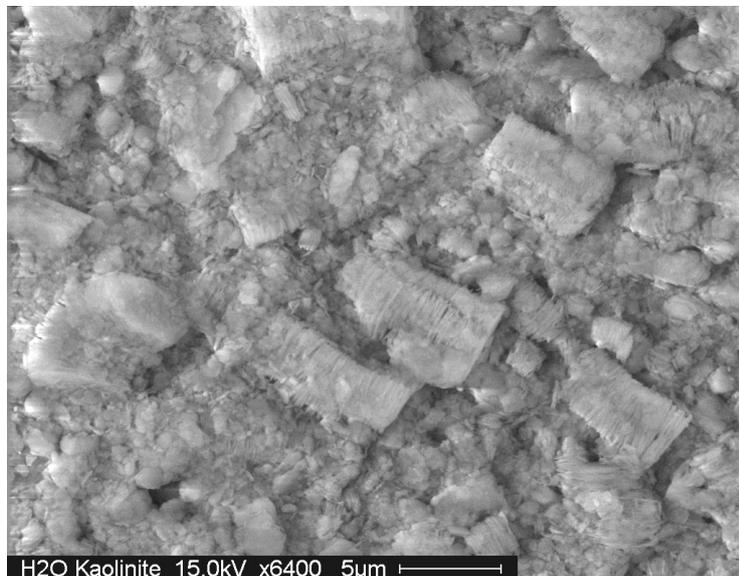


Figure 4. SEM images of aggregated kaolinite particles that have been in suspension.

We are not aware of any “significant body of literature” that specifically shows that coagulation does not reduce the surface area available for nucleation and would be grateful to be directed to this literature.

Additionally, the authors have not compared their results against all of the available data from experiments with the same materials. Comparison with literature data

shows that the Manchester ice cloud chamber data is inconsistent with other dry-dispersed instruments such as continuous flow diffusion chambers.

It is true that data from the Manchester chamber are slightly higher than some of the CFDC counters. CFDC counters also suffer from artefacts and many of the scientists who work with them are trying to understand these very useful instruments. One issue is that, even when operated at supersaturated conditions, the CFDC counters do not guarantee that the 100% of the sample activate into drops. This is relevant because we are considering immersion / condensation freezing in our paper. A specific sentence from the published literature where this is stated is actually in the Hiranuma intercomparison paper (that Benjamin Murray co-authored) just before section 3.3. Here it is very clearly stated that, ***“the lower  $n_s$  of CSU-CFDC may be a consequence of the underestimation of  $N_{ice}$ , possibly due to its constrained RH<sub>w</sub> (at 105%) and the disturbance of aerosol laminar between two plates in a CFDC (DeMott et al. 2015).”***

An important aspect of the results we present here is that the slopes of the  $n_s$  vs temperature curves are consistent with those for natural dusts (e.g. those shown in Niemand et al. 2012) whereas those from wet-suspension (Murray et al. 2011; Broadley et al. 2012; Atkinson et al 2013) tend to be much steeper. This is illustrated in the recent publication by Atkinson et al. (2013) where a comparison is made between observed and modelled ice nuclei concentrations using curves derived from wet suspension experiments for the modelled ice nuclei.

We have reproduced data from Atkinson et al. (2013, figure 4 f) and added an assessment based on the Niemand curve (that our data are consistent with) in Figure 5, essentially rescaling the Atkinson et al. figure 4 f by the ratio of the Niemand curve to the scaled Feldspar line.

Admittedly there are many uncertainties in such an analysis, but we note that there is arguably better 1 : 1 agreement between model and observations if the Niemand curve is used instead of the wet-suspension data. Figure 5 thus shows that when data are adjusted to  $n_s$  curves that have a slope that is closer to those of natural dust (and our data) that agreement is better between observations and model.

Thus we consider that the wet suspension technique may be underestimating  $n_s$  by some means to be a strong possibility. We looked at several aspects of the problem, including the distribution of particles within the suspension (see Figure 1 and Figure 2) and arrived at the conclusion that aggregation may be an important loss of particle surface area.

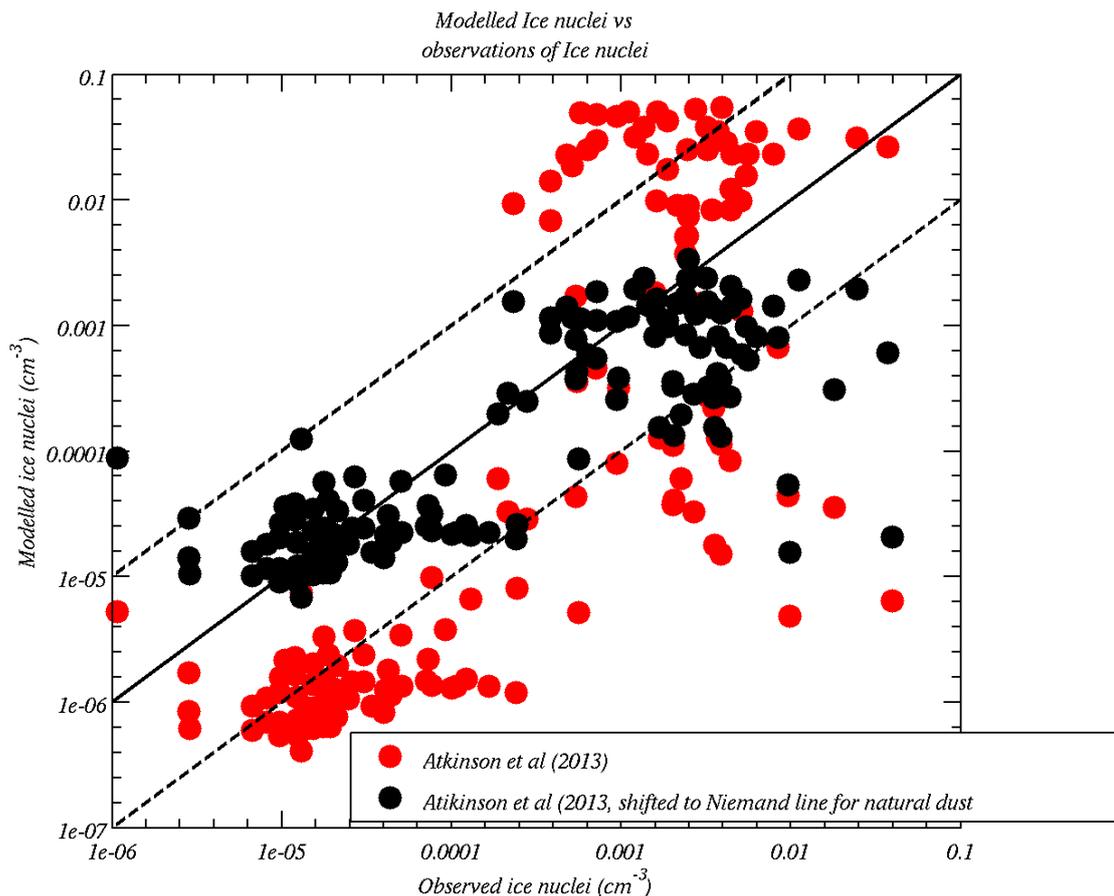


Figure 5. Data reproduced from Atkinson et al. (2013, figure 4f) red lines as well as the same data shifted to the Niemand curve, which has a slope that is consistent with the data presented in our article.

In fact, the wet-dispersed droplet freezing experiments are consistent with a number of data sets with dry-dispersed dusts. This brings into question the basis on which the paper is founded. Emersic et al. claim to be motivated by the ‘discrepancy between wet-suspended and dry-dispersed derived ice nucleation’ efficiencies (as stated very boldly in the title).

our response above addresses this statement. The title of our manuscript picks up on the current status of the literature and specifically the paper on Hiranuma paper on illite-NX, where it is stated that:

“the ice nucleation activity expressed in ns was smaller for the average of the wet suspended samples and higher for the average of the dry-dispersed aerosol samples between about -27C and -18C”

But, there is not a clear cut discrepancy between dry-dispersed and wet-suspended particles and the reference to Hiranuma et al. (2014) has been taken out of context. We reproduce the key plots from Hiranuma et al. to illustrate that there are

discrepancies between different instruments rather than a simple divide between dry-dispersed and wet-dispersed instruments

Benjamin's comment above is referring to the fact that some CFDC techniques also do not agree. This point was raised above and our response is that the Hiranuma et al paper clearly states ***“the lower  $n_s$  of CSU-CFDC may be a consequence of the underestimation of  $N_{ice}$ , possibly due to its constrained RHw (at 105%) and the disturbance of aerosol laminar between two plates in a CFDC (DeMott et al. 2015).”***

### Specific comments

1. Emersic et al. make the argument that coagulation of particles occurs when mineral dust particles are suspended in water and assume that this reduces the surface area available for nucleation by many orders of magnitude at high particle concentrations in microliter volume droplets. However, the evidence in the literature (discussed below) shows that surface area is not significantly reduced through coagulation

We contest that the data presented in the referees comment show that “surface area is not significantly reduced.” The data presented by Benjamin Murray actually show that  $n_s$  values are consistent over a wide range of weight percents when microlitre droplets are used. We believe that aggregation can occur in the wet suspensions over a wide range of concentrations. Several details also depend on sample preparation, for instance, if a stock suspension is made up and then diluted this can also lead to aggregation at the time when the high concentrations are present in the suspension.

Putting these difficulties aside we have performed some model simulations that show that the aggregation effect is high, but relatively insensitive to wt % over the regime  $0.05 < \text{wt \%} < 2.0$  as shown in Figure 6. We discuss this in more detail in response to a similar point made below.

and cannot account for the differences between the  $n_s$  datasets.

See above.

It is already very well known that mineral dust particles tend to form aggregates. The vast majority of particulates in both dry dispersed and wet-suspended experiments are already aggregates of smaller particles. I include an image of a typical dry particle of nx-illite in which we can see that it is made up of many aggregated individual grains of just a few 10s of nanometres in size. This is prior to any aggregation in suspension and is representative of the particles used by Emersic et al. in their chamber.

We agree there is some degree of aggregation in the dry samples; however, we argue that the aggregation is amplified in the wet suspension. See Figure 4, which shows SEM images of kaolinite particles that have been in suspension and then dried out. The layered nature of the particles is evident and one can see that this particular particle has aggregated face-to-face many times.

So, is the total surface area of wet suspended particles strongly influenced by aggregation? Here we present multiple lines of evidence which show that there is not a strong effect and that most of the 'internal' surface area of an aggregate remains available for ice nucleation.

i. The authors correctly state that aggregation becomes more important for higher particle concentrations in suspension, but their claim that this will substantially reduce the surface area available for nucleation is unsubstantiated. Aggregation leading to loss of surface area is something which has been tested within the remit of the INUIT intercomparison (Hiranuma et al., 2014).

They state on page 22 that “agglomeration may conceivably affect the surface area exposed to liquid water” and in section 4.4 “Further quantification...is an important topic for future works”.

Wet suspended experiments were performed with several droplet freezing instruments each using droplets containing a range of nx-illite concentrations. For example, in BINARY (instrument based in Bielefeld) the surface area was varied by a factor of 100, in NIPI (the Leeds instrument) it was varied by a **factor of 10** and in the North Carolina instrument it was varied by 4 orders of magnitude. The resulting ns values are all self-consistent within a single system which shows that there is no impact on ns values by particle aggregation.

The interesting point here is that within this range of wt% in micro litre drops the modelled area fractions are not that sensitive to the initial wt%. Figure 6 below shows coagulation calculations over the course of a day for wt %=0.05, 1.0 and 2.0. Here it is shown that the surface area of particles divided by initial surface area tends towards similar values in all three simulations.

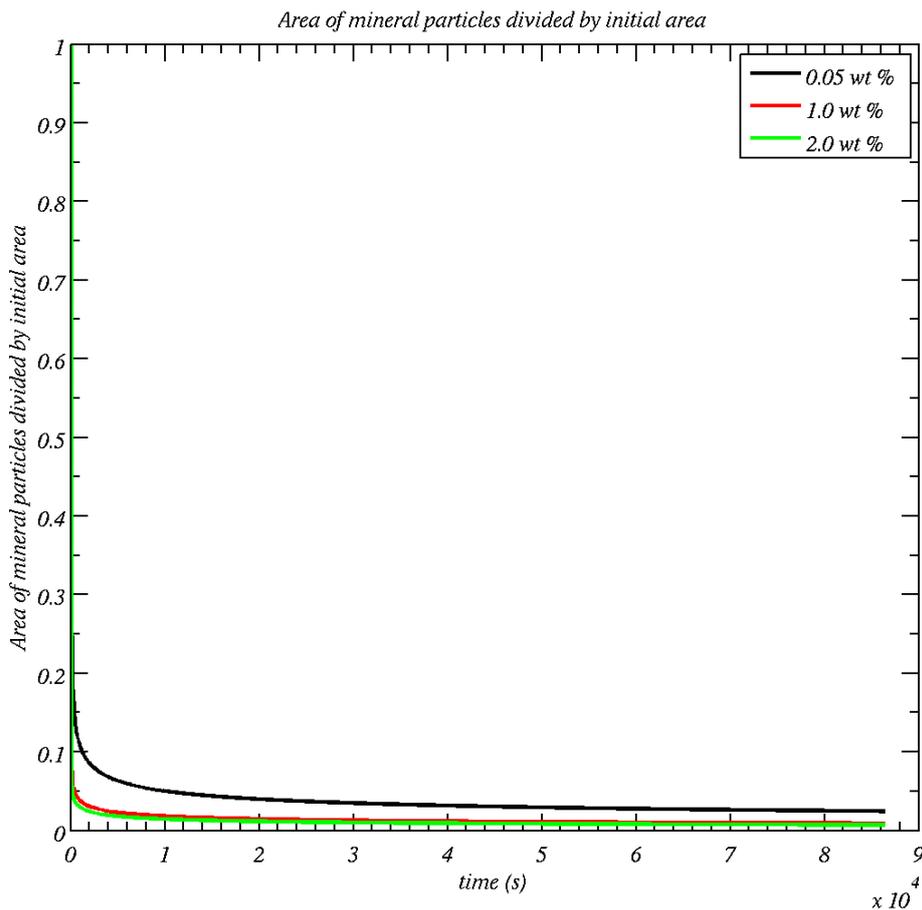


Figure 6. Sensitivity of aggregation to wt % in the range  $0.05 < \text{wt \%} < 2.0$

A caveat in these calculations is that you should not trust them to be 100% accurate, but only to an order of magnitude because there are several uncertain parameters in the calculations. For instance the zeta potential is very important to determining how effectively the particles are able to come together and stick, but its value is quite uncertain. Another area of uncertainty is in how the particles aggregate together (ie. do they form quasi-spheres or to form stacked plates?): it is not clear how they should aggregate from first principles but either assumption will lead to different results. In addition to this we have not taken into account enhancement of the coagulation kernel by shear motion in the fluid. Nevertheless the picture that emerges from this first cut treatment is that the surface area ratio is relatively insensitive to particle number.

This is all assuming the wt% does not affect the zeta potential of the mineral particle, but in actual fact the wt% could slightly alter the zeta potential. Slight changes in zeta potential can make large differences to the coagulation kernel.

To reinforce this view we have plotted new data from NIPI for nx-illite in microliter volume droplets in Figure 2. The dust concentration was varied from 0.05 to 2 wt%. The values of  $n_s$  from the experiments with widely varying dust concentrations overlap, hence  $n_s$  is independent of dust concentration and therefore independent of aggregation.

To be explicit, we do not believe this offers evidence that aggregation is not affecting all of the results presented (see Figure 6 above, which shows the fractional area left over after aggregation is relatively insensitive to wt % in this regime, but that it is very much lower than the initial value).

ii. The individual mineral dust grains which make up a mineral dust aggregates are irregular and stack in an irregular manner leaving space between the grains for gas or liquid, i.e. aggregation only has a minor impact on total surface area.

In our opinion this argument is invalid. The very fact that they “stack” can lead to a large difference in surface area (see Figure 4 for instance). A more quantitative counterargument is needed to rule it out in our opinion.

This view is borne out by both gas adsorption measurements and methylene blue adsorption on particulates in aqueous suspension. Broadley et al. (2012) showed that the BET gas adsorption surface area implied a primary particle size for nx-illite of 10s nm. This was consistent with electron microscope images where aggregates of 100s-1000s nm in size were composed of many smaller primary grains of 10s nm in size (Figure 1).

The soil science community also uses a method to quantify surface area of clay minerals suspended in water (Hang and Brindley, 1970). This technique involves placing a known quantity of methylene blue in an aqueous suspension and recording how much adsorbs onto the clay mineral from which they determine the surface area. They show that the BET and methylene blue specific surface areas are consistent which unambiguously shows that the internal surfaces of aggregates are accessible to molecules much larger than water such as methylene blue

The paper by Hang and Brindley uses a much lower wt% than those under consideration here. For example, at the bottom of page 204 of the Hang and Brindley article (left column) they say they use 5 mg in 200 ml of water, which is  $2.5 \times 10^{-3}$  wt%.

In addition in the technique described by Hang and Brindley (end of page 204) they start with mineral particles dispersed in methylene blue solutions and observe that the absorption of methylene blue increases with time. They do observe flocculation of the clays (as stated on page 204), and they consider a plot of methylene blue concentration vs amount absorbed. They argue that where the gradient of this curve starts to drop off is the point that defines the specific surface area, because the particles are flocculating. Central to this assumption is that there is only one

monolayer of methylene blue on the mineral particles at this point, which is not a given.

Another point is that the BET vs MB surface areas reported in the Table of Hang and Brindley only agree to within a factor of two. Hence, the agreement is more order of magnitude OK, rather than exactly the same.

2. Emersic et al. also suggest that coagulation 'removes the particles from the drops by sedimentation'. The mechanism through which the authors envisage micron scales particles to pass across the air-water interface through the side of a droplet is not discussed. But, the fact that aggregation is expected to be mineral dust concentration dependent and that we observe no dependence of  $n_s$  over a wide range of mineral dust concentrations (discussed in 1i) shows this is not a major loss of surface area.

We think this is a misinterpretation. We are suggesting that the particles sediment in the bulk suspensions...but they can still aggregate within the drops. We will make this clear.

3. Potential problems with measuring  $n_s$  at the Manchester Ice Cloud Chamber (MICC). This paper represents the first ever published measurement of ice nucleation efficiency in the MICC chamber. Despite the many issues which could affect the results from a complex instrument and the subsequent analysis of the data the resulting  $n_s$  values are regarded as 'truth'. Rather than validating their own instrument and results, they focus on why other instruments might be wrong.

They need to show that their instrument is capable of making these measurements.

We have compared our results to the AIDA published data for NX-illite and they agree – see figure 8 in our manuscript. This is good validation of our experiment.

Here are some selected issues that we think should be clarified:

i. Background measurements are mentioned, but are not shown. Is a measurement of 2 ice crystals per  $\text{cm}^3$  really significantly above the background? The background runs need to be performed with all the possible artefact aerosol sources, such as mixing fans, valves, inlet pipes, etc, used with clean filtered gas. ii. What has been done to test for temperature gradients in the chamber? What standard experiments have been done? Can MICC reproduce homogeneous freezing rates, for example?

Figure 7 shows a background experiment at -12 to -20C. You see the activation of cloud drops on the CDP (middle plot) by the presence of a closed drop mode and the lack of ice is indicated by two pieces of evidence: (1) in the middle plot the lack of particles outside of that mode; (2) in the bottom plot by the lack of ice on the 3V-CPI.

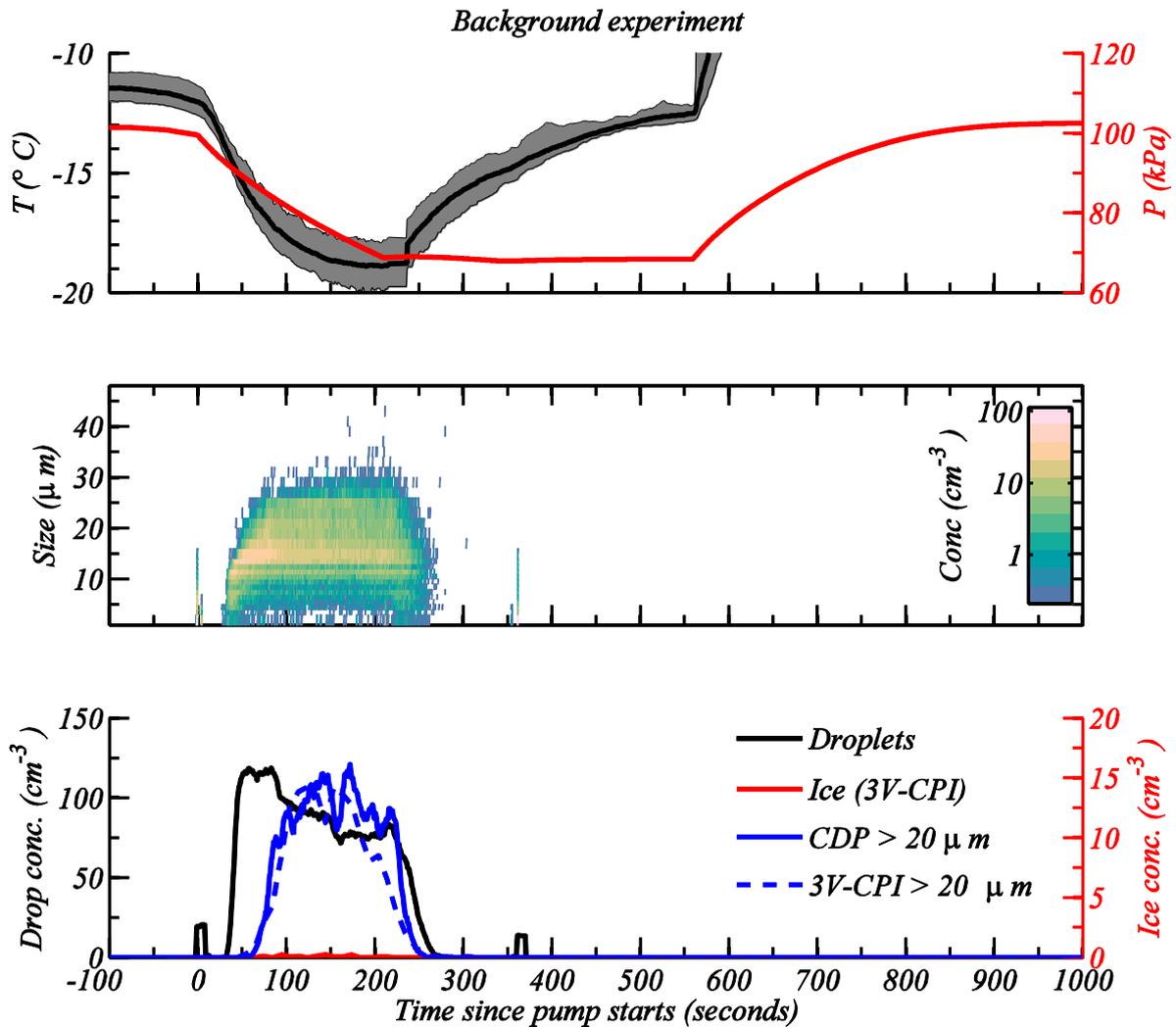


Figure 7. Background experiment at -12 to -20C.

Figure 8 shows a background experiment at -20 to -28C, the same point is true although here the background ice concentration is slightly higher (about  $<0.2 / \text{cc}$ ). Ignore the spike at the end of the run – this is due to electromagnetic interference when the valves close. We have also done this at -25C, but there we get to temperatures as low as -33 - -34C and see evidence of homogeneous nucleation at the end. We have not done the analysis to see if this reproduces homogeneous freezing nucleation rates because that is a separate problem.

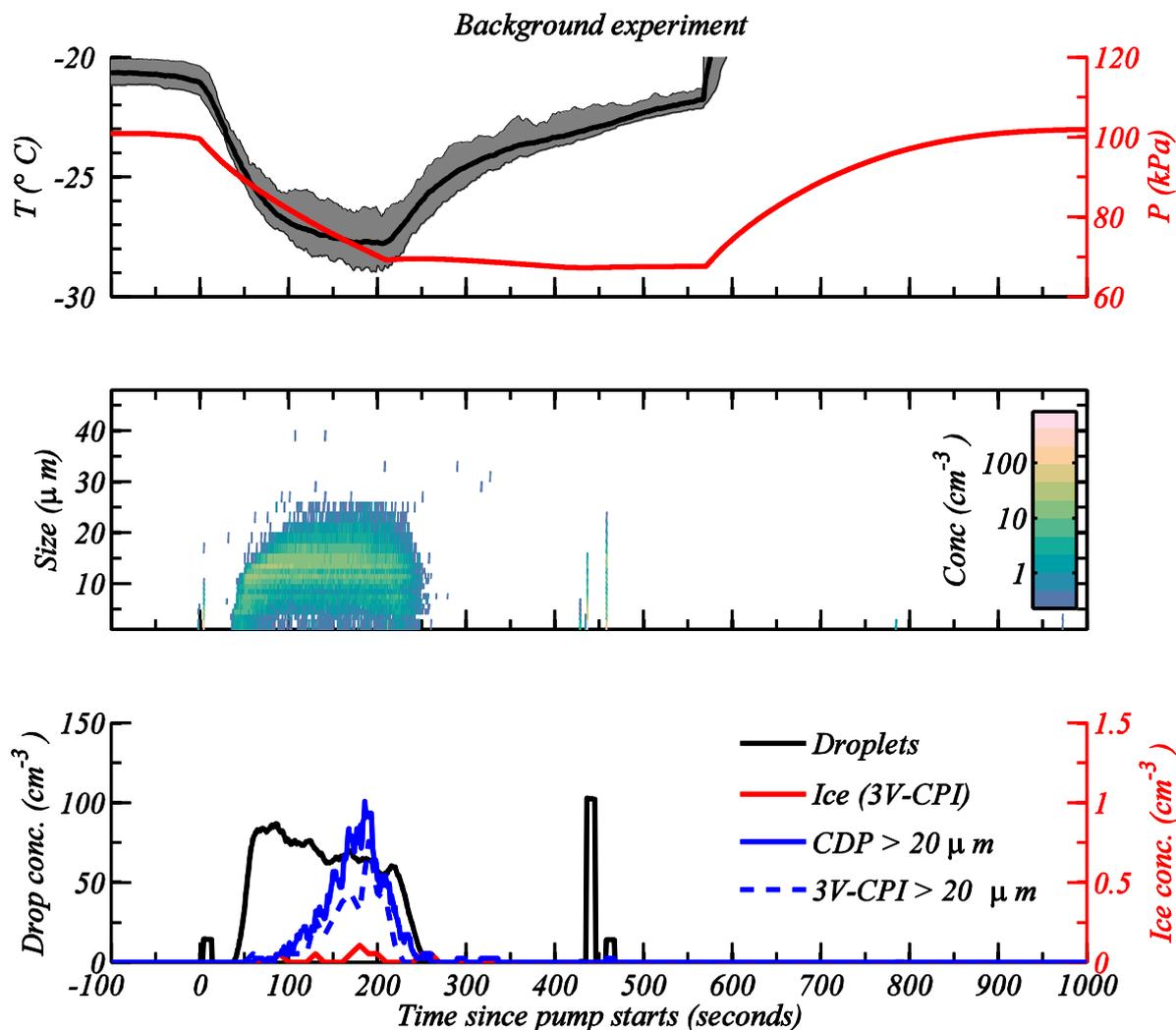


Figure 8. Background experiment at -20 to -28C.

iii. The geometry of the chamber is quite different from chambers which are focused on cloud nucleation research. The MICC chamber is 10 m tall and just 1 m wide in contrast to the AIDA chamber which is 7 m tall and 4 m wide. The geometry of the AIDA chamber minimises interaction of the cloud with the walls. The MICC chamber is described by Emersic et al. as a fall tube and has only been used in the past for ice aggregation work (at least this is the only published work from the chamber: Connolly et al. ACP. 2012).

In addition to the aggregation work, the chamber has also been used to study a wide variety of problems including:

Kaye, P. H., Hirst, E., Greenaway, R. S., Ulanowski, Z., Hesse, E., DeMott, P. J., Connolly, P. J. (2008). Classifying atmospheric ice crystals by spatial light scattering. *Optics Letters*, 33(13), 1545–1547.

Ávila, E. E., Castellano, N. E., Saunders, C. P. R., Bürgesser, R. E., & Aguirre Varela, G. G. (2009). Initial stages of the riming process on ice crystals, DOI: 10.1029/2009GL037723

Smith, H. R., Connolly, P. J., Baran, A. J., Hesse, E., Smedley, A. R. D., & Webb, A. R. (2015). Cloud chamber laboratory investigations into scattering properties of hollow ice particles. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 157, 106–118. doi:10.1016/j.jqsrt.2015.02.015

The instrumentation to detect droplets and ice is all located at the base of the chamber, up to 10 m away from the region in which nucleation could occur. Are artefacts introduced by having to rely on sedimentation of crystals out of the main volume of the chamber to the detectors?

No because we do not rely on sedimentation. We sample air from the chamber, so actively suck the air out. In addition are data agree well with AIDA for illite-NX as shown in our Figure 8.

How homogeneous is temperature? Cold spots 3-4 K colder in the warmer temperature experiments might explain the discrepancies in ns.

Temperatures are slightly inhomogeneous – it is not as well mixed as AIDA, but the temperature difference measured at 8 separate locations is less than 1K as can be seen by the margin of error values in the time series of temperature in Figs 2-7 (which show the full range rather than standard deviation values).

iv. What is the background INP concentration with the rotating brush generator running with just gas flowing through? This is a rather vigorous way of making aerosol and I worry that flakes of metal and previous dusts make it into the chamber. When measuring just 2 ice crystals in 2000 dust grains minor impurities will become problematic.

See Figure 7 and Figure 8 on the background issues. Additionally, the rotating brush generator was completely dismantled and vigorously washed clean of any powder then dried each time we changed the mineral powder under investigation. This yielded a good background (see above).

v. What are the error bars on the measurements in figure 8? There seems to be a very large spread in estimated ns values. For example, the nx-illite data around -21°C varies by 2 orders of magnitude. Is this within the experimental uncertainty or does it indicate that there is some other uncontrolled dependency which is not addressed.

No, this is just removal of the most effective IN during several repeat experiments. The difference is a factor of about 30, which is attributed to the most effective IN being used up. In the Hiranuma paper only the first expansions were shown, so we will make this clear in our paper.

This could be something like a dust preparation dependency.

We don't believe this is the case, due to the argument above.

4. Emersic et al. have focused their comparison plot (their fig 8) on the data from my team and show just the dry-dispersed and wet-dispersed average data from Hiranuma et al. (2014). This is odd because there now exists a wealth of literature data using the exact materials used here which the authors could also compare their results to (see below). It is our opinion that the omission of the literature data from this comparison is a major error and has led Emersic et al. to make incorrect claims. We suggest that data for each material is plotted on a separate plot together with the pertinent literature data.

Below I explore how the new Emersic et al. data compares with literature data:

i. Nx-illite. There is a wealth of information available in the Hiranuma et al. (2014) intercomparison paper where many of the world's ice nucleation research teams used their respective instruments (17 in total) to quantify ice nucleation with the same material. This dataset cannot be simply summarised in two lines – the dry-dispersed and wet-dispersed lines in Emersic et al.'s Fig 8. I have reproduced the data set in Figure 3 and have added the Emersic et al. data to Figure 4 in which the data are split into dry-dispersed and wet-suspended. The discussion in the Hiranuma et al. paper is far more subtle and caveated than Emersic et al. suggest (and has also been modified in the accepted ACP article; they cite only the ACPD version). If you take a simple average of the two groups of data, you apparently get wet suspended lower than the dry dispersed ns. But, taking a closer look it is clear that the CFDC, a dry-dispersed technique that cannot be susceptible to aggregation effects described by Emersic et al., are consistent with the wet-suspended experiments.

**This comment about the CFDCs is addressed in an earlier comment above.**

The Manchester data is inconsistent with the CFDC data from ETH (PINC) and Colorado State (Instrument name?). Discussion of why the new Emersic et al. data is inconsistent with the CFDC data needs to be included in the paper.

**We will address the concerns over the discrepancy with CFDCs as stated above: in short the literature clearly state that the CFDCs may underestimate  $n_s$  (see Hiranuma et al. prior to section 3.3).**

ii. Kaolinite KGa-1b. Again, Emersic et al. have ignored most of the literature data.

Tobo et al. (2014) summarise some kaolinite results together with recent literature data for KGa-1b in their Fig A1. This figure is reproduced here together with the Emersic et al. data superimposed (Figure 5). There is a mixed picture here. The dry-dispersed CFDC data from Tobo et al. (2014) and the dry dispersed Wex et al. (2014) data are in good agreement with the wet-dispersed Murray et al. (2011) data, but the Kanji et al. (2013) data also from a CFDC, is somewhat higher. The new Emersic et al. data sits between these two extremes, but is more than one order of magnitude greater than the Murray et al. (2011), Tobo et al. (2014) and Wex et al.

(2014) data. This does not support the premise that there is a strong difference between dry dispersed and wet-suspended experiments.

We reproduce Benjamin Murray's plot below. There are several things to point out:

- First of all, our data at low temperatures has been omitted. This data, at around -32C, agrees with all of the data except the Kanji (2013) results.
- Secondly, we address the comparison to the other instruments at warmer temperatures, where our results are higher than the others.
  - The results from Schill et al are using wet suspensions and may also suffer from the problems we are discussing.
  - The results from Tobo et al are fitted to data from a CFDC (see above argument)
  - The results cited as being from Wex et al. are also a fit to the same CFDC data as Tobo et al. because the original article says that measurements with LACIS were made at temperatures -30, -34 and -38C (see page 5536) and the other measurements were with the CSU CFDC.
  - The operator of the CSU CFDC admits that there may be an issue in activating all particles to drops (in the Hiranuma paper)

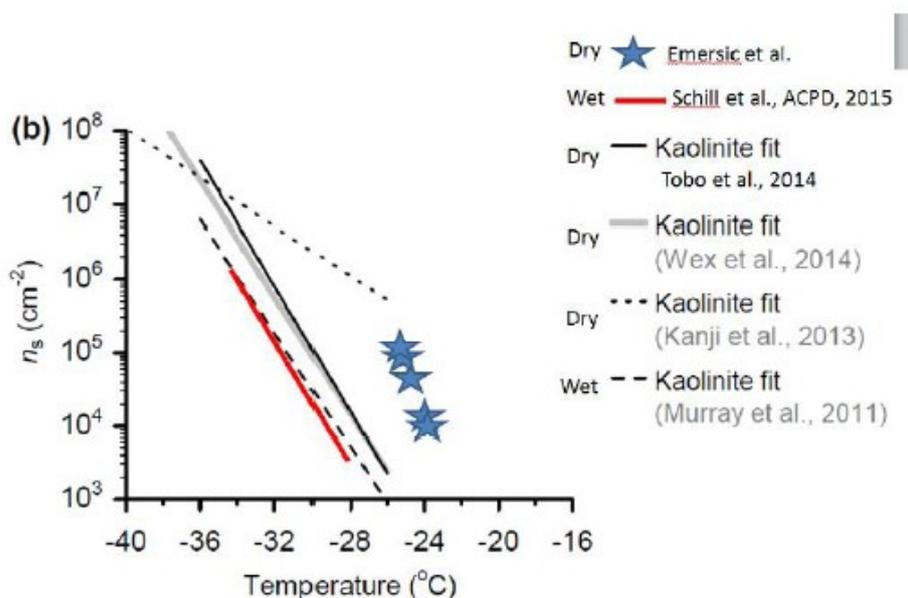


Figure 1. Figure comparing data for Kaolinite KGa-1b adapted from Tobo et al. (2014) with the addition of the Emersic et al. data and that of Schill et al. (2015). The dry dispersed results of Wex et al. (2014) and Tobo et al. (2014) are in good agreement with the wet dispersed data of Murray et al. (2011) and Schill et al. (2015). The results of Kanji et al. (2013) are somewhat higher above about -34°C. The data of Emersic et al. are inconsistent with all data sets and substantially higher than two of the dry-dispersed datasets which is inconsistent with their aggregation hypothesis.

5. Emersic et al. have extrapolated the fits presented in Murray et al. (2011), Broadley et al. (2012) and **Atkinson et al. (2013)** well beyond the regime where measurements were made and the stated validity range of those parameterisations. They then use these extrapolations to claim that there is a difference between the chamber and droplet freezing approaches. This is not valid. The nx-illite ns polynomial parameterisation (Broadley et al. (2012)) extends up to -25 C, whereas Emersic et al. quote data around -21oC. In Broadley et al. (2012) we made it very clear that extrapolation would be incorrect, stating: 'since this parameterisation is based on experimental data with surface areas  $2 \times 10^{-6}$  cm<sup>2</sup> it may under predict ice nucleation above 247 K. Similarly, for Kaolinite we only quote data up to -27oC, whereas Emersic et al. assume in their argument that there is a discrepancy on experiments at warmer temperatures. The fits in Fig 8 need to be limited to the range where measurements were made and the discussion modified accordingly.

The measurements from Broadley are superseded by the INUIT measurements in any case. The conclusion is the same regardless. We dispute that we have extrapolated results from Atkinson et al. (2013): the K-feldspar curve from Atkinson et al. spans the range 247 K to 270 K (see their Figure 3) and our results span 247 to 255 K.

6. The ns data for from Murray et al. (2011) and Broadley et al. (2012), plotted in their Fig 8, is based on droplets with diameters of 10's micrometers. These droplets are closer to picolitre in volume rather than microliter. Emersic et al. suggest that it is the microliter volume droplets where there is an aggregation problem. Given the Murray et al. (2011) and Broadley et al. (2012) data is not based on microliter experiments they should not suffer from aggregation issues according to the analysis of Emersic et al. Hence, aggregation cannot account for the differences between the chamber and these droplet freezing studies.

We are not saying it is not an issue for the pico litre-sized drops. We are saying that it probably does not happen within the drops when they are pico litre sized, but it could still happen in the bulk suspension. Whether or not it does will depend on sample preparation. Whether or not the particles stay in an aggregated state when making the drops will depend on whether clays or feldspars are under consideration. Clays tend to form strong aggregates because of they are platelets, whereas feldspars form looser aggregates.

7. The authors claim that feldspar is not susceptible to coagulation and should therefore not be affected. However, their data is still more than one order of magnitude higher than the Atkinson et al. (2013) parameterisation at around -18oC. Doesn't this imply we need to look for a different explanation other than aggregation?

This is a misinterpretation, what we mean by that is that the Feldspar sample forms weaker aggregates because of their morphology. Hence, we are suggesting that the

Feldspar aggregates can be easily disrupted when introduced into pico-litre sized drops.

8. Quoting from Emersic et al.: 'Illite and kaolinite particles may behave differently and could coagulate during the stirring process.' The authors suggest that aggregation of particles occurs during stirring. The action of stirring breaks up aggregates, not the other way around. This is the whole point of stirring – it breaks up aggregates to create a more stable suspension.

We disagree that stirring will always act to break up the aggregates. One only needs to consult the wide body of literature on this subject to learn that aggregation / flocculation can be greatly enhanced by shear within the fluid under certain conditions. These are text books that cover some of these details:

*Jacobson, M. Z. (1999). "Fundamentals of atmospheric modelling". "Cambridge University Press".*

*Crowe, C. T. (2006). MULTIPHASE FLOW HANDBOOK. City, 1218, 6092–101. doi:10.1016/j.chroma.2011.01.063 (see page 6-11)*

9. 'Ben Murray' in the acknowledgments: The draft which I saw was very different to this one and I should not be acknowledged for comments. We should be acknowledged for providing the samples as part of the ACID PRUF consortium.

We will make this change on your request.

## Comment from Heike Wex

The main comment to address here is the statement that data from the LACIS chamber agrees with data from Benjamin Murray's group

We have reproduced the figure included in this communication and would like to point out that the red line starts to come away from the orange line at around  $T = -24^{\circ}\text{C}$ . This is completely consistent with our data for K-feldspar, but unfortunately the data do not extend far enough to lower temperatures. The error bar for NX-illite is too large to say much.

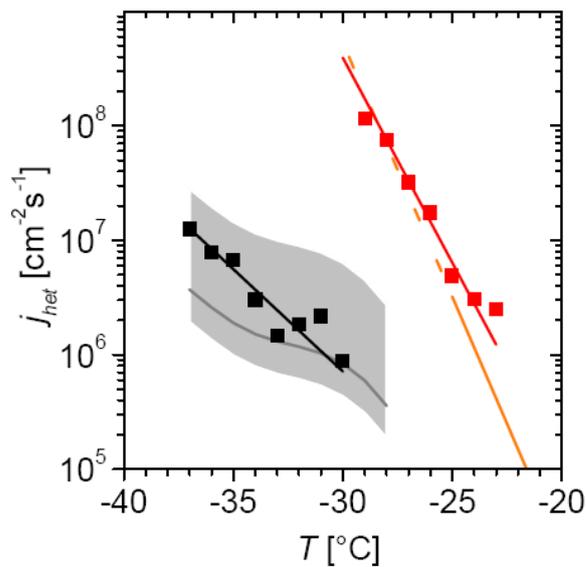


Figure S1 (from Augustin-Bauditz et al., GRL (2014), supplement): Calculated nucleation rate coefficients for K-feldspar and illite NX as function of temperature. Symbols in red (K-feldspar) and black (illite NX) show data obtained from LACIS, together with the respective fits (lines). The orange and grey lines represent data from Atkinson et al., Nature (2013) for K-feldspar and Broadley et al., ACP (2012) for illite NX, respectively. The grey shaded area represents the uncertainty in the conversion from surface areas based on BET to those based on the assumption of spherical particles.

Furthermore, although they are interesting, we do not wish to comment on the biological samples as it is not relevant to the present study.