Atmospheric
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Interactive comment on "Investigating the discrepancy between wet-suspension and dry-dispersion derived ice nucleation efficiency of mineral particles" *by* C. Emersic et al.

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These comments are a result of discussions between myself (Ben Murray), Danny O'Sullivan, Theo Wilson and Thomas Whale at the University of Leeds.

General comments

Emersic et al. present a paper in which they compare chamber derived ns 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 ns 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. However, Emersic et al.'s explanation for smaller ns 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.

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. 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). 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.

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 and cannot account for the differences between the ns datasets. 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. 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). 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

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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.

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 ns from the experiments with widely varying dust concentrations overlap, hence ns is independent of dust concentration and therefore independent of aggregation.

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. 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.

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

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dependent and that we observe no dependence of ns over a wide range of mineral dust concentrations (discussed in 1i) shows this is not a major loss of surface area.

3. Potential problems with measuring ns 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 ns 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. 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 cm3 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?

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). 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? How homogeneous is temperature? Cold spots

3-4 K colder in the warmer temperature experiments might explain the discrepancies in ns.

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.

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 -21oC 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. This could be something like a dust preparation dependency.

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. 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.

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.

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 $2 \times 10-6$ cm2, 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.

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.

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?

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.

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.

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Figure 1. Scanning Electron Microscope (SEM) images of nx-illite. An aggregate of several micrometers in size is shown on the left and a close up (right) reveals that it is composed of many particles on the order of 10–100s of nanometres across. This is consistent with the gas adsorption measurements, which suggested average particles sizes of 20 nm (assuming smooth spheres – see (Broadley et al., 2012) for details.

Figure 2. Values of ns for nx-illite from experiments where the weight fraction of dust in microliter volume droplets was varied from 0.05 to 2 wt %. Aggregation is expected to change over this range of concentrations. The ns values are independent of dust concentration which shows that the surface area available for nucleation is independent of aggregation.

Figure 3. nx-illite ns data from Hiranuma et al. (2014) showing the range of existing nx-illite data.

Figure 4. nx-illite ns data from Hiranuma et al. (2014) split into dry-dispersed (red) and wet-suspended (blue) instruments. Emersic et al.'s data have been superimposed on this plot (green stars). The Emersic et al. chamber data are in disagreement with dry dispersed CFDC (continuous flow diffusion chamber) data from two groups (ETH-

PINC and Colorado state). Aggregation as envisaged by the authors is not an issue in these experiments yet the CFDC data is in agreement with the wet-suspension measurements. The CFDC data is therefore inconsistent with Emersic et al.'s aggregation hypothesis.

Figure 5. 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 -34oC. 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.
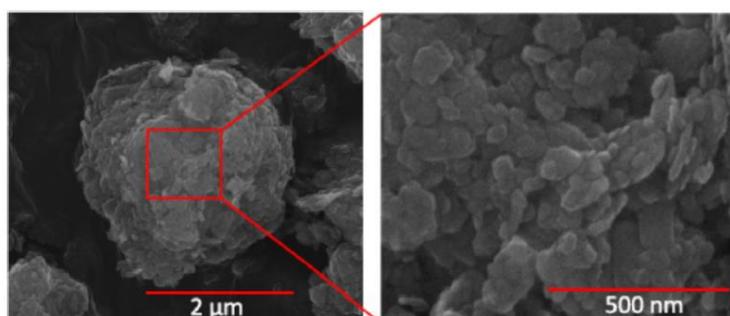
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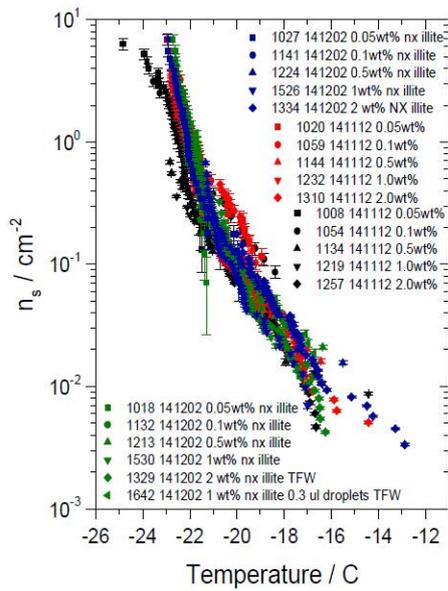
Fig. 1.

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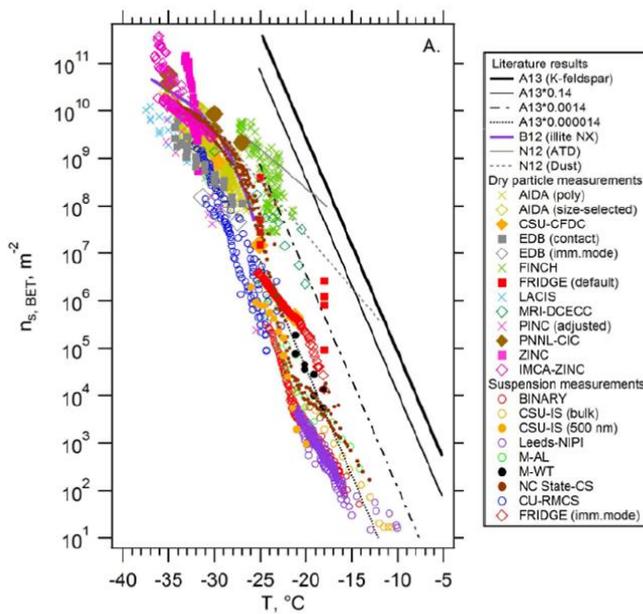
Fig. 2.

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Figure 1. nx-illite n_s data from Hiranuma et al. (2014) showing the range of existing nx-illite data.
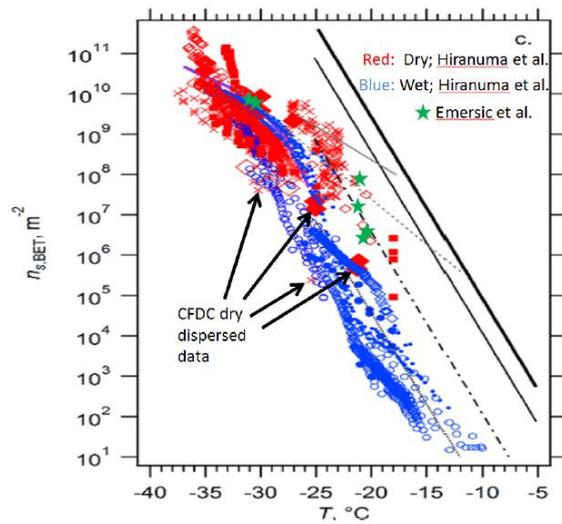
Fig. 3.

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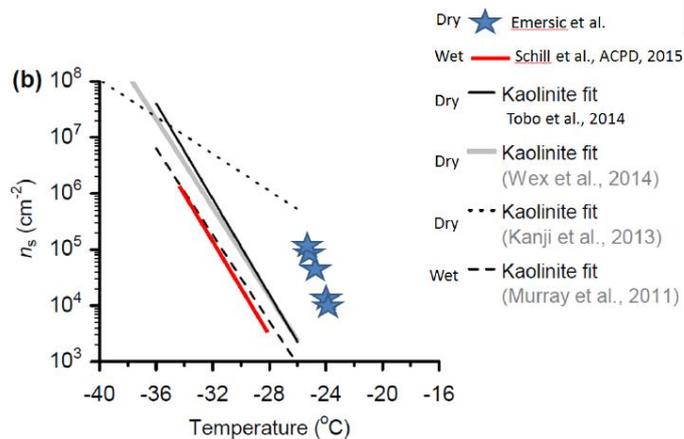
Fig. 4.

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Fig. 5.

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