Response to Referee #3

We would like to thank the referee for their insightful comments and have responded below. The referee comments are highlighted in red with our responses in black.

This is a well-written paper with an interesting experimental approach that fits perfectly well into the journal Atmospheric Measurement Techniques. The authors describe an instrument for quantifying heterogeneous ice nucleation: the InfraRed-Nucleation by Immersed Particles Instrument (IR-NIPI). They use multiwell plates and an infrared camera for detection of the freezing process. For comparison, they have investigated homogeneous ice nucleation of ultrapure water, and the heterogeneous freezing of two mineral dust samples. The manuscript should be published in AMT after major revisions.

Comments

In line 72, the authors claim "Here we propose a new technique,. . .". Unfortunately, this is not entirely true. A quick literature research shows that there are other instruments with very similar approaches. In particular, I would like to mention the set-ups of Zaragotas et al. and of Kunert et al. It is good scientific practice to search, to describe, and to discuss the findings of other scientists when presenting a new set-up. I expect that the authors make up the leeway in the revised version of the manuscript. Concerning the set-up of Kunert et al., I could not find any peer-reviewed publication, but I have been the organizer of two ice workshops (Kunert 2016b, 2017b) and the convener of two EGU General Assembly sessions (Kunert 2016a, 2017a) and a speaker at the INUIT Final Conference and 2nd Atmospheric Ice Nucleation Conference (Kunert 2018), where this research has been presented. At all these meetings, also the authors were present and in the case of the latter have even been the organizers. Therefore, the Twin-plate ice nucleation assay (TINA) with infrared detection by Kunert et al. is well-known to them and should be described in their manuscript for comparison with IR-NIPI.

The omission of Zaragotas *et al*. (2016) was a major oversight and we thank the reviewer for bringing this to our attention. The instrument discussed is applied to the cryobiology field but is a similar set up to the IR-NIPI and supports the use of IR cameras for this application.

With regards to the various conference presentations made by Kunert et al. there was no peer reviewed literature for this technique at the time of submission and hence it was not cited or discussed. However on the 24th of July Kunert et al. have had a publication accepted for review and posted on the AMT discussion forum. We are then happy to include this reference and have altered the text to include it.

We have included the references to these papers in sections 1 and 2.4.

In section 1: "While many instruments use optical cameras to detect freezing events (Whale et al., 2015; Budke and Koop, 2015; Häusler et al., 2018; Beall et al., 2017), some researchers have used techniques to detect the release of latent heat associated with freezing. For example differential scanning calorimetry (Marcolli et al. 2007; Pinti et al. 2012) and infrared emissions (Zaragotas et al., 2016; Kunert et al. 2018) have been used. Zaragotas *et al*. (2016) use a thermal camera to measure the temperature of individual aliquots within a 96 multiwell plate partially submerged within an alcohol bath. This study investigated plant samples but suggested that the technique may be adapted for atmospheric purposes. Very recently, Kunert *et al*. (2018) presented a similar set up to investigate biological samples and collected aerosol. Unlike Zaragotas *et al.* (2016), Kunert *et al.* (2018) do not measure individual droplet temperatures via infrared emissions but instead use multiple thermistors embedded in the sample holders to infer temperature for the droplet array."

In section 2.4: "It should be noted that one of the limitations of the setup used by Zaragotas *et al*. (2016) was that the IR camera was calibrated only once by the factory, however our calibration method mitigates this limitation."

In line 48, the authors list some droplet freezing assay experiments but the list is rather incomplete, e.g. Häusler 2018 is missing. I strongly recommend a table with all technical parameters of each experiment listed, e.g. number of observed volumes, volume of the droplets, homogeneous ice nucleation temperature, etc. Finally, for all experiments a discussion of the pros and cons in comparison to IR-NIPI should be added.

This list was not intended to be exhaustive, but representative. We have now added the reference of Häusler *et* al. (2018) to the list of drop assay references.

We think that a table reviewing all previous droplet freezing assays is beyond the scope of this techniques paper. A table of such a nature would be much better suited in a review or intercomparison paper. There are papers already available which describe such advantages and disadvantages of the various styles of instruments and are referenced in the text "For more information on the capabilities and limitations of the various techniques see the comprehensive reviews and intercomparisons conducted by Hiranuma *et al*. (2015) and (DeMott et al., 2018). Haüsler *et al*. (2018) also presents a summary of the features of various techniques. ". In addition, we are aware of a paper describing many techniques from the FIN02 activities which has recently been submitted to AMTD and added to the references in text.

Instead, the authors compare only their own set-ups, i.e. µL-NIPI and IR-NIPI. However, the volume of the respective droplets is very different, 1µL versus 50µL, respectively.

We have compared a wide variety of different techniques when investigating the NX-illite sample. We chose NX-illite as it allowed a direct comparison to literature data of a similar experiment in terms of droplet volume (the AIS instrument) as well as a wide range of other instruments (Hiranuma *et al*., 2015). This included a direct comparison to another technique using 50 µL droplets (AIS). It should be noted there is limited literature data for 50µL droplets and NX-illite is the only material we can compare directly to as a result of this. We compared to our ul-NIPI technique for other samples, because this is available in our laboratory and we could operate the two instruments side by side with the same sample.

This is not only important for homogeneous ice nucleation, which shows strong volume dependence, but also is important for heterogeneous ice nucleation because larger volumes carry more INPs and the abundance of efficient INPs rises. The authors have discussed this only partly and a more elaborated discussion might be necessary.

The text has now been amended to expand on this topic to read "The alternative approach is therefore to increase the number of particles within each aliquot of water. In principle, increasing the number of particles per droplet, and therefore the surface area of nucleator per droplet, will increase the sensitivity of the experiment to rarer INP. This enables quantification of lower INP concentrations" To increase the number of aerosol particles per volume of liquid the time period over which an atmospheric sample is collected can be extended, but in doing so temporal resolution would be lost. A method of increasing the sensitivity of an immersion mode technique is to increase the volume of the collected suspension used in each aliquot, while maintaining the concentration of particles per unit volume. This increases the number of particles per aliquot of liquid and therefore makes it more likely that rarer INP will be detected."

In particular, I miss plots of the homogeneous freezing events and a detailed study of the freezing of single droplets (marked with numbers on a picture of the multiwell assay). I also recommend adding the diameter of the droplets to the volume to make the study more comparable to other studies.

We are unable to reach homogenous in this setup, as with all techniques employing such large droplets. The expected homogeneous curve can be seen in figure 5 and our blanks are well above this. We do not see the value of numbering specific droplets in an array, this is not information we routinely collected.

Our droplets are not spheres in the multiwell plates so a diameter is not relevant but we have quoted a volume equivalent diameter to help compare to other studies. "The most useful for this freezing assay are the 96 x 200 µL or 384 x 50 µL aliquot arrays and in the tests reported here 50µL droplets (~2300µm volume equivalent diameter) are used in 96 well plates."

The authors make the point that their set-up is more sensitive for low concentrations of INPs, which is particularly true for strong INPs. However, they don't mention the disadvantage of their set-up, which is that they cannot easily measure weak INPs. In the atmosphere, the number of strong INPs is extremely low, which makes µL-NIPI a valuable technique. However, often strong INPs are entirely missing and weak INPs will be much more abundant. Therefore, the authors should discuss the limitations of their set-up and should also show experiments at the detection threshold and should investigate proxies for weak INPs e.g. cellulose or soot.

We have now tried to clarify the point that the IR-NIPI instruments compliment smaller droplet techniques. The section of text added reads "These large volume assays capture the rarer, more active INP but often miss the

more abundant but less active INP. Hence they should ideally be used alongside a smaller droplet instrument to generate complimentary datasets."

Also I miss biological INPs or proteins and polysaccharides been emitted by biological sources. Therefore, beside ns values of solid INPs also nm values of soluble INPs should be measured and discussed.

We accept that this would be interesting to investigate but again believe it is beyond the scope of this paper which is to outline the concept of the technique. We have some interesting results from biological materials and would like to use these in another paper and do not think this is the best place to present this data. We believe that we have already provided sufficient examples of materials used in the IR-NIPI system.

Specific comments

Where is the homogeneous freezing temperature (T50) of ultrapure water in your IRNIPI set-up?

Homogenous freezing (T50) for 50µL droplets is ~-32.5°C based on Murray and Koop (2016). This is presented in figure 5. We have not accessed homogeneous freezing and do not claim to do so.

Line 99: Also indicate the formula for nm and add respective water soluble samples.

We do not think this is necessary as explained above.

Line 182: "standard deviation ±0.5◦C"

Thank you. This has been changed.

Line 190: "after the first equilibrium step at +5◦C"

Thank you. This is changed to the suggested.

How is the temperature uncertainty in the range between -20◦ and -30◦ C?

We are unable to quantify the uncertainty as the thermocouples and water often freezes before this point but we assume that it is similar to that stated for the temperature range above -20°C. We are mainly interested in the temperature of samples above -20°C as below this we enter our baseline. The uncertainty within this temperature range is of secondary importance for our experiments.

You have only used ultrapure water for temperature calibration. How about other samples such as aqueous salt solutions, higher alcohols or alkanes?

As you have rightly pointed out we have only calibrated on the basis of ultrapure water. We have done this because we are only using water suspensions and have not attempted to study nucleation in different solutions or other materials. Furthermore, using solutions or other liquids for a calibration would not be applicable for water, since they have different thermal conductivities and different thermal emissivity. The IR camera is already corrected based on the thermal emissivity of water and hence using other solutions or liquids would introduce new errors.

Line 215: What kind of filter has been used for purification?

Thank you for highlighting this. It has now been added to the text. "Sartorius Ministart, non-pyrogenic, single use filters were used for this (product code 17597-K)."

A figure, similar to that in fig. 7B, should be plotted also for feldspar samples including comparison data from other groups.

We believe that is not needed for this paper as for the same reasons as mentioned earlier. We believe we have already demonstrated the use of the IR-NIPI with sufficient materials and that this would be more applicable for an intercomparison paper and has been done so by DeMott *et al*. (2018). In addition there is also no published literature data for feldspar in the droplet regime for the IR-NIPI so no direct comparison can be made. This was one of the reasons we chose to include a comparison with NX-illite.

In figures 2, 3, 4, and 7 capital letters have been used in the graph but small letters have been used in the figure caption, respectively.

Thank you. This has been amended.