

Answer to reviewer's comments on the manuscript by Thomas Häusler, Lorenz Witek, Laura Felgitsch, Regina Hitzemberger and Hinrich Grothe "Heterogeneous freezing of super cooled water droplets in micrometre range- freezing on a chip"

All three referees have suggested that the manuscript would be more suitable for AMT. After correspondence with the handling editor and Chief editors of both AMT and ACP, the editors recommended to proceed with the regular review process in ACPD as a manuscript under consideration for publication as a Technical Note in ACP. Therefore the title of the manuscript has been changed to: "*Technical note: Heterogeneous freezing of super cooled water droplets in micrometre range- freezing on a chip*"

The revised manuscript was uploaded separately and is available as *author comment*.

Reviewer 1

The authors would like to thank the reviewer for the constructive comments!

Comment

1. Several recent studies addressed freezing of INP suspension droplets placed either in individual compartments (Budke, 2015), or placed on a substrate (Whale, 2015, Harrison, 2016, Peckhaus, 2016). These studies used suspensions of INPs prepared with different concentrations to cover the broad range of freezing temperature. In all these studies, it was clearly shown that freezing temperature is a function of cooling rate and average number of INP particle per droplet. Other studies (Hader, 2013, Wright, 2013a, Wright, 2013b) have shown significant effect of cooling rate on the freezing curves, and Herbert, 2014, and Peckhaus, 2016 have shown that this behavior is consistent with the stochastic theory of ice nucleation. None of these studies is mentioned in this manuscript. The conclusion of instrument "accuracy" (Abstract, Conclusion, and elsewhere) is drawn based on the comparison of median freezing temperatures, but the data used for this comparison has been obtained with droplets of different sizes and different concentrations of INP (Figure 9 of the manuscript)! It is also not clear how accuracy can be derived by comparison to other instruments? These issues have to be fixed.

Answer:

This paper is intended to be a technical description of a new technique to determine freezing behaviour. It was not intended to show again the influence of concentration, cooling rates or the average number of INP per droplet in immersion freezing. Therefore this paper is going to be resubmitted as a *Technical Note*. Wright and Petters, 2013, Polen, 2016 and Peckhaus, 2016 were added to the references. The comparability of the measurements is discussed later on.

Changed text on page 2 line 28 ff:

"In order to observe freezing processes in the laboratory, several experimental approaches have been employed in the past, such as cloud chambers (DeMott, 1990;Möhler et al., 2006;Niemand et al., 2012;Rudek et al., 1999), continuous-flow diffusion chambers (Kanji and Abbatt, 2009;Rogers et al., 2001;Salam et al., 2006;Stetzer et al., 2008), levitation in an electrodynamic balance (Stockel et al., 2005), acoustic levitator (Diehl et al., 2014) and different kinds of droplet-freezing setups (Peckhaus et al., 2016;Polen et al., 2016;Whale et al., 2015;Wright and Petters, 2013;Zolles et al., 2015)."

Comment

2. Peckhaus (2016) has used up to 1000 identical 0.2 nL droplets deposited on a silicon substrate and coated with oil. It was shown there that pure water droplets froze homogeneously and no effect of substrate on ice nucleation has been found. The setup used by Peckhaus (2016) has much in common with the instrument described in this manuscript (droplet size, automatic detection of freezing events, use of a substrate and oil coating), and a comparison might be instructive for the reader. It would be interesting to explore the role of etching on the heterogeneous freezing, as no effect on the monocrystalline silicon substrate was observed in their study (I am referring to your statement “Tests of an uncoated silicon plate indicated that the silicon itself is IN active.” (page 5 line 25). Consider using their SBM-based parameterization scheme to compare your measurements with the literature data.

Answer:

The untreated silicon plate does not show any ice nucleation activity before the etching process. After the application of the cavity pattern via RIE (Reactive Ion Etching), a freezing temperature shift of ultrapure water was found. We suspect a reaction of the silicon surface with the etching reagents, leading to an ice nucleation active silicon compound.

Changed text on page 5 line 29 ff:

“Peckhaus et al. (2016) found no effect of a silicon substrate on ice nucleation. After the RIE-treatment, however, a shift of the freezing temperature of ultrapure water from $-37,5^{\circ}\text{C}$ to approx. -20°C was found. This shift might have been caused by a reaction of the etching agents with the silicon surface leading to an ice nucleation active compound. After the etching process, a gold layer (thickness 500 nm) was sputtered on top of the pattern, leading to an ice nucleation neutral surface. As an alternative to a gold sputtered silicon plate, a pure gold chip of similar dimensions was ion milled with a Focused Ion Beam (FIB) to introduce the same kind of pattern. Due to the thermodynamically stability of pure gold, no ice nucleation active compounds are formed on the surface during the introduction of the cavity pattern. Therefore no further treatments of its surface are necessary. If the surface of the gold sputtered silicon plate is scratched accidentally and the silicon is exposed, the chip becomes ice nucleation active again. Small scratches on the surface of the pure gold chip as well as the slight surface irregularities in the cavities were not found to have any influence on the INA. Anyway they have to be avoided to not damage the cavity pattern.”

Comment

3. The whole discussion of droplet volume dependence is a mystery to me. Clearly, changing the size of the droplet containing suspended INPs would change the total surface available for critical ice embryo formation. The same effect can be achieved by changing the concentration of INPs. The median freezing temperature measured with two droplet assays can only be compared if droplets of the same size and the same concentration have been cooled down with the same cooling rate until freezing. To compare results obtained with different setups and under different conditions, the ice nucleation community came up with the notion of ice nucleating active surface (INAS) site density (n_s), which authors introduce (equation 1), but don't use. By carrying out the freezing experiments with the different concentration of INPs and using the INAS density parameterization a much wider range of temperature can be accessed (see Budke, 2015, or Wex, 2015).

Is there any reason for not using this approach?

Is that because the volume of the droplets has not been measured?

The only information that is provided is the cavity diameter (20 to 80 μm) which is not sufficient since the cavity depth and geometry is not given.

Answer:

The correct approach to compare results obtained with different techniques and under different conditions is now used. The ice nucleation active surface/mass site densities are now provided in Figure 6 and 8, compared, described and discussed. The droplets form was assumed to be spherical and was not experimental determined. The droplets shape is assumed to be independent of the geometry of the bottom of the cavity. We would like to emphasize to all cavities on one chip have exactly the same diameter within an error of about $\pm 1\mu\text{m}$. The diameter description in the text (20 – 80 μm) refers to the range being accessible by the RIE and FIB techniques.

Changed text on page 3 line 24 ff:

“The ice nucleation activity can be also well expressed by referring to the mass of INP per droplet (n_m) instead of the surface per droplet. This is often used when the surface of the investigated INP is not accurately quantifiable.”

Changed text of chapters *Results* and *Conclusion*:

See the revised manuscript as uploaded separately as *author comment*.

Changed text on page 13 line 5 ff:

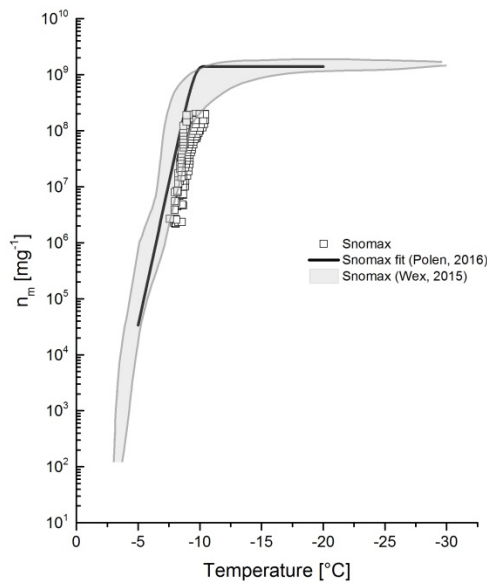


Figure 6 The ice nucleation active mass site density n_m of Snomax[®] determined with the freezing ship is in consistence with the results published by Wex et al. (2015) and Polen et al. (2016). A shift of the n_m values to lower temperatures due to degradation processes can be observed and is in agreement with Polen et al. (2016).

Changed text on page 14 line 5 ff:

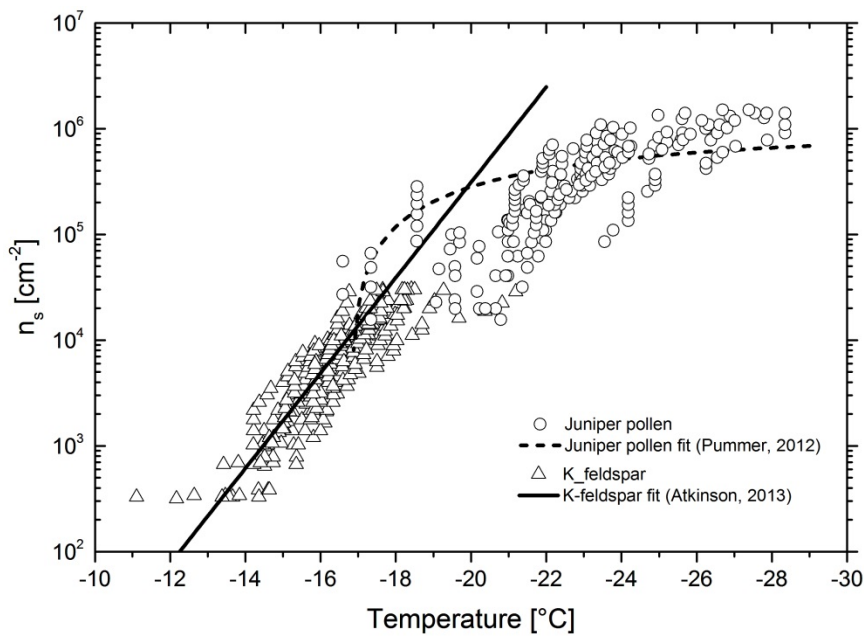


Figure 8 Comparison of ice nucleation surface site densities n_s of measurements done using the freezing chip with already published data. The n_s values of K-feldspar fit well to the published data of Atkinson et al. (2013). Minor deviations of the obtained juniper values occur in comparison to Pummer et al. (2012).

Comment

4. (a) Give the reader more information on the method of spreading of particle suspension.
- (b) Can you be sure that no particle residuals are left on the surface between the etch pits?
- (c) What is the variability of INP concentration inside the etch pit introduced by spreading?
- (d) Have you tried to analyze the residuals in the pits: is the distribution homogeneous? If not, what is the mass distribution? These issues have to be addressed if you plan to resubmit the manuscript.

Answer:

- (a) The method of spreading the suspension is now described in more detail.
- (b) We agree that INPs remain between the cavities, since water between the cavities is evaporating. This is not true for the water inside the cavities. Due to the pre cooling of the freezing chip to $+5^{\circ}\text{C}$, the evaporation of the droplets is prevented.
- (c) It is assumed that no variabilities of concentration are introduced by spreading.
- (d) The suspension of INP in water is deposited on the chip immediately after vortexing and therefore assumed to be distributed homogeneously. No analysis of the mass distribution of droplet residues were performed.

Changed text on page 7 line 18 ff:

“By reabsorbing the suspension into the pipette, a thin film of suspension is left on the freezing chip. By precooling the chip to approx. 5°C right before applying the suspension, the liquid between the cavities evaporates while the cavities stay filled.”

Comment

5. The size of a single etch pit would allow for tremendous assay dimensions. Taking the pits center-to-center separation distance of 0.1 mm (as estimated from the figure 6), one would be able to create 10.000 etch pits on a 10 by 10 mm chip. I see, however, only 24 25

s in the video frame shown in figure 5 and this is appr. The number of individual data points on the freezing curves. What is the reason for not using more of the cavities? Is that because of the limited field of view of the microscope or difficulties with the freezing detection at lower magnification? Please discuss these issues.

Answer:

The field of view, specified by the parameters of the light microscope, limits the observation of about 25 cavities at a time with a center-to-center distance of 100 μ m.

Changed text on page 6 line 7 ff:

“The field of view, specified by the parameters of the light microscope, enabled the observation of about 25 droplets with a center-to-center distance of 100 μ m for each experiment.”

Comment

6. Provide the value of the cooling rate for all presented experiments. I estimate the cooling rate to be around $\sim 8\text{K/min}$ (from the temperature and time readings of the supplemental video). Such cooling rate can be responsible for up to 1 K difference in T50 (Wright et al. (2013) and Herbert et. al. (2014), Peckhaus (2015)).

Answer:

For all experiments, the cooling rate was set to 2K/min . The supplemental video was intended to be a short systematic example. Therefore the cooling rate was increased to shorten the video. The cooling rate is now provided in the manuscript and the cooling rate for the video is provided as well (see answer to comment 8)

Changed text on page 6 line 24 ff:

“The temperature control was set to a cooling rate of 2K/min for all measurements.”

Comment

7. The claim of automatic detection of the freezing events is not very convincing. Indeed, the liquid and frozen droplets shown in figure 6 are distinctively different. Looking at the video record of the freezing droplets available in the Supplement, I doubt that an automatic routine is capable of capturing the freezing based on the change of brightness, at least not in the given example. If I compare frames 1 and 2 captured from the Supplemental video (see my figure 1 below), the difference in individual droplets is hardly detectable by eye, and yet all of them must have been frozen at this temperature. If I am wrong, please provide in the supplement the “contrast graphs” for each droplet from the supplemental video to convince the reader that the automatic software is indeed capable of capturing the individual freezing times.

Answer:

The contrast graphs and a figure of the droplet numbering were added to the supplements (Fig. S1 and S2), to convince the reader that the automatic software is indeed capable of capturing the individual freezing temperatures. The abrupt increase of contrast (see Fig. S2) indicates the freezing and is identified by the software automatically.

To avoid a misleading impression of the contrast change during the freezing process, the pictures in Figure 6 have been exchanged with pictures of the freezing event in the provided video.

Changed text on page 4 line 1(Supplements):

“Contrast graphs of each droplet in the freezing video provided in supplements.”

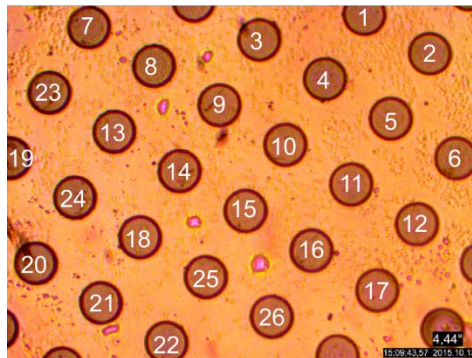


Figure 4 Numbering of the droplets from the provided freezing video in supplements as listed in the contrast graph (see Figure 5).

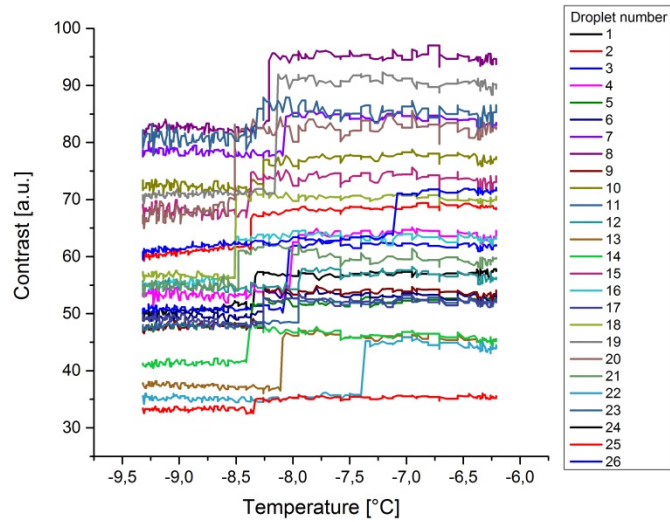


Figure 5 Contrast trend of each frozen droplet as listed in Figure 4 from the provided freezing video in the supplements. Differences in light scattering behaviour of water and ice lead to a contrast increase during the freezing process, which is used to determine the freezing temperature.

Changed text on page 12 line 5 ff:

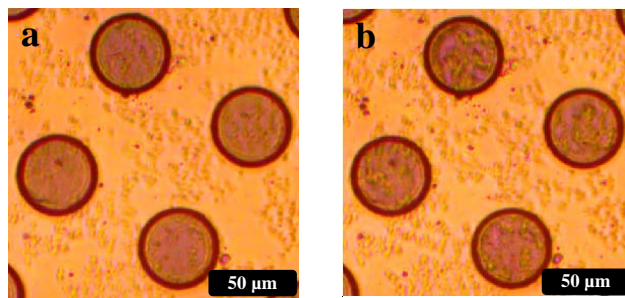


Figure 4 Details of the freezing mask. Comparison of cavities filled with unfrozen and frozen ultrapure water. Differences in light scattering behaviour of water (a) and ice (b) lead to a decreased brightness for ice compared to liquid droplets. This change in brightness is used to determine freezing temperatures (see Supplements for contrast trends).

Comment

8. Such high cooling rate can be responsible for false temperature reading. The frame 3 of my Figure 1 (above) recorded at 0.55°C still shows some structures in the etch pits, which are obviously absent in the frame 4 recorded at 1.84°C, where all droplets are frozen. There must be a time lag in the temperature measurement, caused by thermal inertia of temperature sensor, thermal contact between the sensor and the chip, or response time of the readout electronics. Please check carefully your data.

Answer:

For all experiments, the cooling rate was set to 2K/min and is now provided in the manuscript. The supplemental video is intended to be a short systematic example for demonstration purpose only. Therefore a higher cooling rate was chosen intentionally to provide a shorten video. The cooling rate of ~6K/min and the explicit note “Demonstration video” was added into the video to avoid confusion.

The thawing process is not regulated by the TEC, which can result in heating rates of up to 50K/min. Therefore no statements are done concerning the thawing process since the high rates result in temperature delays and false temperature reading. To avoid confusion, the thawing process was removed from the video.

Changed text in the supplementing video:

“Demonstration video of the freezing chip with Snomax® (concentration 0,5g/l; cooling rate 6K/min)”

Changed text on page 6 line 24 ff:

“The temperature control was set to a cooling rate of 2K/min for all measurements.”

Specific comments:

Comment

1. The authors put such a strong emphasis on not using the oil matrix that it is rather surprising to see some solid inclusions in their own oil layer covering the chip (Supplemental video, particulate movement on the right side of the frame starting from 15:12:07). I suppose these are particles left on the chip surface after spreading the suspension?

Answer:

Residues of INP between the cavities can't be avoided using this preparation technique. They do not affect the measurements and are removed before the next experiment.

Comment

2. What would be the cleaning procedure for the chip between the measurements? How durable is the gold coating?

Answer:

The cleaning process depends on the investigated INP (solubility, hydrophobicity...). After each measurement (e.g. mineral dust), the freezing chip is processed in an acetone/isopropanol (50/50) bath, a toluol and an ultrapure water bath, each for 20 minutes. To confirm the accomplished cleaning process, freezing measurements of ultrapure water were performed before a new sample was put on the chip.

Changed text on page 6 line 16 ff:

“A cleaning process of the chip was applied after each measurement, consisting of a treatment in acetone/isopropanol (50/50), toluol and an ultrapure water solution, each for 20 minutes. Depending on the previous investigated INP, additional steps had to added (e.g. for Snomax[®]: heat treatment at 150°C for one hour).”

Comment

3. Abstract, page 1: “Finally, it opens a temperature window down to -38°C for freezing experiments which was not accessible with many former approaches and allows determination of IN also with weak nucleation activity”. Contrary to your statement, the freezing curves you show occupy a very narrow temperature range (within 2 K, except for Juniper pollen), indicating a very concentrated solution and a high cooling rate. To demonstrate applicability of the instrument for measurements of the INPs with weak nucleation activity you would have to do measurements with diluted samples and present your results in form of INAS surface site densities.

Answer:

We show a temperature window down to about -38°C by measuring ultrapure water at the predicted homogeneous freezing temperature for 40µm water droplets. In this paper we concentrate on INPs also investigated by others. Of course we plan to use the system in later studies to investigate other INPs with possible weak nucleation activity. Furthermore the ice nucleation active surface/mass site densities are now provided in Figure 6 and 8 (see before).

Changed text on page 1 line 26 ff:

“Finally, it opens a temperature window down to -38°C for freezing experiments which was not accessible with many former approaches and will allow the determination of INPs also with weak nucleation activity.”

Comment

4. Page 3, lines 13-14: “INP distribution and surface site location are random events which do not involve time sequences and therefore behave according to the singular model”. I do not understand this statement. Neither distribution of INPs between the droplets nor the distribution of active sites on the total surface of INPs in the droplets are “events”, that is, they are not distributed along the time axis. Anyway, the singular hypothesis is not about that, it is about prescribing certain fixed freezing temperature to each individual active site. By the way, singular hypothesis does not predict cooling rate dependence of median freezing temperature.

Answer:

The statement has been corrected.

Changed text on page 3 line 13 ff:

“The molecular floating of embryos is a stochastic process. The INP distribution in subsamples i.e. samples obtained by dividing aqueous INP suspensions into individual droplets and surface site locations are expected to be random (Vali, 2014).”

Comment

5. Page 3, line 26. Is the reference to Stan et al., 2009, correct here? There is nothing about free-falling droplets in this work. Please check.

Answer:

We agree, Stan et al., 2009 refers to free-fall experiments. However, this section is just an overview over existing measurements and techniques.

Comment

6. Page 4, lines 3 to 9. I count only four main problems with the oil emulsions, a) to d).

Answer:

It has been corrected.

Changed text on page 4 line 11 ff:

“In this procedure four main problems occur:”

Comment

7. Page 6, line 14. Could you provide more information on the microcline used in your study? Any microcline contains a certain amount of Na-rich feldspar, and the microstructure can be very different. Harrison (2016) compared several feldspars and found a tremendous spread of freezing efficiency. Any additional information would be useful, like place of origin, composition, crystal structure (via powder diffractometry) etc. How the grain size has been determined? Have you measured the effective surface, e.g. via BET? Otherwise, comparison with another “microcline” is rather useless.

Answer:

The surface values obtained via BET and the composition obtained via XRD and EDX have been added to the manuscript. Comparisons were done with K-feldspar (Atkinson, 2013) and the same batch of K-feldspar used by Zolles, 2015 (Alfa Aesar, microcline, LOT: H23P37). The description of the grain size has been removed.

Changed text on page 6 line 26 ff:

“Microcline (K-feldspar, KAlSi_3O_8 , 70-80% microcline, rest: albite, LOT: H23P37) is a naturally occurring mineral and was supplied by Alfa Aesar GmbH & Co KG. The mineral was freshly milled with a swing mill (Retsch MM400) for 4 minutes and 30 swings per second immediately before the experiments. The surface area value of $6,6 \text{ m}^2/\text{g}$ was determined using the physical adsorption of gas molecules on solid particles (BET Brunauer-Emmett-Teller technique). Microcline was suspended in ultrapure water (concentration 20 g/L).”

Comment

8. Page 8, lines 16 – 18: “Different milling parameters result in variable surface textures (as e.g. cracks, edges and steps) which play an important role in the INA of microcline. The higher freezing temperature found in our experiment might be due to varied milling parameters.” This is a speculation unless you compare the freezing efficiencies in terms of $n_s(T)$. The difference may result from the fact that this was a different “microcline”.

Answer:

Comparisons were done with the same batch of K-feldspar used by Zolles, 2015 (see above). INAS site density plots are now provided and compared with Atkinson et al., 2013. INAS site density values obtained using the freezing chip is in good agreement with Atkinson et al., 2013 (see Fig. 8). Zolles et al., (2015) didn't provide n_s values, therefore just the T_{50} values can be compared. Since the same batch of K-feldspar, concentration and droplet size range was used we assume that different milling parameters led to the difference in T_{50} values.

Comment

9. Page 8, lines 26-27: “Wex et al. (2015) worked with Snomax® concentrations of about 0,5 g/L (the same as here), but they generated droplets with diameters about 1200µm...” Wex et al., (2015) has derived the $n_m(T)$, a number of ice active entities per mass of dry Snomax, which is the mass-based analogue of $n_s(T)$. In the intercomparison study of Wex et al. (2015) the data of seven different instruments fit perfectly into a very narrow range disregarding all different experimental methods and measurements conditions. Their work is a good example of how the experimental data should be treated and I strongly recommend using their approach to compare your data to experiments of other groups.

Answer:

INA mass surface site densities were added for Snomax and compared with Polen et al., (2016) and Wex et al., (2015) (see Fig. 6) to compare the experimental data properly. Furthermore we changed the description of Snomax (information about the storage and age of Snomax used) according to another reviewer. They are now provided and discussed.

Changed text on page 7 line 9 ff:

“It was stored at -20°C for 3 years before the measurements were performed.”

Changed text of chapters *Results* and *Conclusion*:

See the revised manuscript as uploaded separately as *author comment*.

Comment

10. Page 9, lines 22 -23: “We were able to show the efficiency and accuracy of our setup by comparing the measurements of freezing temperatures of different INPs with already published results (Figure 9).” Again, accuracy cannot be demonstrated by comparing your results with the literature data. Accuracy (or more precisely, “uncertainty”) is a measure of your confidence in the reported results, obtained from the measurements according to certain mathematical rules. This reminds me of the fact that there is no discussion of the measurement uncertainty in the whole manuscript, apart from the error bars that are visible in the figure 9. The values of median freezing temperature, however, are given with a precision of 0.1K (see Conclusion section). This has to be changed.

Answer:

Using the measured T_{50} values of ultrapure water and the homogeneous freezing temperature of 40µm water droplets at -37°C according to Pruppacher and Klett, (1997) as a reference, a standard deviation of the temperature of $\pm 0,5^\circ\text{C}$ was calculated (confidence level of 90%, ten degrees of freedom, t- distribution: 1,812). The evaluation is now mentioned in the manuscript and the uncertainties were corrected.

Changed text on page 5 line 19

“The uncertainty of the temperature was calculated by using the homogeneous freezing temperature of -37°C of water droplets with a diameter of 40µm calculated by Pruppacher and Klett (1997) using the classic nucleation theory, as a reference and comparing it to the obtained $T_{99,9}$ values (temperature where 99,9% of the droplets are frozen) of ultrapure water using the freezing chip. Applying a confidence level of 90%, a standard deviation of the temperature of $\pm 0,5^\circ\text{C}$ was calculated (t- distribution: 1,812).“

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