Answer to reviewer's comments on the manuscript by Thomas Häusler, Lorenz Witek, Laura Felgitsch, Regina Hitzenberger 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 2

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

Comment

1) The authors mentioned that "After the etching process, a gold layer (thickness 500 nm) was sputtered on top of the pattern, leading to an ice nucleation neutral surface. Tests of an uncoated silicon plate indicated that the silicon itself is IN active. A shift of freezing temperatures of ultrapure water from -38◦C to approx. -20◦C was found for droplets on the uncoated plate. (Page 5, Lines 24-26)". If this is true, the authors need to show evidence that the use of "gold surface" instead of "silicon surface" indeed plays a crucial role in improving the quality of their freezing experiments. For example, other studies on similar freezing techniques have prepared droplets on a hydrophobic silicon slide and immersed them in oils, such as squalene (Wright and Petters, 2013; Hader et al., 2014; Polen et al., 2016) and silicon oil (Peckhaus et al., 2016). Since these studies also reported that freezing of pure water droplets is limited at temperatures above the homogeneous freezing temperature, I doubt if the types of substrates (gold or silicon) might not be a key issue when using microliter-sized droplets covered with oils.

Answer:

We found that the untreated silicon plate does not show any ice nucleation activity before the etching process, ultrapure water froze at T_{50}= -37,5°C. After the application of the cavity pattern, 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°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 activity compounds are formed on the surface during the introduction of the cavity pattern. Therefore no further treatments of its surface are necessary.

Comment

2) The authors should provide the information on the numbers of droplets and the cooling rate for each experiment.

Answer:

The cooling rate and the numbers of droplets observed for each experiment are now given in the manuscript.

Changed text on page 6 line 24ff:

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

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 100µm for each experiment.”

Comment

3) As described by the authors, “Homogeneous nucleation depends on the droplet volume (Vali, 1971). (Page 2, Line 32)”. However, the authors compare their freezing experiments with 40 µm pure water droplets with the results of different droplet sizes (= 10-20 µm; Pruppacher and Klett, 1997). In addition, since the authors note that “The freezing spectra (Figure 7) are well comparable to the extended singular model VS66 as described by Vali (2014). (Page 8, Lines 3-4)”, the authors would need to show the values obtained from the extended singular model VS66. Or I would like to suggest to calculate the fice values for 40 µm pure water droplets predicted by the classical nucleation theory (e.g., see Murray et al., 2010; Whale et al., 2015; Tobo, 2016).

Answer:

As this manuscript is a technical note and had to be shortened, we decided to remove comparisons with the VS66 model. The comparison of the freezing temperatures between our own measurements and literature data from Pruppacher and Klett, 1997 is now correctly related to 40µm droplets, provided in Figure 9.

Changed text on page 15 line 1 ff:

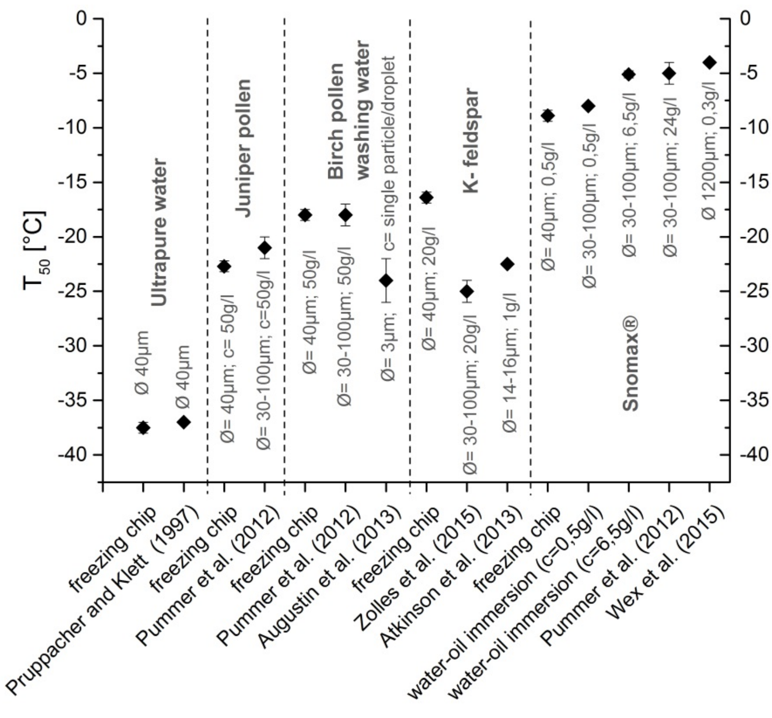

Figure 9 T_{50} values of several INPs compared with already published values. Diameters of the droplets and concentrations at each experiment are given in the figure.

Comment

4) The comparison of the T50 values obtained from droplets with different sizes and mass concentrations is quite problematic. I strongly suggest to calculate the ice nucleation active site density per unit surface area (ns) and/or (nm) to compare the results from this study and the literature data. Or if the authors want to use the T50 values instead of the ns and/or nm values, they should compare the T50 values at the same droplet sizes (volumes) and mass concentrations. Otherwise, it is difficult for the readers to judge whether the cold-stage-based approaches proposed by the authors are valid or not.

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.

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 4 ff:

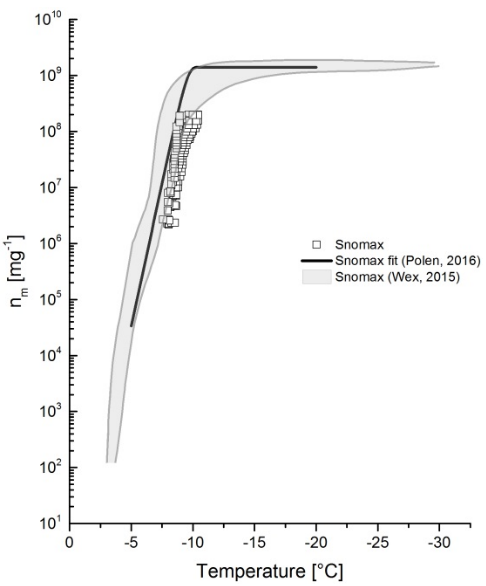

Figure 6 The ice nucleation active mass site density n_m of Snomax® determined with the freezing ship is in consistence with the results published by Wex et al. (2015) and Polen et al. (2016). A shift of the n_m values to lower temperatures due to degradation processes can be observed and is in agreement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

Changed text on page 14 line 6 ff:

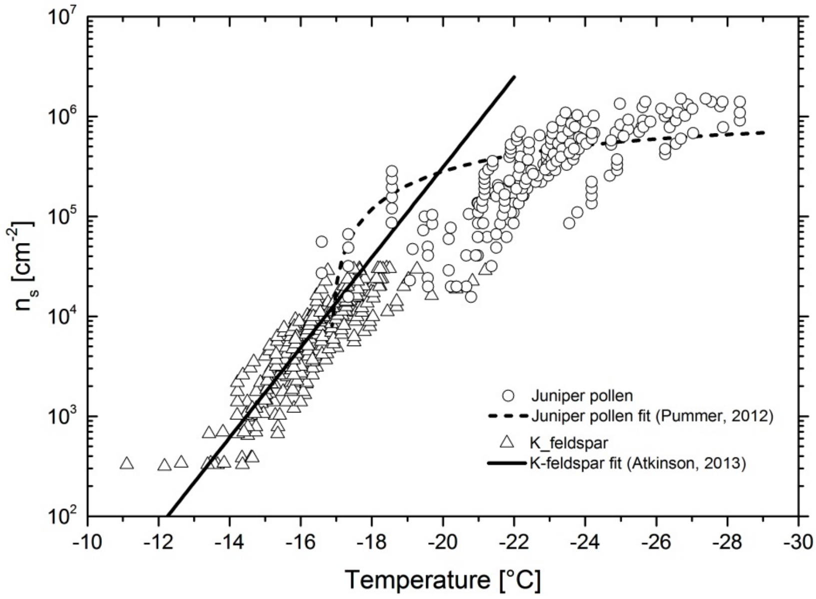

Figure 8 Comparison of ice nucleation surface site densities n_s of measurements done using the freezing chip with already published data. The n_s values of K-feldspar fit well to the published data of Atkinson et al. (2013). Minor deviations of the obtained juniper and birch pollen values compared to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

Comment

5) To discuss the results from Microcline (Page 8, Lines 14-18), the authors would need to compare the results based on the ns and/or nm values (see “General Comment 4”). In addition, the authors should explain the details of the difference of milling processes between this study and Zolles et al. (2015). Otherwise, I don’t know whether “The higher freezing temperature found in our experiment might be due to varied milling parameters. (Page 8, Lines 17-18)”.

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).

INAS site density plots are now provided in Fig. 8 and compared with Atkinson et al., 2013 (see above). INAS site density values obtained using the freezing chip is in good agreement with Atkinson, 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, droplet size range and cooling rate was used we assume that different milling parameters led to the difference in T_{50} values.

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 m^2/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).”

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

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

Comment

6) It is hard to understand whether the discussion on the results from Snomax® (Page 8, Lines 21-29) are reasonable or not. First, the authors would need to compare the results based on the ns and/or nm values (see “General Comment 4”). In addition, the authors would need to provide the detailed information on the conditions of Snomax® samples used here, since recent studies reported that the ice nucleation properties of Snomax® are considerably unstable and can change dramatically depending on their conditions (Polen et al., 2016).

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) in Fig. 6 and 8 to compare the experimental data properly (see above). Furthermore we changed the description of Snomax (information about the storage and age of Snomax) according to reviewer #3. 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*.

Specific comments

Comment

1) In Abstract, the authors need to explain what "the T50 values" mean.

Answer:

The T_{50} value is now explained in the abstract.

Changed text on page 1, line 17 ff:

"To describe the freezing behaviour of INPs, freezing spectra, T_{50}, i.e. the temperature where 50% of the droplets in a sample are frozen), and ice nucleation active surface/mass site density $n_{s/m}$ values are used."

Comment

2) I could not find the descriptions of Figures 1 and 2 in the main text.

Answer:

Figure 1 and 2 have been removed from the manuscript.

Comment

3) Page 2, Line 5: ice nuclei (INPs) => ice nucleating particles (INPs)

Answer: Ice nuclei has been changed to ice nucleating particles.

Changed text on page 2 line 4 ff:

"In all these processes, aerosol particles play a crucial role by acting as cloud condensation nuclei (CCN) for liquid droplets or as ice nucleating particles (INPs) for the formation of ice particles."

Comment

4) Page 2, Line 28: Demott, 1990; Mohler et al., 2006 => DeMott 1990, Möhler et al., 2006

Answer: References has been corrected.

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),…"

Comment

5) The authors need to explain what the "V66 model (Page 3, Lines 7)" is.

Answer: As this manuscript is a technical note and had to be shortened, we decided to remove comparisons with the VS66 model.

Comment

6) As mentioned by the authors, “Whale et al. (2015) have shown that ultrapure water droplets with a diameter of approx. 1 mm are often so strongly contaminated with INPs that the homogeneous freezing temperature is not reached and freezing occurs at around -25◦C heterogeneously (Page 3, Line 27-29)”. On the other hand, recent work reported that despite the use of such large droplet sizes, freezing of pure water droplets placed on a Vaseline layer is limited at temperatures above a homogeneous freezing limit (Tobo, 2016).

Answer: Tobo (2016) is now mentioned in the manuscript. We assume his water to free of any impurities.

Changed text on page 4 line 2 ff:

“Whale et al. (2015) have shown that ultrapure water droplets with a diameter of approx. 1 mm are often so strongly contaminated with INPs that the homogeneous freezing temperature is not reached and freezing occurs at around -25°C heterogeneously. On the other hand Tobo (2016) demonstrates that the CRAFT (Cryogenic Refrigerator Applied to Freezing Test) setup allows the observation.”

Comment

7) Section 4.2: I cannot understand why the title of this section is “Snomax®” since the authors describe the results of freezing experiments with Juniper, Birch pollen, Microcline and Snomax®. The authors should describe only the results from Snomax® and the other results should be presented in different sections appropriately.

Answer: The titles have been revised.

Comment

8) Figure 9: Pruppacher et al. (1997) => Pruppacher and Klett (1997)

Answer: The reference has been corrected.

Comment

9) Figure 9: It is a little difficult to understand the difference between “freezing chip” and “water-oil immersion”, since the freezing chip also uses oil cover (immersion). Is it correct? If so, I would suggest to use a different wording to avoid misunderstanding.

Answer: We decided not to change the wording. On the freezing chip, INPs are suspended in water only, and the chip contains droplets of this aqueous suspension. These droplets are not embedded in the oil. The oil only covers the freezing chip, while in the oil-immersion technique, the droplets with the aqueous suspension of INP are dispersed within the oil matrix.

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