Point-by-point explanation of the changes made to the manuscript in response to the comments received during the open discussion

First of all, we would like to thank both anonymous referees for their valuable comments and suggestions. They were very helpful to us in the revision process and we think they have considerably contributed to a substantially improved, revised manuscript.

For clarity and easy visualization, the referee's comments are shown from here on in black.

> The authors' replies are in blue font with an increased indent below each of the referee's statements. Page and line numbers (in blue) refer to the original manuscript as in the online ACPD version.

>> The authors' comments about the changes made to the original manuscript are stated in green, with a further increased indent.

>> Furthermore, the relevant changed sections from the revised manuscript are copied below in red. Page and line numbers (in red) refer to the revised version of the manuscript (without track changes).

Authors' response to Anonymous Referee #1

Review from Anonymous Referee #1 received and published: 28 August 2018

General comments

The manuscript shows results of cold stage tests from samples taken at Jungfraujoch with the aim of illustrating secondary ice formation at an "individual hydrometeor level". These analyses could yield quantitative estimates of ice crystal enhancement, but the data are too few to make a publication-worthy conclusion in my opinion. The authors note that Hoffer and Braham attempted a similar per-particle analysis more than 50 years ago. Their sample size was 300 snow pellets, 150% that presented here, and they note in their abstract that "a firm statement could not be made as the number of observations is limited." The burden is on the authors to explain why it is sufficient to show ground-based data from only 10 days.

> We thank Anonymous Referee #1 for his/her assessment and valuable suggestions. In a 'short comment' we have already clarified the valid point about the sample size. We will discuss that the number of snow crystals found to have formed through heterogeneous freezing determines how firm a conclusion can be drawn and not the total number of snow crystals analysed and we will add the uncertainty of the multiplication factor during revisions. The uncertainty associated with the observed multiplication factor is about 20% (square root of 24 divided by 24). The detailed answer can be found in the short comment posted on 5th September 2018.

>> We have clarified that Hoffer and Braham (1962) could not make "a firm statement" about the multiplication factor with their sample size of 300 in the introduction by adding the following sentence:

>> However, an ice multiplication factor (i.e. the number of all ice particles divided by the primary ice particles) could not be estimated because the number of primary ice particles was zero. (page 3, lines 14-16)

> In our case the number of primary ice particles was not zero but 24 out of 190. Therefore, we can derive an uncertainty of the primary ice number (√24/24) and estimate a multiplication factor (190/24). We have mentioned the uncertainty associated with our findings regarding the number of primary ice crystals in the result section with:
>
> The uncertainty associated with the number of primary crystals in our observations is about 20% (√24/24). (page 7, lines 14-15)

Thereafter, the introduction needs to be expanded in my opinion. Right now, there is not a thorough discussion of existing literature. Approximate values and measurement techniques for INPs and IRs in mixed-phase clouds should be mentioned, in particular the abundance of measurements from Jungfraujoch (e.g. with the Ice Selective Inlet (Kupiszewski et al. 2015), the Ice Counterflow Virtual Impactor (Mertes et al. 2007), and the Horizontal Ice Nucleation Chamber (Lacher et al. 2017) as discussed in Cziczo et al. Measurements of Ice Nucleating Particles and Ice Residuals).

> We will expand our introduction and refer to the mentioned studies to make clear already in the introduction the novelty of our approach. By sampling small ice particles (few tens of micron in aerodynamic diameter) at Jungfraujoch earlier studies were not able to separate ice which had formed in clouds from aerosolised parts of hoar frost growing on surrounding surfaces (Lloyd et al., 2015; Farrington et al., 2016; Beck et al., 2018). By sampling larger, regular ice particles (e.g. dendrites) we minimised the influence of local surfaces on our results (page 6 line 10-14) and can draw a conclusion regarding secondary ice formation within mixed-phase clouds.
>
> > We have expanded the introduction and mentioned the measurement techniques for INPs and ice residuals which we think are relevant for our study. This was done mainly by adding a new paragraph about ice residuals and the trade-off when selecting small pristine crystals on mountain-top stations. Also, we refer to the studies by Mertes et al. (2007), Kupiszewski et al. (2015), and Cziczo et al. (2017). Please note that we haven't mentioned Lacher et al. (2017) because they have measured INPs at much lower temperatures (~ -30°C) than those at which we have measured INPs.
> >
> > While modelling studies accounting for secondary ice production can to some extent explain the observed ice crystal numbers (e.g. Sullivan et al., 2018b), field measurements have not been conclusive as to the contribution of secondary ice production mechanisms until present days. Kumai (1951, 1961) and Kumai and Francis (1962) found an insoluble particle of 0.5 to 8 µm in size in the centre of almost every one of the about 1000 snow crystals they collected. The particles they found were clay and related minerals and were assumed to have initiated the formation of the crystals. Bigg (1996) suggested to repeat the experiments by Kumai and Francis (1962) and to look at the ice nucleation properties of these particles. One reason why it can be misleading to equate ice residuals with INPs is that MPC-generated ice crystals can contain cloud condensation nuclei (CCN) which have been collected upon riming but have not acted as INPs. One possibility to overcome this issue is to sample ice residuals of freshly formed, small ice crystals (< 20 µm), which are assumed to have grown by the initial phase of vapour diffusional growth only (Mertes et al., 2007; Kupiszewski et al., 2015). On mountain-top stations, where such crystals can be collected in-cloud, however, hoar frost (cloud droplets frozen

onto surfaces) can be a strong source of small (i.e. < 100 µm) ice crystals (Lloyd et al., 2015; Farrington et al., 2016; Beck et al., 2018). Hoar frost grows in saturated conditions, breaks off when windy, and broken-off segments can become ingested into clouds and commonly mistaken for secondary ice (Rogers and Vali, 1987). Residuals in hoar frost particles are CCN that had not been activated as INPs. Only droplets freeze upon contact with an iced surface while ice particles bounce off and remain in the airflow, a principle applied in counterflow virtual impactor inlets used to separate ice from liquid in MPCs (Mertes et al., 2007). Current ice selective inlets are not able to separate primary from secondary ice (Cziczo et al., 2017). (page 2, lines 15-31).

The analyses also need to be fleshed out. A more complete picture of the meteorology could be given by including the range and variability of air temperatures and wind velocities during the sampling periods. If photos of all the crystals were taken with a high-quality camera, some of these should be shown. Is there a more rigorous means of classifying the crystals than what is “considered to be planar, branched”? If the size of the crystals was measured with ImageJ, could some of these statistics also be presented? In Section 2.3, there is also a mention of rime analyses with a second cold plate, but it was not clear to me how this fit in. The results shown in Figures 2 and 3 are from pristine, unrimed dendrites, right?

We will provide the range and variability of air temperatures and wind velocities in a revised version. We are ready to show representative pictures of the crystals that were taken in the main paper or all pictures as supporting information. As mentioned on page 3 line 31, we classified the crystals by habit and riming degree using the ‘global classification scheme’. There are some variations in crystal shape. We considered as planar, branched crystals, crystals that can be classified into the following classes: R1c, R2c, R3a, R4a, P4, P3, P2 according to Kikuchi et al. (2013) (see first paragraph in Section 3; please note that the paper by Kikuchi et al. contains representative images of all the crystal classes mentioned in our paper). Figures 2 and 3 show the results of the 190 crystals. A large fraction of them are ‘rimed dendrites’ or ‘densely rimed dendrites’ (see page 5 line 6). Rime itself was analysed to determine the fraction of analysed crystals that possibly had scavenged through riming an INP active at -17 °C or warmer. This fraction was smaller than 1% (page 6, lines 32-33).

We have extended the methods section in various ways. We have provided the standard deviations of the daily temperatures and wind velocities in Table 1 and the standard deviation of the mean air temperature and wind velocity during the sampling periods.

The mean air temperature at the station during the sampling periods was -11.0 °C (±3.6) and the mean wind velocity was 9.1 m s^{-1} (±3.9). (page 4, lines 9-10)

We have added example images of the analysed dendrites in the supplement (see Fig. S3 in the revised version).

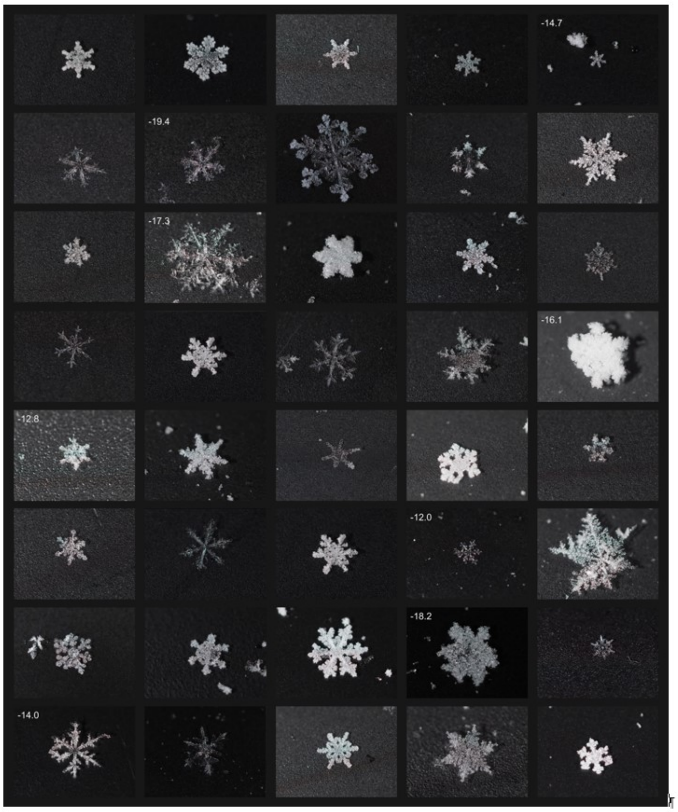

Figure S3. Examples of images of the analysed dendrites taken by macro (1:1) photography. Crystals of which the residues immersed in a water droplet froze above -20 °C have this freezing temperature added in the upper left corner of their image. Each image shows an area of 8.6 mm x 6.4 on the black surface where the crystals had been collected.¶

We have clarified our selection criteria of the analysed crystals in section 2.2.

2.2 Single crystal selection and analysis

We collected snow crystals on a black aluminium plate (40 cm x 40 cm) at about 1 m above the floor of the main terrace of the Sphinx Observatory at Jungfraujoch and analysed the crystals inside a small, naturally cold (-1 °C to -7 °C) anteroom between the terrace and the laboratory. Among a usually wide variety of shapes and sizes precipitating onto the plate we selected what we considered to be single, planar, branched or dendritic ice crystals (from here on “dendrites”), which can safely be assumed to have grown within MPCs at temperatures around -15 °C (Nakaya, 1954; Magono, 1962; Magono and Lee, 1966; Takahashi et al., 1991, Takahashi, 2014; Libbrecht, 2017). Our selection criteria exclude hoar frost particles which might have been generated by local surface sources around the station (Llyod et al., 2015; Farrington et al., 2016; Beck et al., 2018). Rime on selected crystals is of little concern in our approach and was accounted for (see Sect. 2.3).

Selected crystals were documented by macro (1:1) photography (camera: OM-D E-M1 Mark II, pixel width: 3.3 µm; objective: M.Zuiko ED 60mm f2.8; flash: SFT-8; all items from Olympus, Tokyo, Japan) stabilised by a focusing rack (Castel-L, Novoflex, Memmingen, Germany) propped up on the aluminium plate. The size of our crystals was determined by using ImageJ (Rueden, 2017; Schindelin, 2012). Images were later analysed more exactly for the habit, including the degree of riming both categorized according to the latest ice crystal classification scheme, as presented by Kikuchi et al. (2013). The scheme catalogues solid precipitation particles into a total of 121 categories and provides for each category a representative image.

After selecting the crystals, we tested them for the most efficient insoluble INP they contain that can be activated through immersion freezing using a custom-built cold-stage (Fig. 1; more details in supplement). A cold-stage is a drop freezing apparatus, on which droplets are deposited onto a cooling surface and the temperature at which they freeze is observed (Vali, 1971a). This technique is commonly used today to assess the activation temperature of INPs immersed in droplets. Observations have shown that an overwhelming majority of ice particles originate from supercooled liquid clouds at temperatures > -27 °C, which strongly suggests that the initial process of ice formation in MPCs > -27 °C occurs through immersion freezing (Westbrook and Illingworth, 2011). The cold-stage used in this study is meant to be taken into the field, can be set up within minutes and operated without additional infrastructure (i.e. no cooling water or lined power is required). It consists of a gold-plated copper disk with a surface diameter of 18 mm, which is large enough to easily accommodate simultaneously two dendrites and two control droplets (roughly 1 cm apart from each other).

With a fine brush, two crystals are transferred onto the cold-stage surface thinly covered with Vaseline® petroleum jelly (Tobo, 2016; Polen et al., 2018) before being analysed within the next minutes (Fig. 1a). The manual application of Vaseline® requires precision and clean gloves in order to get an as uniform and clean cover as possible. At the transfer of the crystals, the surface of the stage was at a temperature between +1 °C and +5 °C, which is a common temperature range to store INPs in water for several hours before analysis (e.g. Wilson et al., 2015). Upon deposition onto the cold-stage the crystals melted into liquid droplets. To aid visual detection of freezing, we increased the size of the melted crystal droplets by adding 3 µL of ultrapure water (Molecular Biology Reagent, Sigma-Aldrich) with a pipette (using a new tip for each measurement run). The melted crystal containing all residuals and potentially the INP that had triggered its formation, has a rather small volume compared to the added water. For each crystal a control droplet (3 µL) of the same ultrapure water was placed next to the melted crystal droplet and served as control (blank) (Fig. 1b). Then we ramped the temperature of the cold-stage down to -25 °C. Shortly after the cold-stage temperature reached a value below the surrounding air temperature, we covered it with a transparent hood to minimise the chance for contamination from the environment surrounding the droplets and to prevent condensation on the cold-stage (Polen et al., 2018). From -12 °C and below we limited the cooling rate to 3 °C min-1. The freezing of the droplet and thus the presence of the most efficient INP was detected visually, and the corresponding temperature was recorded manually (Fig. 1c). The presence of an INP active at -17 °C and warmer (INP-17) was taken as evidence for the tested dendrite to have been generated through primary ice formation. Nevertheless, extending the drop freeze assay down to -25 °C is useful to determine the fraction of rime associated with single crystals (see Sect. 2.3). After a test was complete, we cleaned the cold-stage carefully with isopropanol. In total, the procedure (i.e. collecting and analysing two samples) takes ~15 minutes. (pages 4-5, lines 12-26)

We formulated more precisely why we have analysed rime samples with a second cold plate in section 2.3.

2.3 Accounting for riming

> A rimed ice crystal has collected liquid cloud droplets, each of them containing a CCN that may cause freezing of the droplet containing the residuals of this crystal. Such a CCN may be activated on the cold-stage as INP (from here on: scavenged INP), although it had not initiated the formation of the collected dendrite. The median concentration of INPs active at -25 °C or warmer (INP_{-25}) was determined for bulk rime samples collected on impactor plates ($conc_{rime}$) and used to estimate the mass of rime associated with a single dendrite (m):
>
> $$m\ [g\ rime\ crystal^{-1}] = \frac{\ln((1-FF_{crystal})^{-1}))}{conc_{rime}}\ [\ INP_{-25}\ crystal^{-1}/INP_{-25}\ \ g^{-1}\ bulk\ rime\ ], \qquad (1)$$
>
> with $FF_{crystal}$: the frozen fraction of INP_{-25} in the analysed dendrites (after subtracting the control).
>
> This step was necessary to estimate the contribution of scavenged INP_{-17} representing false positives of primary ice crystals in our results. They were estimated from the average mass of rime associated with a single dendrite (Eq. 1) and the concentration of INP_{-17} within the independent rime samples as described next.
>
> Independent rime samples were collected with a plexiglass impactor plate (Lacher et al., 2017) suspended on the railing of the terrace at Jungfraujoch for a few to several hours (~1-13h). In total, 30 samples of aggregated rime droplets were collected between 15 February and 11 March. The freezing experiments of the rime samples were done with a drop freezing assay similar to the set up described above which was used for the single crystal analysis. However, rime samples were melted and portioned with a sterile syringe into 2.5 µL droplets and analysed with a drop freezing cold plate following the description in Creamean et al. (2018a). Of each sample 300 droplets were cooled until all droplets were frozen. The cumulative number of INPs active at a certain temperature (with a temperature interval of 0.5 °C) was calculated by taking into account the observed numbers of frozen droplets at a temperature, the total number of droplets and the analysed volume of sample (Vali, 1971b). The main reason for the use of a second cold-stage was to ensure that the custom-build one was always ready for single crystal analysis in case dendrites were precipitating. Other than that, the drop freezing cold plate has a larger surface on which more droplets can be analysed at a time making it more suitable for rime analysis. However, it also requires an external refrigerated circulation bath, lined power and it is relatively large, making it impossible to put it into the anteroom and to analyse single crystals. (pages 5-6, lines 27-19)

With additional data and stronger analysis, more could be gleaned from this study. If the cold plate measurements are subject to any contamination, then 12.6% of the droplets refreezing is actually an overestimation. And a limited crystal geometry has been used to define secondary ice; at -15°C and lower supersaturations, other geometries are possible. So perhaps the multiplication factor of 8 is more of a lower bound. Quantitative estimates of this factor are needed for models, and field measurements at the hydrometeor level, rather than the bulk cloud level, are a new, if labor intensive, technique.

With the same number of control droplets as droplets from crystals we assessed potential contamination. For temperatures at which the analysed crystals had formed (-12 °C to -17 °C) only 0.5% (1 in 190) of the droplets were contaminated. Indeed, at lower supersaturations other crystal geometries are possible at around -15 °C. However, as we were sampling within mixed-phase clouds, we were always within highly supersaturated conditions. We would like to recall that our aim was to find reliable evidence for secondary ice formation at around -15 °C in clouds. For this reason, we had to exclude as rigorously as possible the influence of secondary ice formed and aerosolised from local surfaces (e.g. hoar frost). This requirement called for selecting crystals with a regular shape that forms in clouds and a size large enough to tell they have not grown from splinters emitted locally (see page 6, lines 5-14). We agree that the estimated ice multiplication factor may therefore be a lower bound, a point we will make clear when revising the manuscript.

Our multiplication factor is based on the total number of crystals analysed and the number of ice crystals that froze at -17 °C and warmer (INP_{-17}). At this temperature and above only one of 190 control droplets froze. Furthermore, we have clarified that the number of crystals that froze at -25 °C is not relevant for the multiplication factor at around -15 °C. However, it was useful to determine the fraction of rime associated with single crystals, for which the number of frozen control droplets (at -25 °C) were taken into account (see Eq. 1).

The presence of an INP active at -17 °C and warmer (INP_{-17}) was taken as evidence for the tested dendrite to have been generated through primary ice formation. Nevertheless, extending the drop freeze assay down to -25 °C is useful to determine the fraction of rime associated with single crystals (see Sect. 2.3). (page 5 lines 23-25).

The ice multiplication factor we found is only valid for dendrites. Therefore, we have added the following sentence in the conclusion:

However, we do not know whether the ice multiplication factor we found for dendrites is the same for other crystal habits found in the same MPCs. (page 9, lines 7-8)

Specific comments

Page 1, Lines 18-20: The conclusion that “secondary ice can be observed at temperatures around -15°C” is not an especially compelling one, given that many previous studies have already shown this. Is there a hypothesized mechanism? Or was observed multiplication factor higher under certain conditions?

As far as we know, no previous study has directly observed secondary-produced ice at around -15 °C in natural mixed-phase clouds. What has been reported were large discrepancies between number concentrations of ice crystals and INPs. We could only speculate which mechanisms is responsible for the secondarily produced ice by referring to the papers by Field et al. (2017) and Sullivan et al. (2018), both cited in the manuscript. As shown in Figure 3 the daily fraction of primary crystals was relatively constant and varied around the mean value of the pooled data. When considering the uncertainty of those days where we had at least four primary crystals (black dots), their means are not distinguishable from the pooled data (mean +/- standard deviation of the pooled data).

We have kept the conclusion as it was as we think that this is a new type of evidence for secondary-produce dendrites at around -15 °C. However, the referee's comment has led us to change the title of the manuscript to:

New type of evidence for secondary ice formation at around -15 °C in mixed-phase clouds

Furthermore, we have put more emphasis on the novelty of our study in the abstract.

The novelty of our approach lies in comparing the growth temperature encoded in the habit (shape) of an individual crystal with the activation temperature of the most efficient INP contained within the same crystal to tell whether it may be the result of primary ice formation. (page 1, lines 14-16)

We have added a sentence in the conclusion section to clarify that based on our results we do not know which mechanisms were responsible for the secondary ice production.

No conclusion regarding the process of secondary ice formation can be drawn from our observation. (page 9, lines 8-9)

Page 1, Line 23 – "These freezing pathways" as there can be contact or deposition or immersion freezing.

Correct, thank you.

The sentence has been changed to:

In mixed-phase clouds (MPCs), heterogeneous freezing is expected to generate ice crystals, but also secondary ice production mechanisms can enhance the ice crystal number concentration (Cantrell and Heymsfield, 2005). (page 1, lines 25-27)

Page 1, Line 26 – A few additional, more recent observations might be cited. For example, Lasher-Trapp et al. JAS [2016], Ladino et al. GRL [2017], and Jackson et al. ACPD [2018].

We will add them.

We have added them see page 2, line 3 and page 3, line 1 in the revised manuscript.

Page 2, Line 19 – For completeness, you could mention the correction of such shattering artifacts in more recent data by inter-arrival time algorithms and K-tip probes.

Thank you for mentioning; we will do that.

Not applicable anymore. The related sentence fell victim to the substantial revision of the manuscript.

Page 2, Line 22 – I would define rime when you first discuss rime splintering above in Lines 4-5.

O.k., we will define rime there.

We have done so.

For example, secondary ice crystals can result from rime splinters that are released upon riming (i.e. supercooled cloud droplets that freeze upon contact with a solid hydrometeor) of ice crystals at temperatures between -3 °C and -8 °C (Hallett and Mossop, 1974; Jackson et al., 2018). (page 2, lines 1-3)

Section 2.2 and Figure 2 – The authors have taken a number of concerns about cold-stage measurements into consideration with their setup, which I appreciate. I would cite Tobo 2016 for the use of a semi-sold, hydrophobic substrate, and you might mention the possibility that INP settle out or aggregate within your large-volume droplet [e.g., Emerstic et al. 2015 ACP]. I am still concerned, however, that 20% of the control droplets have frozen by -25°C, almost 10°C above the threshold temperature for homogeneous freezing. Could the estimated enhancement factor be adjusted to account for these "false positives"?

The estimated enhancement factor relates to the temperature window in which the collected ice crystals were likely to have formed (-12 °C to -17 °C). In this temperature window we had only one false positive in 190 tested controls. The number of droplets frozen by -25 °C only plays a role when estimating the average mass of rime associated with a single crystal. In this estimate we have accounted for the false positives (subtracted frozen controls from frozen droplets; please see page 6, line 27).

We have cited Tobo (2016) and Polen et al. (2018) regarding the cover of petroleum jelly.

With a fine brush, two crystals are transferred onto the cold-stage surface thinly covered with Vaseline® petroleum jelly (Tobo, 2016; Polen et al., 2018) before being analysed within the next minutes (Fig. 1a). (page 5 lines 9-10)

That 20% of the control droplets are frozen at -25 °C is not unusual for drop freezing assay. It is rather low compared to the results obtained by Polen et al. 2018.

A frozen fraction of 21% of the control droplets at -25 °C is a rather low fraction compared to the results with pure water droplets (1 µL) on a Vaseline-coated substrate presented recently by Polen et al. (2018). (page 7, lines 7-9)

Page 4, Line 1 – I would add a sentence that summarizes what this 'global classification scheme' is because it is not so widely used, as far as I know.

We will add a sentence that summarizes the global classification scheme.

We have added a sentence.

Images were later analysed more exactly for the habit, including the degree of riming both categorized according to the latest ice crystal classification scheme, as presented by Kikuchi et al. (2013). The scheme catalogues solid precipitation particles into a total of 121 categories and provides for each category a representative image. (page 4 lines 25-29)

Page 4, Line 27 – Is there a reason that the "custom-built cold stage" used for single crystal analysis was not also used for the rime?

Unlike traditional cold plate systems, the custom-built cold stage is mainly made to be easily field transportable to remote locations. It was however not used for the rime samples as it has a rather small surface (surface diameter of 18 mm, page 4 line 5). Analysing rime with it would have led to less measurement time for the single crystals. Our goal was to get as much measurement time for the single crystals as possible. This requires a cold stage which is ready to be used when the specific type of crystals precipitate. The second cold stage i.e. the NOAA Drop Freezing Cold Plate has a larger surface, therefore more droplets can be placed on it, which is convenient for the rime analysis. Please note that the NOAA Drop Freezing Cold Plate requires an external refrigerated circulation bath, lined power and is relatively large. We could not put it into the anteroom and analyse single crystals. We used the most suited cold stage type available for each sample type. We will add the reason why we used two different cold plate systems in the revised manuscript and discuss whether the results of both plates are comparable.

We have listed the reasons why the custom-build cold stage was not also used for the rime in the section 2.3. Please note that the naming “NOAA Drop Freezing Cold Plate” has been changed to simply “drop freezing cold plate”.

The main reason for the use of a second cold-stage was to ensure that the custom-build one was always ready for single crystal analysis in case dendrites were precipitating. Other than that, the drop freezing cold plate has a larger surface on which more droplets can be analysed at a time making it more suitable for rime analysis. However, it also requires an external refrigerated circulation bath, lined power and it is relatively large, making it impossible to put it into the anteroom and to analyse single crystals. (page 6, lines 15-19)

Page 4, Lines 28-29 – I am not sure what is meant by “droplets of molten rime”. You are melting the aggregation of frozen droplets and then refreezing them upon a cold plate? Or somehow separating the droplets within a single aggregate? Please clarify here.

Indeed, we are melting the aggregation of the frozen rime droplets and then refreezing them. We will clarify this in a revised manuscript.

We have rephrased this part.

However, rime samples were melted and portioned with a sterile syringe into 2.5 µL droplets and analysed with a drop freezing cold plate following the description in Creamean et al. (2018a). (page 6, lines 10-12)

Page 5, Lines 19-21 – Measurement uncertainty and / or variability for this estimate needs to be included.

Measurement uncertainty will be included on page 5, lines 19-21.

We have included the uncertainty.

The uncertainty associated with the number of primary crystals in our observations is about 20% (√24/24). (page 7, lines 14-15)

Page 5, Line 32-Page 6, Line 1 – The mention of INP from soils does not seem particularly relevant to me, as those will not be the INP source at Jungfraujoch.

This sentence presents one of three examples from the literature that illustrate the ice nucleation temperature stability during repeated melting and freezing and therefore we think that it is worthwhile to mention it. Besides that, we think that aerosolised soil particles, or soil dust, potentially emitted from fields in northern Italy, southern France, southern Germany, and the Swiss Plateau might make a relevant contribution to INPs active at relatively high temperatures (i.e. > -17 °C) at Jungfraujoch. Note that the most prominent particle classes (reflecting particles in the size range between 0.5 um and 5 um) determined at Jungfraujoch were carbonaceous particles (Hinz et al., 2005). Furthermore, most of the fields within the fetch of Jungfraujoch are not covered by snow during winter and wind blown dust emissions are relatively high during that season in Europe (Korcz et al., 2009).

We think that it is still worth mentioning it because of the above mentioned reasons and therefore we kept it.

Page 6, Lines 5-14 – Blowing snow is a very important consideration here, given several existing studies on this mechanism at Jungfraujoch. You are considering pristine dendrites here, right? Otherwise, there is the potential for riming growth, not just depositional growth.

We are considering planar, branched crystals including rimed crystals. This is the reason why we have also analysed the INP spectra of rime itself. Our results show that less than 1% of the analysed crystals may have scavenged an INP active at a similar temperature as the INP which might have catalysed the formation of a dendrite (page 6 lines 23-34).

We have emphasized which crystals we have selected in section 2.2.

Among a usually wide variety of shapes and sizes precipitating onto the plate we selected what we considered to be single, planar, branched or dendritic ice crystals (from here on "dendrites"), which can safely be assumed to have grown within MPCs at temperatures around -15 °C (Nakaya, 1954; Magono, 1962; Magono and Lee, 1966; Takahashi et al., 1991, Takahashi, 2014; Libbrecht, 2017). Our selection criteria exclude hoar frost particles which might have been generated by local surface sources around the station (Llyod et al., 2015; Farrington et al., 2016; Beck et al., 2018). Rime on selected crystals is of little concern in our approach and was accounted for (see Sect. 2.3). (page 4, lines 15-20)

As they were not necessarily pristine, we have accounted for riming as described in section 2.3.

A rimed ice crystal has collected liquid cloud droplets, each of them containing a CCN that may cause freezing of the droplet containing the residuals of this crystal. Such a CCN may be activated on the cold-stage as INP (from here on: scavenged INP), although it had not initiated the formation of the collected dendrite. The median concentration of INPs active at -25 °C or warmer (INP-25) was determined for bulk rime samples collected on impactor plates (concrime) and used to estimate the mass of rime associated with a single dendrite (m): (see Eq.1). This step was necessary to estimate the contribution of scavenged INP$_{-17}$ representing false positives of primary ice crystals in our results. (pages 5-6, lines 28-4)

Table 1 – For periods that last as much as 14 hours, it would be more rigorous to give mean and standard deviation for values like air temperature / wind velocity since a single value will not be characteristic. Are there are any vertical wind measurements?

O.k., we will add standard deviations for air temperature and wind velocity. No vertical wind measurements were taken though.

We have added the standard deviations for air temperature and wind velocity (see Table 1.)

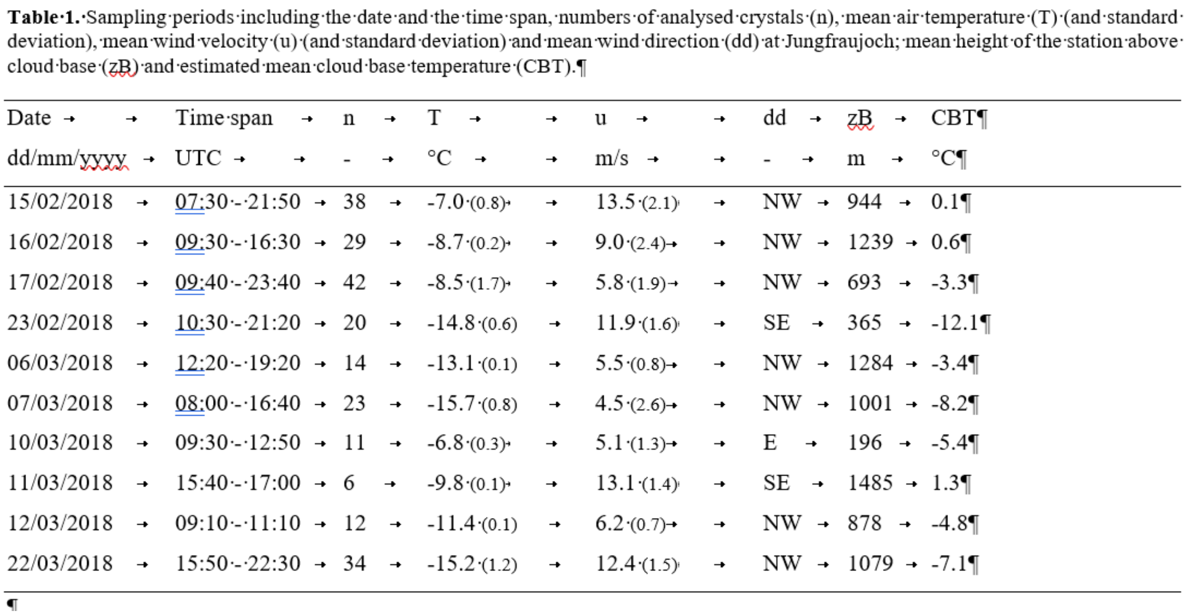

Table 1. Sampling periods including the date and the time span, numbers of analysed crystals (n), mean air temperature (T) (and standard deviation), mean wind velocity (u) (and standard deviation) and mean wind direction (dd) at Jungfraujoch; mean height of the station above cloud base (zB) and estimated mean cloud base temperature (CBT).

Date dd/mm/yyyy	Time span UTC	n -	T °C	u m/s	dd -	zB m	CBT °C
15/02/2018	07:30 - 21:50	38	-7.0 (0.8)	13.5 (2.1)	NW	944	0.1
16/02/2018	09:30 - 16:30	29	-8.7 (0.2)	9.0 (2.4)	NW	1239	0.6
17/02/2018	09:40 - 23:40	42	-8.5 (1.7)	5.8 (1.9)	NW	693	-3.3
23/02/2018	10:30 - 21:20	20	-14.8 (0.6)	11.9 (1.6)	SE	365	-12.1
06/03/2018	12:20 - 19:20	14	-13.1 (0.1)	5.5 (0.8)	NW	1284	-3.4
07/03/2018	08:00 - 16:40	23	-15.7 (0.8)	4.5 (2.6)	NW	1001	-8.2
10/03/2018	09:30 - 12:50	11	-6.8 (0.3)	5.1 (1.3)	E	196	-5.4
11/03/2018	15:40 - 17:00	6	-9.8 (0.1)	13.1 (1.4)	SE	1485	1.3
12/03/2018	09:10 - 11:10	12	-11.4 (0.1)	6.2 (0.7)	NW	878	-4.8
22/03/2018	15:50 - 22:30	34	-15.2 (1.2)	12.4 (1.5)	NW	1079	-7.1

Authors' response to interactive comment from Anonymous Referee #1

Interactive comment received and published: 10 September

Thanks very much for your response concerning the uncertainty in the ice multiplication factor estimate given your sample. My concern is more related to the uncertainty in the representativeness of your sample for the population. Assuming that "the population" here is ice in a mixed-phase cloud, then you can estimate the population size ..say conservatively that the cloud is 2 km deep and has an equivalent radius of 3 km, then it already has a volume on the order of 10ˆ10 cubic meters. Even if the ice crystal concentration in the cloud is only a crystal per cubic meter, you have sampled a very small portion of the population for which you are making a conclusion. This is how I am thinking, but I understand that there are all sorts of subtleties related to representativeness and that your collection process is laborious, so let us see what other reviewers say.

The number of crystals we have sampled and analysed is indeed a very small fraction of all crystals in all clouds that have passed Jungfraujoch between 15 February and 22 March 2018. If we had sampled the crystals from a small fraction of a cloud volume and would extrapolate our findings to a much larger volume in which primary and secondary crystals are very heterogeneously distributed, we would face a problem. However, we have sampled crystals on 10 days in different clouds spread over a period of 36 calendar days. To estimate the total path of clouds crossing Jungfraujoch during our sampling events, we can multiply the sampling duration of an event with the mean wind speed (values in Table 1). By doing so and taking the sum of all the sampling events, we get a total path of 2368 km within clouds along which we have taken our samples. We think that this is a representative distance of cloud passage and thus a representative sample for this year's winter clouds at Jungfraujoch. Figure 2 shows that the ice multiplication factor for individual days is similar to the mean of the pooled data, considering the larger uncertainty of daily estimates as compared to the estimate for the whole period. Hence, the average of the period is not subject to bias of a single day with substantially different multiplication factor from the rest of the days.

We have mentioned that we have taken samples from a long pathlength within different clouds.

They had been collected from a pathlength of 2368 km through a large number of MPCs from different wind directions (sum of sampling duration multiplied by average wind speed; see Table 1). (page 6, lines 25-26)

Authors' response to Anonymous Referee #2

Review received and published: 11 September 2018

Authors present the experimental work where they collected the snow crystals, melted the crystals and visually observed the freezing of the crystal droplet. These results were used to understand more about the secondary ice formation and ice multiplication factors. These questions are challenging, and the community needs an understanding of these cloud processes for better representation in the cloud model. However, this study lacks appropriate experimental technique/methodology to answer these questions, and for this reason, the paper is not ready for the publication. I'm not sure if the major review could improve the paper further as substantial experimental work is involved. There are a number of issues in the present experimental study.

We thank Anonymous Referee #2 for openly sharing his/her ideas on our recent manuscript. We agree that the questions about secondary ice formation and multiplication factors are challenging and that the community needs to answer them to improve cloud parametrizations in models. There are different approaches to answer these questions. The work presented here addresses them by applying an unconventional, new method. The study combines the growth temperature encoded in the habit of snow crystals with a drop freezing assay and thus complements previous observations of secondary ice formation. Our experimental technique is appropriate for detecting insoluble ice nucleation particles (INPs) in single crystals and enables us to estimate with an uncertainty of about 20% the lower bound of the ice multiplication factor in clouds during our sampling campaign at Jungfraujoch. Herewith, we would like to dispel the referee's doubts and elucidate how we will make use of the referee's comments in a revised version of the manuscript. Furthermore, we are confident that our manuscript constitutes a valuable contribution to ACP and we appreciate the opportunity to openly stand up for and constructively discuss our work.

We have clarified in the revised version of the manuscript how we addressed the quantification of secondary ice in MPCs by applying a new and appropriate experimental methodology. The changes made with regard to the general comment above are too numerous to list here at once. They are indicated in the more detailed sections below.

Section1

If no INP was observed within the crystal, it does not mean that crystal was formed through secondary ice formation mechanism. It is possible that a INP may have induced nucleation of ice, and still while INP is floating within the atmosphere may have detached from the ice crystal because the crystal evaporated or through some turbulent process. Now, this crystal when sampled had no INP.

We are not aware of any literature describing the mechanisms to which this statement could refer to. Does Anonymous Referee #2 have supportive evidence for ice crystals losing their INP through evaporation, sublimation, or through "some turbulent process" in the atmosphere that are resulting in ice particles without INP?

In the atmosphere, ice nucleation has been observed at temperatures warmer than that of homogeneous freezing (Ansmann et al., 2005). Four main pathways of heterogeneous freezing have been identified: contact, deposition, condensation, and immersion freezing (Pruppacher and Klett, 1997). In our study, we investigated freezing through the immersion freezing mechanism. Immersion freezing refers to the initiation of ice nucleation by a solid and insoluble INP immersed in a water droplet. To our understanding, the immersed INP will catalyse an initial crystal, in which the INP is embedded. This initial crystal then grows through vapour deposition. In this process, the INP in the initial crystal will increasingly become encased in ice that grows thicker around it. If this crystal then begins to sublimate, the ice covering the initial droplet surrounding the INP will become thinner again, which we expect to evolve rather uniformly from the outside (i.e. edge of the crystal) towards the inside (i.e. initial droplet that froze by immersion). The INP will be released from the ice only once the ice of the very initial frozen droplet has sublimated, resulting in an INP without ice, but not in ice without an INP.

Besides that, we are also not aware of observations that show how “some turbulent processes” may detach the INP from a crystal. How should the INP get out of the crystal structure? Is there at all relevant turbulent friction at the submillimetre-scale in the free atmosphere? We would however be happy to discuss such mechanisms in our manuscript if they have a theoretical or observational basis.

As already mentioned in our published reply above, we are not aware of any literature describing the mechanisms to which this statement could refer to and therefore we were not able to change the revised manuscript accordingly.

Section 2

It is also possible that INP is present, but was deactivated while it went transformation (change in physical and chemical properties) during sampling, heating or droplet preparation. There are numerous studies in the literature that discusses the deactivation of INP. Such discussion is missing.

Indeed, studies exist that discuss the deactivation of INP during transformation. In our experiment, the crystals were sampled below melting temperatures, and melted or “heated” to between +1 °C and +5 °C (page 4, line 12) before being analysed within the next minutes. It is not unusual to store INPs in water at +4 °C for several hours before analysis (e.g. Wilson et al., 2015). Studies reporting deactivation through heating typically refer to heating temperatures close to the boiling point of water (e.g. Christner et al., 2008).

There is also convincing evidence in the literature that INPs, which are active at temperatures relevant for our study, can be repeatedly activated, going through multiple cycles of freezing and melting. We have discussed and referred to these studies on page 5 line 30 to page 6 line 3. Furthermore, we have clearly formulated that our findings are based on the assumption that the cited evidence also applies to our samples, see page 5 line 23.

Several laboratory studies have investigated the role of coating of mineral dust particles and the related changes in ice nucleation efficiency (e.g. Knopf and Koop 2006, Cziczo et al., 2009; Kanji et al., 2018). Soluble coating or soluble INPs could be altered through melting or droplet preparation. However, the work presented here is not investigating the effect of soluble coating and neither of soluble INPs. Soluble INPs probably do not play a role at temperatures warmer than about -27 °C (Knopf et al., 2018, see their Fig. 5). Based on the referee’s comment, we will emphasize in a revised version, that we are focusing on insoluble INPs in dendrites that can be activated through immersion freezing at temperatures above -17 °C for at least two freezing cycles (one when forming the crystal and one when doing the measurement).

We have clarified that we have only tested the crystals on insoluble INPs through immersion freezing.

After selecting the crystals, we tested them for the most efficient insoluble INP they contain that can be activated through immersion freezing using a custom-built cold-stage (Fig. 1; more details in supplement). (page 4, lines 30-31)

Furthermore, we have added a note that the temperature at which we have melted the samples is a common temperature at which samples can be stored for a few hours before for INP analysis

At the transfer of the crystals, the surface of the stage was at a temperature between +1 °C and +5 °C, which is a common temperature range to store INPs in water for several hours before analysis (e.g. Wilson et al., 2015). (page 5, lines 11-13)

Also, we have added in the conclusion that our findings are based on a number of assumptions in the conclusion section, which were discussed before.

The habit of a planar, branched ice crystal, growing exclusively around -15 °C, enables the verification of whether it derived from primary or secondary ice formation based on a number of reasonable assumptions. (page 9, lines 2-3)

Section 3

Experiments are needed that investigate the ice nucleation efficiency of crystal melted droplets up to -37 degC (below this temperature homogeneous freezing is the dominant mode of ice nucleation) to understand more about the insoluble INPs, but for soluble INPs experiments should be investigated at homogeneous freezing temperatures too. Without such results, the conclusions regarding secondary ice formation cannot be inferred.

Heterogeneous freezing at temperatures below -25 °C and homogenous freezing at even colder temperatures are certainly important topics of research, especially when investigating cold mixed-phase clouds or cirrus clouds. Observations have shown that an overwhelming majority of ice particles originate from supercooled liquid clouds at temperatures > -27 °C, which strongly suggests that the initial process of ice formation in mixed-phase clouds > -27 °C occurs through immersion freezing (Westbrook and Illingworth, 2011). Therefore, we assume that homogeneous freezing does not play an important role in mixed-phase clouds surrounding Jungfraujoch during our campaign where temperatures were clearly higher (see Table 1). Further, every experimental study has a limited parameter space. We set the frame for our study in the second part of the introduction. Briefly, our objective was to detect the presence of INPs active at around -15 °C in dendrites, which typically grow around that temperature. By investigating ice nucleation down to -25 °C we already expanded our measurements well beyond the necessary to answer the question to what proportion dendrites are the result of primary ice formation.

We have clarified why immersion freezing experiments down to -25°C are a suitable way to address the question addressed in the presented study (ice multiplication at around -15 °C). In addition to the two short paragraphs below, please also see the substantially revised Sect. 2.3 in the new manuscript.

Observations have shown that an overwhelming majority of ice particles originate from supercooled liquid clouds at temperatures > -27 °C, which strongly suggests that the initial process of ice formation in MPCs > -27 °C occurs through immersion freezing (Westbrook and Illingworth, 2011). (page 5, lines 2-4)

The presence of an INP active at -17 °C and warmer (INP_{-17}) was taken as evidence for the tested dendrite to have been generated through primary ice formation. Nevertheless, extending the drop freeze assay down to -25 °C is useful to determine the fraction of rime associated with single crystals (see Sect. 2.3). (page 5, lines 23-25)

Section 4

Supporting experiments are needed to say why there was no INPs present (page 5 line 14). It would be just that the limitation of the experimental setup. In this study, the sample collection onto the cold stage is not done in clean air conditions. It is possible that crystals were contaminated with room air particles. Further, it is possible that these particles may have induced nucleation of ice but not the primary INP (the first INP that was responsible for freezing the droplet in the atmosphere before sampling). Without knowing the composition of residue it is difficult to infer which INP (primary or room air particulates) was responsible for freezing.

Indeed, it is very important in a first step to avoid contamination as much as possible and in a second step to quantify it. We examined contamination with control droplets of molecular grade water (blanks). If contamination, including deposition of INP from the room air would have been a problem, we would have seen it in the freezing of control droplets. As shown in Fig. 2 and discussed in the text, of 190 control droplets only one froze within the temperature range where the analysed crystals may have formed (-12 °C to -17 °C). Deposition of “room air-INPs” is only one out of several possible reasons why this control droplet may have frozen. Another reason could have been surface contamination of the cold stage. Please note that the control droplets were exposed to the same room air during the same time as were our sample. Thus, even without knowing the composition of residue, we can show, with the results of the control droplets, that INPs deposited from room can not have been responsible for the freezing of the crystal droplets.

It is not a limitation of our experimental setup that no INP active around -15 °C was found in a large proportion of the analysed dendrites. A possible explanation for the absence of INPs are crystals formed through secondary ice formation processes. Our results are consistent with findings and conclusions from other studies (page 1 line 26). Several studies measured much lower INP concentrations than ice crystal number concentrations in clouds by using different approaches and measurement techniques from ours.

We have added a section in the introduction clarifying why the composition of ice residuals will not help us to answer our question.

One reason why it can be misleading to equate ice residuals with INPs is that MPC-generated ice crystals can contain cloud condensation nuclei (CCN) which have been collected upon riming but have not acted as INPs. One possibility to overcome this issue is to sample ice residuals of freshly formed, small ice crystals (< 20 µm), which are assumed to have grown by the initial phase of vapour diffusional growth only (Mertes et al., 2007; Kupiszewski et al., 2015). On mountain-top stations, where such crystals can be collected in-cloud, however, hoar frost (cloud droplets frozen onto surfaces) can be a strong source of small (i.e. < 100 µm) ice crystals (Lloyd et al., 2015; Farrington et al., 2016; Beck et al., 2018). Hoar frost grows in saturated conditions, breaks off when windy, and broken-off segments can become ingested into clouds and commonly mistaken for secondary ice (Rogers and Vali, 1987). Residuals in hoar frost particles are CCN that had not been activated as INPs. Only droplets freeze upon contact with an iced surface while ice particles bounce off and remain in the airflow, a principle applied in counterflow virtual impactor inlets used to separate ice from liquid in MPCs (Mertes et al., 2007). Current ice selective inlets are not able to separate primary from secondary ice (Cziczo et al., 2017). (page 2, lines 20-31)

We have accounted for false positive through riming as described in section 2.3.

A rimed ice crystal has collected liquid cloud droplets, each of them containing a CCN that may cause freezing of the droplet containing the residuals of this crystal. Such a CCN may be activated on the cold-stage as INP (from here on: scavenged INP), although it had not initiated the formation of the collected dendrite. The median concentration of INPs active at -25 °C or warmer (INP_{-25}) was determined for bulk rime samples collected on impactor plates ($conc_{rime}$) and used to estimate the mass of rime associated with a single dendrite (m): (see Eq.1). This step was necessary to estimate the contribution of scavenged INP_{-17} representing false positives of primary ice crystals in our results. (pages 5-6, lines 28-4)

Also, we have changed the following sentence to more precisely state how we avoided contamination.

Shortly after the cold-stage temperature reached a value below the surrounding air temperature, we covered it with a transparent hood to minimise the chance for contamination from the environment surrounding the droplets and to prevent condensation on the cold-stage (Polen et al., 2018). (page 5, lines 18-21)

Furthermore, we have added supporting literature which found larger ice crystals number concentrations than INP number concentration:

Most such studies report large discrepancies between measured INPs and ice crystal numbers (e.g. Hobbs and Rangno, 1985; Lasher-Trapp et al., 2016; Ladino et al., 2017; Beck et al., 2018) the latter being several orders of magnitudes higher than the former. (page 2-3, lines 34-2)

Section 5

It is not clear how section 2.3 supports the secondary ice formation analysis. Details such as validation and performance calibration of the cold stage (shown in Fig 1) under different temperature and humidity conditions are missing.

The majority of analysed crystals were rimed. Rime could have added INPs active at around -15 °C to initial crystals (page 2 line 23-24). Therefore, we analysed not only (rimed) crystals but also rime itself (method in section 2.3). Our results show that riming had only a very minor influence on our results (page 6 line 23-34).

The cold stage was used to test for INPs in immersion freezing mode. Details of the cold stage as well as calibration can be found in the supplement, including the result of tests at a range of temperatures. We are not sure why we should perform validation and calibration at different humidity conditions. These would play a role only, if we would study deposition or condensation freezing.

We have extended section 2.3 in order to clarify why the collection and analysis of rime samples was necessary and how it supports our study.

2.3 Accounting for riming

A rimed ice crystal has collected liquid cloud droplets, each of them containing a CCN that may cause freezing of the droplet containing the residuals of this crystal. Such a CCN may be activated on the cold-stage as INP (from here on: scavenged INP), although it had not initiated the formation of the collected dendrite. The median concentration of INPs active at -25 °C or warmer (INP_{-25}) was determined for bulk rime samples collected on impactor plates ($conc_{rime}$) and used to estimate the mass of rime associated with a single dendrite (*m*):

$$m\ [g\ rime\ crystal^{-1}] = \frac{\ln\left(\left(1-FF_{crystal}\right)^{-1}\right)}{conc_{rime}}\ [\ INP_{-25}\ crystal^{-1}/INP_{-25}\ \ g^{-1}\ bulk\ rime\ ], \qquad (1)$$

with $FF_{crystal}$: the frozen fraction of INP_{-25} in the analysed dendrites (after subtracting the control).

This step was necessary to estimate the contribution of scavenged INP_{-17} representing false positives of primary ice crystals in our results. They were estimated from the average mass of rime associated with a single dendrite (Eq. 1) and the concentration of INP_{-17} within the independent rime samples as described next.

Independent rime samples were collected with a plexiglass impactor plate (Lacher et al., 2017) suspended on the railing of the terrace at Jungfraujoch for a few to several hours (~1-13h). In total, 30 samples of aggregated rime droplets were collected between 15 February and 11 March. The freezing experiments of the rime samples were done with a drop freezing assay similar to the set up described above which was used for the single crystal analysis. However, rime samples were melted and portioned with a sterile syringe into 2.5 µL droplets and analysed with a drop freezing cold plate following the description in Creamean et al. (2018a). Of each sample 300 droplets were cooled until all droplets were frozen. The cumulative number of INPs active at a certain temperature (with a temperature interval of 0.5 °C) was calculated by taking into account the observed numbers of frozen droplets at a temperature, the total number of droplets and the analysed volume of sample (Vali, 1971b). The main reason for the use of a second cold-stage was to ensure that the custom-build one was always ready for single crystal analysis in case dendrites were precipitating. Other than that, the drop freezing cold plate has a larger surface on which more droplets can be analysed at a time making it more suitable for rime analysis. However, it also requires an external refrigerated circulation bath, lined power and it is relatively large, making it impossible to put it into the anteroom and to analyse single crystals. (pages 5-6, lines 27-19)

Section 6

Any results from previous studies who had attempted to study secondary ice formation should be shown in Figure 2 and 3.

It would make sense to compare our results with previous studies. However, the results of previous studies are based on completely different approaches. Their results are not directly comparable to ours. One of the main differences is that we have analysed relatively large snow crystals (several millimetres in diameter) to make sure our results are not influenced by local surface sources of secondary ice formation. We will discuss differences regarding results and methodology between previous studies and this study in more detail in a revised version of our manuscript.

We clarified the difference between our and previous studies mainly in the introduction and in the methods section.

Section 7

Discussion regarding nature of INP is missing. What are their composition and size? One should use Ice-CVI (Mertes et al 2007) to sample only ice crystals, sublimate/evaporate these crystals, count the residues and investigate the ice nucleation propensity of a single residue. By comparing inlet ice crystal and residue concentrations one can infer some understanding regarding secondary ice formation.

Mertes et al. (2007) sampled very small ice particles, between 5 and 20 micron (aerodynamic diameter). Lloyd et al. (2015) concluded for Jungfraujoch that “hoar frost crystals generated at the cloud enveloped snow surface could be the most important source of cloud ice concentrations.” The same may apply to other mountain stations (Beck et al., 2018). Therefore, repeating the experiments of Mertes et al. (2007) would tell us mainly about ice residues in hoar frost particles generated by local surfaces. This is not what we are interested in. We would like to know more about secondary ice formation in mixed-phase clouds themselves. This is the reason why we have sampled larger crystals with a regular shape that are unlikely to have resulted from surface processes and tested these crystals for the presence of INPs active within the temperature range they typically form.

We could not use an Ice-CVI to determine the multiplication factor, because such an inlet is not able to separate primary from secondary ice. We have clarified this in a new paragraph in the introduction.

One reason why it can be misleading to equate ice residuals with INPs is that MPC-generated ice crystals can contain cloud condensation nuclei (CCN) which have been collected upon riming but have not acted as INPs. One possibility to overcome this issue is to sample ice residuals of freshly formed, small ice crystals (< 20 µm), which are assumed to have grown by the initial phase of vapour diffusional growth only (Mertes et al., 2007; Kupiszewski et al., 2015). On mountain-top stations, where such crystals can be collected in-cloud, however, hoar frost (cloud droplets frozen onto surfaces) can be a strong source of small (i.e. < 100 µm) ice crystals (Lloyd et al., 2015; Farrington et al., 2016; Beck et al., 2018). Hoar frost grows in saturated conditions, breaks off when windy, and broken-off segments can become ingested into clouds and commonly mistaken for secondary ice (Rogers and Vali, 1987). Residuals in hoar frost particles are CCN that had not been activated as INPs. Only droplets freeze upon contact with an iced surface while ice particles bounce off and remain in the airflow, a principle applied in counterflow virtual impactor inlets used to separate ice from liquid in MPCs (Mertes et al., 2007). Current ice selective inlets are not able to separate primary from secondary ice (Cziczo et al., 2017). (page 2, lines 20-31).

Authors' response to Anonymous Referee #2, RC4

Review received and published: 3 October 2018

Thanks for providing more information about these experiments. However, authors do not address the concerns that are outlined. I will describe one example here. One of the conclusions of this study (page 5 main paper) is that if no INP was found in a crystal – this crystal was categorized as formed through the process of secondary ice formation. This is based on an observation that this particular crystal (now supercooled droplet) did not freeze until -25C. However, it is possible that this droplet may freeze at colder temperatures than -25C, and if the composition is made up of dissolved organics/inorganics, the droplet may require homogeneous freezing temperatures (< -37C). This possibility is not explored in this study. How to assure that this crystal (or super- cooled droplet) is free of any residue/foreign substance that may trigger nucleation of ice? If the droplet could freeze at < 25C temperatures, then conclusions will change. To verify this possibility an experimental evidence is needed. In response (page 3), it is mentioned that "A possible explanation for the absence of INPs are crystals formed through secondary ice formation processes.", but this is a conclusion which is drawn in this paper based on limited observations, not an explanation. Further, papers from the literature are highlighted saying that low INP concentrations compared to N_ice concentrations are observed previously, but this response does not answer the above question. There are no results regarding the nature of INPs or the freezing spectra of droplets at colder temperatures to understand this concern. My all other questions are somewhat related to this concern. Additional experimental evidence (for example as above) is needed to support the claims made in the paper.

In additional experiments we certainly would find residues or foreign substances in the planar branched crystals we categorise as secondary ice. Such residues could be cloud condensation nuclei in rime droplets, scavenged interstitial aerosol particles, or others. Some of these residues may indeed be capable of triggering ice at temperatures colder than -25 °C. However, initial ice formation at such cold temperatures would not have resulted in the form (habit) of crystals we have analysed. For this reason, we are convinced that they resulted from an ice multiplication process. There is strong evidence supporting this view, which we would include in a revised version of the manuscript:

The temperature range from -20 °C to -70 °C is the so-called "polycrystalline regime" dominated by crystal shapes with a range of different angles between branches or plates extending in three dimensions (Bailey and Hallett, 2009). These crystals will continue to grow when falling into warmer layers of air, as long as these layers are supersaturated with respect to ice. Otherwise, the crystals will sublimate. The growth habit of the falling crystals may change depending on temperature and supersaturation, but it will remain polycrystalline and irregular (c.f. Fig. 6 and 7 in Bailey and Hallett, 2009). Polycrystalline ice particles are highly unlikely to grow into the kind of crystals we have sampled, which had the same angle (60°) between all branches, and branches only extending in a single plane (i.e. dendrites; c.f. Schwarzenboeck et al., 2009).

We have moved the sentence mentioned by the referee from the introduction section to the results and discussion section.

The lack of INP_{-17} indicates that the formation of these crystals was most likely not triggered by heterogeneous freezing, but through a secondary ice formation process. (page 7, lines 4-5)

We have added the second paragraph in our comment above to the results and discussion selection (see page 8 lines 7-13 in the revised version of the manuscript).

We think that dendritic crystals either formed through primary or secondary ice formation processes are initially formed at around -15 °C, a temperature which is encoded in their habit. Only around such a temperature these habits are formed, which was shown by many studies cited in our manuscript. We think that formation of these crystals can not have been triggered by INPs that were activated in the atmosphere below -20°C, otherwise they would have grown into polycrystalline, not single planar crystals. Therefore, we are convinced that the freezing of melted crystal droplets below -20 °C was caused by CCN scavenged during rime formation on the dendrites. Some CCN that had not been activated as INP before or during collision with the dendrites, will have been activated as INP on our cold stage when its temperature dropped below -20 °C and caused the test droplets to freeze.

Finally, we think that our study has shown that temperature information contained in the habit of an ice crystal can be a starting point to quantify multiplication in clouds.

~~Direct~~New type of evidence for secondary ice formation at around -15 °C in mixed-phase clouds

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Abstract. Ice crystal numbers can exceed the numbers of ice-nucleating particles (INPs) observed in mixed-phase clouds (MPCs) by several orders of magnitude also at temperatures that are colder than -8 °C~~required for the Hallett-Mossop process (-3 °C to -8 °C).~~. This disparity~~ese observations~~ provides circumstantial evidence of secondary ice formation also other than via the Hallett-Mossop process. ~~Attempting~~In a ~~more direct observational~~new approach, we made use of the fact that planar, branched ~~snow~~ice crystals (e.g. dendrites) grow within a relatively narrow temperature range (i.e.~~about~~ -12 °C to -17 °C) and can be analysed individually for INPs using a field-deployable~~suitable~~ drop freezing assay~~ technique. During~~. The novelty of our approach lies in comparing the growth temperature encoded in the habit (shape) of an individual crystal with the activation temperature of the most efficient INP contained within the same crystal to tell whether it may be the result of primary ice formation. In February and March 2018, we analysed a total of 190 dendritic crystals (~~an average of ~~~3 mm median~~in~~ size~~ and between 1.3 to 7.6 mm~~) deposited within ~~mixed-phase clouds~~MPCs at the High Altitude Research Station Jungfraujoch (3580 m a.s.l.~~.), Switzerland.~~). Overall, one in eight of ~~these~~the analysed crystals contained an INP active at -17 °C or warmer, while the remaining seven~~ of eight~~ most likely resulted from secondary ice formation within the clouds. The ice multiplication factor we observed was small (8), but relatively stable throughout the course of ~~the experiment~~documentation. These measurements show that secondary ice can be observed at temperatures around -15 °C ~~in the atmosphere ~~and thus advance our understanding of the extent of secondary ice formation in ~~mixed-phase clouds~~MPCs, even where the multiplication factor is smaller than 10.

1 Introduction

Ice-nucleating particles (INPs) are required to catalyse primary ice formation in clouds at temperatures above -36 °C via heterogeneous freezing (e.g. Vali et al., 2015). ~~This ~~In mixed-phase clouds (MPCs), heterogeneous freezing ~~pathway ~~is expected to generate ice crystals~~ in mixed-phase clouds and is supported for instance by Kumai (1951, 1961) and Kumai and Francis (1962) who found an insoluble particle of 0.5 to 8 µm in size in the centre of almost every of about 1000 snow crystals~~

~~they had analysed. However, in-cloud observations report large discrepancies between measured INP and ice crystal numbers (e.g. Hobbs and Rangno, 1985; Beck et al., 2018) the latter being several orders of magnitudes higher than the former. These observations suggest that not only heterogeneous and homogeneous freezing~~, but also ~~other processes such as~~ secondary ice production mechanisms ~~(i.e.~~ can enhance the ice crystal number concentration (Cantrell and Heymsfield, 2005). The secondary production of ice particles ~~requiring~~requires the prior presence of other ice particles (Vali, 1985)~~) must generate the observed ice particles~~.

For example, ~~S~~secondary ice crystals can ~~for instance~~ result from rime splinters that are released upon riming (i.e. supercooled cloud droplets that freeze upon contact with a solid hydrometeor) of ice crystals at temperatures between -3 °C and -8 °C (Hallett and Mossop, 1974; Jackson et al., 2018). Other than the well-known Hallett-Mossop process, mechanisms proposed for secondary ice production include ice-ice collisional breakup (e.g. Vardiman, 1978), droplet shattering or fragmentation upon freezing (e.g. Takahashi and Yamashita, 1970; Lauber, 2018) and sublimation fragmentation (e.g. Bacon et al., 1998). These processes and indications for their occurrence in the atmosphere are summarised in Field et al. (2017). Sullivan et al. (2018a) have recently studied three of the~~ose~~ above-mentioned secondary ice formation processes in terms of their thermodynamic and primary ice requirements in a parcel model. They showed that INP concentration can be as low as 2 m^{-3} (0.002 L^{-1}) to initiate ice multiplication by ice-ice collisional breakup. Furthermore, the number of INPs is less important with regard to cloud formation than a sufficiently warm ~~enough~~ cloud base temperature and modest vertical updraft velocity for frozen droplet shattering and rime splintering (Sullivan et al., 2018a). When droplet shattering and ice-ice collisional breakup were implemented into a large-scale weather model, secondary ice contributed as much to the ice crystal number concentration ~~than ice from~~as did primary ice nucleation, even though high ice crystal numbers remain underestimated by the model (Sullivan et al., 2018b).

~~Modelling~~While modelling studies accounting for secondary ice production can ~~explain~~ to some extent explain the observed ice crystal numbers (e.g. Sullivan et al., 2018b), field measurements have not been conclusive as to the contribution of secondary ice production mechanisms until present days. Kumai (1951, 1961) and Kumai and Francis (1962) found an insoluble particle of 0.5 to 8 µm in size in the centre of almost every one of the about 1000 snow crystals they collected. The particles they found were clay and related minerals and were assumed to have initiated the formation of the crystals. Bigg (1996) suggested to repeat the experiments by Kumai and Francis (1962) and to look at the ice nucleation properties of these particles. One reason why it can be misleading to equate ice residuals with INPs is that MPC-generated ice crystals can contain cloud condensation nuclei (CCN) which have been collected upon riming but have not acted as INPs. One possibility to overcome this issue is to sample ice residuals of freshly formed, small ice crystals (< 20 µm), which are assumed to have grown by the initial phase of vapour diffusional growth only (Mertes et al., 2007; Kupiszewski et al., 2015). On mountain-top stations, where such crystals can be collected in-cloud, however, hoar frost (cloud droplets frozen onto surfaces) can be a strong source of small (i.e. < 100 µm) ice crystals (Lloyd et al., 2015; Farrington et al., 2016; Beck et al., 2018). Hoar frost grows in saturated conditions, breaks off when windy, and broken-off segments can become ingested into clouds and commonly mistaken for secondary ice (Rogers and Vali, 1987). Residuals in hoar frost particles are CCN that had not been activated as INPs. Only droplets freeze upon contact with an iced surface while ice particles bounce off and remain in the airflow, a principle applied in counterflow virtual impactor inlets used to separate ice from liquid in MPCs (Mertes et al., 2007). Current ice selective inlets are not able to separate primary from secondary ice (Cziczo et al., 2017).

Another possibility to investigate secondary ice is by comparing the concentration of INPs with that of ice crystals in the same cloud. Most such studies report large discrepancies between measured INPs and ice crystal numbers (e.g. Hobbs and Rangno, 1985; Lasher-Trapp et al., 2016; Ladino et al., 2017; Beck et al., 2018) the latter being several orders of magnitudes higher than the former. ~~2018b). However, in-situ evidence of secondarily produced ice has been difficult to obtain to date, one difficulty being crystal fragmentation due to the sampling instrument (Schwarzenboeck et al., 2009).~~ To the contrary, a good agreement between INPs and ice crystals was found by Eidhammer et al. (2010) in an orographic wave cloud. Furthermore, ~~it probably is not possible to estimate the number of primarily nucleated ice crystals in clouds from the~~ INP ~~spectrum~~ concentrations from bulk~~of~~ precipitation samples ~~(e.g. Petters and Wright, 2015) because INP data from bulk precipitation samples~~ cannot be disentangled to the level of individual hydrometeors (Petters and Wright, 2015). Riming ~~(i.e. supercooled cloud droplets that freeze upon contact with a solid hydrometeor)~~ can affect the INP spectrum of a bulk precipitation sample by ~~potentially~~ adding scavenged INPs immersed in supercooled cloud droplets, which have not been activated under in situ conditions (Creamean et al., 2018b). Further, ice-nucleation active microbes can be scavenged by raindrops below cloud and alter the spectrum (Hanlon et al., 2017).

Another way to separate primary from secondary ice particles could be INP assays on individual hydrometeors collected within MPCs. The first experiment in which individual hydrometeors were analysed for INPs, and the only one to our knowledge ~~we are aware of~~, was conducted by Hoffer and Braham (1962). The hydrometeors they had collected from aircraft were large, frozen water drops that had grown through riming (“snow pellets” or “ice pellets”; Braham, 1964) ~~and collected with an aircraft~~ within summer clouds. They all (n = 301) re-froze at temperatures substantially lower than the expected minimum temperature of the sampled cloud (i.e. the cloud top temperature estimated from~~by~~ radiosonde data~~) from which they were collected,~~), and the authors presumed them to be of secondary origin. However, an ice multiplication factor (i.e. the number of all ice particles divided by the primary ice particles) could not be estimated because the number of primary ice particles was zero.

In this study, similar to the one by Hoffer and Braham (1962), we collected in-cloud hydrometeors to obtain *in ~~-~~situ* evidence of secondary ice formation. ~~The main difference to Hoffer and Braham (1962) is that we collected vapour grown snow crystals in winter clouds at a mountain-top station and estimated the temperature of their formation from their habit (shape). Our idea to observe~~ We concentrated on secondary ice formation at around -15 °C ~~is based on previous studies~~for three reasons. First, Westbrook and Illingworth (2013) observed a long-lived supercooled cloud layer with a cloud top temperature around -13.5

°C, which continued to precipitate ice crystals well beyond the expected exhaustion of its INP reservoir. Second, laboratory investigations revealed ice-ice collision to be most effective in producing secondary ice particles at around -16 °C (Takahashi et al., 1995), or in collisions involving dendritic crystals (Griggs and Choularton, 1986). Third, the growth habit of ice crystals forming in super-saturated conditions between -12 °C and -17 °C is well and distinctively defined. It is a single, planar, sector-type or dendrite-type (branched) habit (dendritic ice; Nakaya, 1954; Magono, 1962; Magono and Lee, 1966; Takahashi et al., 1991; Takahashi,~~,~~ 2014; Libbrecht, 2017) that grows by vapor diffusional growth into a diameter of several millimetres~~ (e.g. forming snow crystals or dendrites)~~ during a vertical fall of a few 100 m (Fukuta and Takahashi, 1999). This in turn restricts the initial~~ir~~ ~~expected ~~nucleation temperature accordingly. These observations suggest that direct evidence for secondarily formed crystals might be obtained by collecting planar, branched snow crystals from supercooled clouds and testing them individually for the presence of INPs that might have catalysed their formation (i.e. INPs that were activated between -12 °C and -17 °C). ~~Absence of such an INP indicates that these crystals are not formed by heterogeneous freezing and would thus be strong evidence for the crystal being a product of secondary ice formation.~~

2 Experimental

2.1 Location and meteorological conditions

Between 15 February and 22 March 2018, we collected and analysed a total of 229 planar, sector- and dendrite-type ~~snow~~ice crystals (i.e. ice crystals of a size larger than 1.3 mm in diameter) during cloudy conditions at the High Altitude Research Station Jungfraujoch (3580 m a.s.l.) in the Swiss Alps. During the collection, cloud base height as measured by MeteoSwiss with a ceilometer located 5 km northwest of Jungfraujoch (Poltera et al., 2017) was on average 950 m below the station (zB, Table 1). Based on air temperature measured by MeteoSwiss at Jungfraujoch, cloud base height and an assumed moist adiabatic lapse rate of 7.5 °C km^{-1} (plausible for approximately 650 hPa and -10 °C) we estimated that daily mean cloud base temperatures (CBT) were between +1 °C and -12 °C. The mean air temperature at the station during the sampling periods was -11.0 °C (±3.6) and the mean wind velocity was 9.1 m s^{-1}~~.~~ (±3.9). On three days air masses arrived mainly from south-east (SE) or east (E), and on seven days from north-west (NW).

2.2 Single crystal selection and analysis

We collected snow crystals on a black aluminium plate (40 cm x 40 cm) at about 1 m above the floor of the main terrace of the Sphinx Observatory at Jungfraujoch and analysed the crystals inside a small, naturally cold (-1 °C to -7 °C) anteroom between the terrace and the laboratory. Among a usually wide variety of shapes and sizes ~~collected on the plate we selected what we considered to be planar, branched snow crystals.~~ precipitating onto the plate we selected what we considered to be single, planar, branched or dendritic ice crystals (from here on “dendrites”), which can safely be assumed to have grown within MPCs at temperatures around -15 °C (Nakaya, 1954; Magono, 1962; Magono and Lee, 1966; Takahashi et al., 1991, Takahashi, 2014; Libbrecht, 2017). Our selection criteria exclude hoar frost particles which might have been generated by local surface sources around the station (Llyod et al., 2015; Farrington et al., 2016; Beck et al., 2018). Rime on selected crystals is of little concern in our approach and was accounted for (see Sect. 2.3).

Selected crystals were documented by macro (1:1) photography (camera: OM-D E-M1 Mark II, pixel width: 3.3 µm; objective: M.Zuiko ED 60mm f2.8; flash: SFT-8; all items from Olympus, Tokyo, Japan) stabilised by a focusing rack (Castel-L, Novoflex, Memmingen, Germany) propped up on the aluminium plate. The size of our crystals was determined by using ImageJ (Rueden, 2017; Schindelin, 2012). Images were later analysed more exactly ~~on a larger screen~~ for the habit, including the degree of riming both categorized according to the ~~'global~~latest ice crystal classification ~~scheme'~~scheme, as presented by Kikuchi et al. (2013). The ~~size~~scheme catalogues solid precipitation particles into a total of ~~the crystals was determined by using ImageJ (Rueden, 2017; Schindelin, 2012).~~121 categories and provides for each category a representative image.

After selecting the crystals, we tested them ~~on freezing~~for the most efficient insoluble INP they contain that can be activated through immersion freezing using a custom-built cold~~-~~-stage (Fig.~~ure~~ 1; more details in supplement). ~~The~~A cold~~-~~-stage is a ~~modified~~ drop freezing apparatus, on which droplets are deposited onto a ~~methodology that~~cooling surface and the temperature at which they freeze is observed (Vali, 1971a). This technique is commonly used today ~~and initially described by Vali (1971a). The device~~to assess the activation temperature of INPs immersed in droplets. Observations have shown that an overwhelming majority of ice particles originate from supercooled liquid clouds at temperatures > -27 °C, which strongly suggests that the initial process of ice formation in MPCs > -27 °C occurs through immersion freezing (Westbrook and Illingworth, 2011). The cold-stage used in this study is meant to be taken into the field, can be set up within minutes and operated without additional infrastructure (i.e. no cooling water or lined power is required). It consists of a gold-plated copper disk with a surface diameter of 18 mm, which is large enough to easily accommodate simultaneously two dendrites and two control droplets ~~at once~~ (roughly 1 cm apart from each other).

With a fine brush, ~~we transferred~~ two crystals are transferred onto the cold~~-~~-stage surface thinly covered with Vaseline® petroleum jelly (Tobo, 2016; Polen et al., 2018) before being analysed within the next minutes (Fig. 1a). The manual application of Vaseline® requires precision and clean gloves in order to get an as uniform and clean cover as possible. At the transfer of the crystals, the surface of the stage was at a temperature between +1 °C and +5 °C ~~(Fig.1a).~~ , which is a common temperature range to store INPs in water for several hours before analysis (e.g. Wilson et al., 2015). Upon ~~contact with~~deposition onto the cold~~-~~-stage ~~these~~the crystals melted into liquid droplets. To aid visual detection of freezing ~~during testing~~, we increased the size of the melted crystal droplets by adding 3 µL of ultrapure water (Molecular Biology Reagent, Sigma-Aldrich) with a pipette~~.~~ (using a new tip for each measurement run). The melted ~~crystals~~ crystal containing all residuals and potentially ~~contained~~ the ~~suspected~~ INP ~~and have~~that had triggered its formation, has a rather small volume compared to the added water. For each crystal a control droplet (3 µL) of the same ultrapure water was placed next to the melted crystal droplet and served as control (blank) (Fig. 1b). Then we ramped the temperature of the cold~~-~~-stage down to -25 °C. Shortly after the cold-stage temperature reached a value below the surrounding air temperature, we covered it with a transparent hood to ~~prevent~~ minimise the chance for contamination from the environment surrounding the droplets and to prevent condensation on the cold-stage ~~of the drops.~~(Polen et al., 2018). From -12 °C and below we limited the cooling rate to 3 °C min^{-1}. The freezing of the droplet and thus the presence of the most efficient INP was detected visually, and the corresponding temperature was recorded manually (Fig. 1c). The presence of an INP active at -17 °C and warmer (INP$_{-17}$) was taken as evidence for the tested dendrite to have been generated through primary ice formation. ~~After a test was complete, we cleaned the cold~~ Nevertheless, extending the drop freeze assay down to -25 °C is useful to determine the fraction of rime associated with single crystals (see Sect. 2.3). After a test was complete, we cleaned the cold-stage carefully with isopropanol. In total, the procedure (i.e. collecting and analysing two samples) takes ~15 minutes.

2.3 Accounting for riming

A rimed ice crystal has collected liquid cloud droplets, each of them containing a CCN that may cause freezing of the droplet containing the residuals of this crystal. Such a CCN may be activated on the cold-stage as INP (from here on: scavenged INP), although it had not initiated the formation of the collected dendrite. The median concentration ~~in~~ of INPs active at -25 °C or warmer (INP$_{-25}$) was determined for bulk rime samples collected on impactor plates ($conc_{rime}$) and used to estimate the mass of rime associated with a single dendrite (m):

$$m\ [g\ rime\ crystal^{-1}] = \frac{\ln\left(\left(1-\cancel{0.41}FF_{crystal}\right)^{-1}\right)}{conc_{rime}\cancel{1100}}\ [\,INP_{-25}\ crystal^{-1}/INP_{-25}\ g^{-1}\ bulk\ rime\,], \qquad (1)$$

with $FF_{crystal}$: the frozen fraction of INP$_{-25}$ in the analysed dendrites (after subtracting the control).

~~We collected rime~~ This step was necessary to estimate ~~how much~~the contribution of scavenged ~~INP~~INP~~ are included~~$_{-17}$ representing ~~in it and thus how riming affects the INP numbers in rimed single~~ false positives of primary ice crystals~~.~~ in our results. They were estimated from the average mass of rime associated with a single dendrite (Eq. 1) and the concentration of INP$_{-17}$ within the independent rime samples as described next.

Independent r~~R~~ime ~~was~~samples were collected with a plexiglass impactor plate (Lacher et al., 2017) suspended on the railing of the terrace at Jungfraujoch for a few to several hours (~1-13h). In total, 30 samples ~~were taken during 15 February and 11 March and they were prepared~~of aggregated rime droplets were collected between 15 February and 11 March. The freezing experiments of the rime samples were done with a drop freezing assay similar to the set up described above which was used for the single crystal analysis. However, rime samples were melted and portioned with a sterile syringe into 2.5 µL droplets and analysed with a ~~the NOAA~~ d~~D~~rop f~~F~~reezing c~~C~~old p~~P~~late following the description in Creamean et al. (2018a). ~~To summarize,~~Of each sample 300 droplets ~~of molten rime of ~2.5 µL each are tested on a cold plate that was~~ were cooled ~~towards~~

~~a temperature where~~until all droplets were frozen. The cumulative number of ~~INP~~INPs active at a certain temperature ~~is~~(with a temperature interval of 0.5 °C) was calculated by taking into account the observed numbers of frozen droplets at a temperature, the total number of droplets and the analysed volume of sample (Vali, 1971b). The main reason for the use of a second cold-stage was to ensure that the custom-build one was always ready for single crystal analysis in case dendrites were precipitating. Other than that, the drop freezing cold plate has a larger surface on which more droplets can be analysed at a time making it more suitable for rime analysis. However, it also requires an external refrigerated circulation bath, lined power and it is relatively large, making it impossible to put it into the anteroom and to analyse single crystals.

3. Results and discussion

Of the 229 crystals analysed in the field 39 had to be excluded retrospectively because a closer inspection of the enlarged photographs showed that they were either not planar or not branched. Most of the excluded crystals were spatial or radiating assemblages of plane-type crystals (P6 or P7, according to Kikuchi et al. (2013)) and may hence been initiated at temperatures < -20 °C (Bailey and Hallett, 2009). The remaining 190 crystals were confirmed as planar and branched, i.e. having a habit that typically forms between -12 °C and -17 °C. They had been collected from a pathlength of 2368 km through a large number of MPCs from different wind directions (sum of sampling duration multiplied by average wind speed; see Table 1). A large fraction of them were rimed (31%) or densely rimed (51%) dendrites (R1c or R2c, according to Kikuchi et al. (2013~~));~~); see Fig. S3 for examples); while the remainder belonged to other categories (in order of decreasing frequency: graupel-like snow of hexagonal shape, hexagonal graupel, composite plane-type crystals, dendrite-type crystals, sector-type crystals or R3a, R4a, P4, P3, P2, respectively, according to Kikuchi et al. (2013)). Their greatest length in the a-axis (outer diameter) ranged from 1.3 to 7.6 mm, with a median of 2.8 mm,~~ and~~ a mean of 3.1 mm and a standard deviation of 1.1 mm.

We found no INP active above -12 °C present in the crystals~~, which corroborates the crystal classification and the temperatures at which they form (Takahashi, 2014)~~. In 24 of the 190 crystals an INP active between -12 °C and -17 °C was present (Fig.~~ure~~ 2). In the other 166 crystals no INP was found between -12 °C and -17 °C. They either refroze below -17 °C (95) or stayed supercooled until -25 °C (71). The lack of INP$_{-17}$ indicates that the formation of these crystals was most likely not triggered by heterogeneous freezing, but through a secondary ice formation process. Blanks that froze above -17 °C were limited to one count, occurring between -16 °C and -17 °C~~.~~ (not accounted for in further analysis). Between -17 °C and -25°C, 40 control droplets froze; the rest (149) stayed supercooled until -25 °C. A frozen fraction of 21% of the control droplets at -25 °C is a rather low fraction compared to the results with pure water droplets (1 µL) on a Vaseline-coated substrate presented recently by Polen et al. (2018).

Throughout the observation period of 10 days the daily fraction of primarily nucleated ice ~~versus ice crystals without an INP~~ was relatively stable (Fig.~~ure~~ 3). From these results, we conclude that about one in eight (24/190) planar, branched crystals found in ~~mixed-phase clouds~~MPCs at Jungfraujoch during winter months in 2018 resulted from primary ice formation and seven of eight were generated through a process of secondary ice formation at temperatures between -12 °C and -17 °C. The uncertainty associated with the number of primary crystals in our observations is about 20% ($\sqrt{24}/24$).

Our preliminary conclusion is based on the following four assumptions: The first assumption is that INPs embedded in natural ~~snow~~ice crystals can be repeatedly activated at the same temperature. Second, that the analysed crystals did not grow from aerosolised parts of hoar frost growing on surrounding surfaces (Lloyd et al., 2015; Farrington et al., 2016; Beck et al., 2018). Third, that initial ice formation leading to the growth of the analysed crystals likely did not occur at a temperature colder than -17 °C. And, fourth, that the detected ~~INP active at -17 °C or warmer (~~INP$_{-17}$~~)~~ were not scavenged during riming of a secondarily formed crystal.

We are confident that the first condition (i.e. that INPs are stable over many refreezing cycles) for our preliminary conclusion is met. Although substantial fractions of bacterial INPs active above -7 °C are deactivated after a single freeze-thaw cycle, those active below -7 °C are typically unaffected even after three freezing cycles (Polen et al., 2016). Further, experiments with ~~INP~~INPs from soils show a remarkable stability of the ice nucleation temperature over tens of repeated melting and freezing cycles, with standard deviations of 0.2 °C (Vali, 2008). Furthermore, Wright et al. (2013) reported~~saw~~ similar results for rain water samples. Since we analysed the collected crystals within minutes after melting, we can also exclude changes due to storage (i.e. aging), which has been observed with bulk snow samples over the course of days or weeks (Stopelli et al., 2014).

Surface frost can be a strong source of very small (i.e. < ~~∼~~100 µm), secondary ice crystals at Jungfraujoch (Lloyd et al., 2015) and at other mountain stations (Beck et al., 2018). ~~Surface frost grows in saturated conditions, breaks when windy, and broken-off segments can become ingested into clouds and commonly mistaken for secondary ice (Rogers and Vali, 1987).~~ During 7 of 10 sampling events air masses approached from northwest. The terrain falls off steeply in this direction and reaches the average observed cloud base (∼1000 m below Jungfraujoch, Table 1) within a horizontal distance of about 2 km. At an average wind velocity of 8 m s^{-1} from this direction ~~of 8 m s^{-1}~~ the distance is covered within less than 5 minutes, which is too short for small, broken off frost crystals to grow to the average size of the crystals we have analysed (average of 3.1 mm). Even in most favourable conditions a dendrite would not grow to 1 mm diameter within that time (Takahashi et al., 1991). Therefore, it seems unlikely that dendrites which were not associated with an INP$_{-17}$ had grown from particles of hoar frost emitted by surfaces in the vicinity of Jungfraujoch.

The temperature range from -20 °C to -70 °C is the so-called “polycrystalline regime” dominated by crystal shapes with a range of different angles between branches or plates extending in three dimensions (Bailey and Hallett, 2009). These crystals will continue to grow when falling into warmer layers of air, as long as these layers are supersaturated with respect to ice.

Otherwise, the crystals will sublimate. The growth habit of the falling crystals may change depending on temperature and supersaturation, but it will remain polycrystalline and irregular (c.f. Fig. 6 and 7 in Bailey and Hallett, 2009). Polycrystalline ice particles are highly unlikely to grow into the kind of crystals we have sampled, which had the same angle (60°) between all branches, and branches only extending in a single plane (i.e. dendrites; c.f. Schwarzenboeck et al., 2009). The lowest temperature at which the formation of the collected crystals may have been initiated by an INP is very likely above -20 °C because INPs activated at colder temperatures would have resulted in polycrystalline crystals (Bailey and Hallett, 2009), a different habit than that of the crystals we had collected. Furthermore, ~~A~~according to Furukawa and Takahashi (1999) a dendrite falls about 400 m while growing to a diameter of around 3 mm. Given a diabatic lapse rate of 7.5 °C km^{-1} an initial ice crystal may have been generated in 3 °C colder conditions than where its growth into a 3 mm dendrite was completed. However, as the deposition velocity of a tiny initial ice crystal is small, the initial ice formation will unlikely have occurred at much higher altitudes than where the main growth into dendrites occurred. Even if we consider all crystals which contained an INP active between -12 °C and -20 °C a large fraction of them (81%) remains to be considered the product of secondary ice formation.

The presence of INPs active at temperatures colder than -17 °C associated with the collected crystals might be explained by riming, i.e. the collection of cloud droplets containing such particles not activated as INP (scavenged INP) because ambient temperatures were not cold enough (Table 1). A majority of our crystals were rimed or densely rimed. The median concentration of INP~~ active at ~~$_{-25}$ ~~°C or warmer (INP$_{-25}$)~~ in the rime samples collected ~~rime~~on an impactor plate at Jungfraujoch was about 1100 ml^{-1} during the period from 15 February to 12 March. Since 41% (background subtracted) of our crystals contained an INP$_{-25}$, the average mass of rime associated with a single crystal (m) must have been about 4.9 x 10^{-4} g (see Eq. 1~~):~~

). ~~$m\ [g\ rime\ crystal^{-1}] = \frac{\ln((1-0.41)^{-1})}{1100}\ [INP_{-25}\ crystal^{-1}/INP_{-25}\ g^{-1}\ rime]$ (1)~~

This is about twice as much as the difference in mass (~2 x 10^{-4} g) between rimed and un-rimed dendrites of 3 mm diameter found at Mount Tokachi, Hokkaido (Nakaya and Terada, 1935). The median of INPs active at -17 °C or warmer in rime was 16 ml^{-1}. Therefore, less than 1% of the crystals we have analysed might have scavenged an INP through riming that was active at -17 °C or warmer (16 [INP$_{-17}$ g^{-1} rime] x 4.9 x 10^{-4} [g rime crystal^{-1}]).

Conclusion~~ and outlook~~

The ~~temperature dependent ~~habit of a planar, branched ~~snow~~ice crystal, growing exclusively around -15 °C, enables the verification of whether it derived from primary or secondary ice formation~~, as long as certain conditions are met~~ based on a number of reasonable assumptions. Although the required experimental procedure including refreezing of dendrites using a drop freezing assay has a low throughput (~15 minutes for two ~~snow~~ice crystals) it can provide ~~robust results that cannot be~~

~~obtained with other approaches. From the single, relatively large dendrites, we found direct evidence~~an estimate for ~~secondary ice formation between -12 °C and -17 °C in winter clouds. The~~ the ice multiplication factor around -15 °C, even when it is smaller than 10, unlike previous *in situ* approaches. The factor we observed was much smaller than the ‘several orders of magnitude’ sometimes inferred from circumstantial evidence. ~~We presume that~~However, we do not know whether the ice multiplication factor ~~close to one order of magnitude was most likely~~we found ~~because we had focused on relatively large crystals which are unlikely~~ for dendrites is the same for~~the~~ ~~product of local surface sources or instrumental interferences,~~other crystal habits found in the ~~latter causing mainly small or broken~~same MPCs. No conclusion regarding the process of secondary ice ~~fragments~~formation can be drawn from our observation. To learn more about the occurrence of secondary ice formation in moderately supercooled clouds, we think it would be valuable to repeat these experiments in other meteorological conditions or in other locations, such as those where most crystals were previously found to contain an insoluble particle in their centre. This study has shown that temperature information contained in the habit of an ice crystal can be a starting point to quantify ice multiplication in clouds.

Data availability

The data are available from the authors upon request.

Competing interests

The authors declare that they have no conflict of interest.

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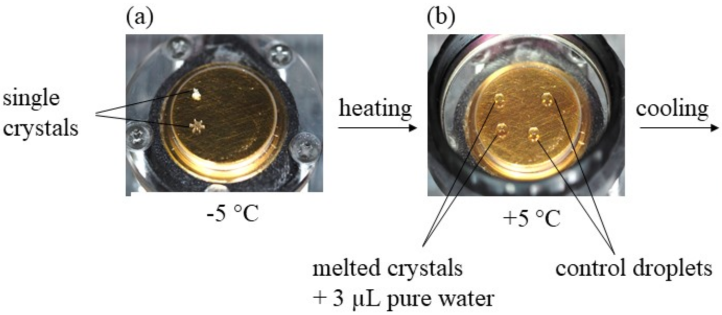
Table 1. Sampling periods including the date and the time span, numbers of analysed crystals (n), mean air temperature (T~~),~~) (and standard deviation), mean wind velocity (u) ~~and~~ (and standard deviation) and mean wind direction (dd) at Jungfraujoch; mean height of the station above cloud base (zB) and estimated mean cloud base temperature (CBT).

Date	Time span	n	T	u	dd	zB	CBT
dd/mm/yyyy	UTC	-	°C	m/s	-	m	°C
15/02/2018	07:~~37~~30 - 21:~~40~~50	38	-7.0 (0.8)	13.5 (2.1)	NW	944	0.1
16/02/2018	09:30 - 16:~~20~~30	29	-8.7 (0.2)	9.0 (2.4)	NW	1239	0.6
17/02/2018	09:40 - 23:~~33~~40	42	-8.5 (1.7)	5.8 (1.9)	NW	693	-3.3
23/02/2018	10:30 - 21:~~10~~20	20	-14.8 (0.6)	11.9 (1.6)	SE	365	-12.1
06/03/2018	12:20 - 19:~~10~~20	14	-13.1 (0.1)	5.5 (0.8)	NW	1284	-3.4
07/03/2018	08:00 - 16:~~30~~40	23	-15.7 (0.8)	4.5 (2.6)	NW	1001	-8.2
10/03/2018	09:30 - 12:~~40~~50	11	-6.8 (0.3)	5.1 (1.3)	E	196	-5.4
11/03/2018	15:40 - ~~16:50~~17:00	6	-9.8 (0.1)	13.1 (1.4)	SE	1485	1.3

12/03/2018	09:10 - 11:~~00~~10	12	-11.4 (0.1)	6.2 (0.7)	NW	878	-4.8
22/03/2018	15:50 - 22:~~20~~30	34	-15.2 (1.2)	12.4 (1.5)	NW	1079	-7.1



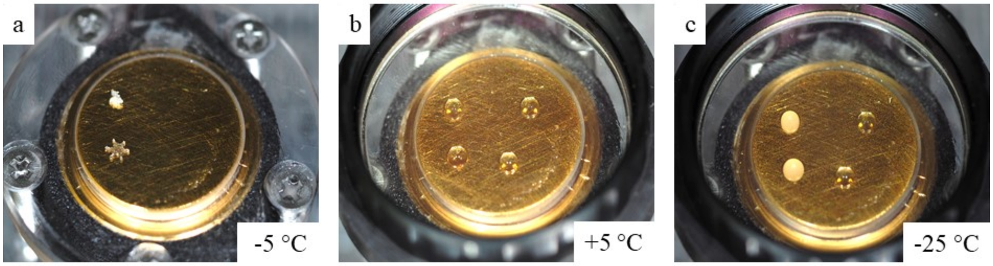


Figure 1. Illustration of ~~a single snow~~ one ice crystal droplet freezing experiment. ~~**(a)** two~~ Transparent droplets are liquid. **(a)** Two single crystals on the cold~~-~~-stage (note: the cold~~-~~-stage was set to below 0 °C for this image~~).~~ and the upper crystals is not a dendrite). **(b)** ~~melted~~Melted ice crystals with addition of 3 µL ultrapure water to increase the detection volume and to fix it (left) and two 3 µL control droplets of the same ultrapure water (right~~),~~). **(c)** ~~the~~The frozen sample (left) and supercooled control (right) droplets after cooling to -25 °C. ~~Here the samples (left) were frozen, and the control droplets (right) were still liquid.~~

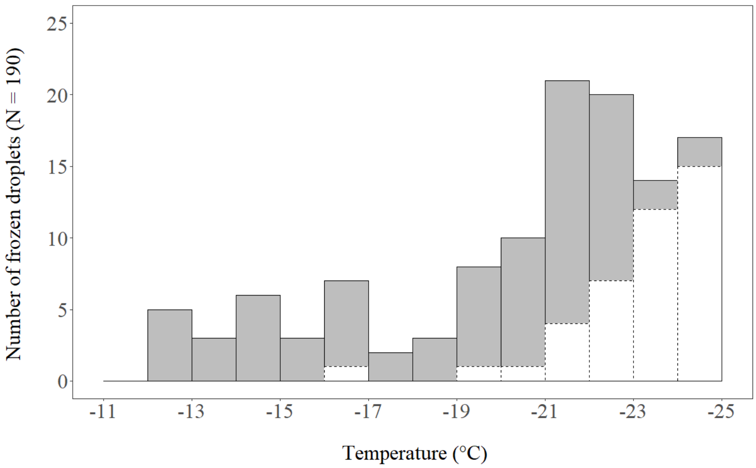


Figure 2. Number of planar, branched ~~snow~~ice crystals that re-froze on a cold~~-~~ stage after having been molten (grey bars with solid contour), thereby confirming they contained an INP active within the respective 1 °C temperature step. Of 190 crystals analysed, 24 re-froze at -17 °C or warmer (INP_{-17}). The white bars with dashed contour indicate the number of frozen control droplets. The total number of control droplets was 190 as well.

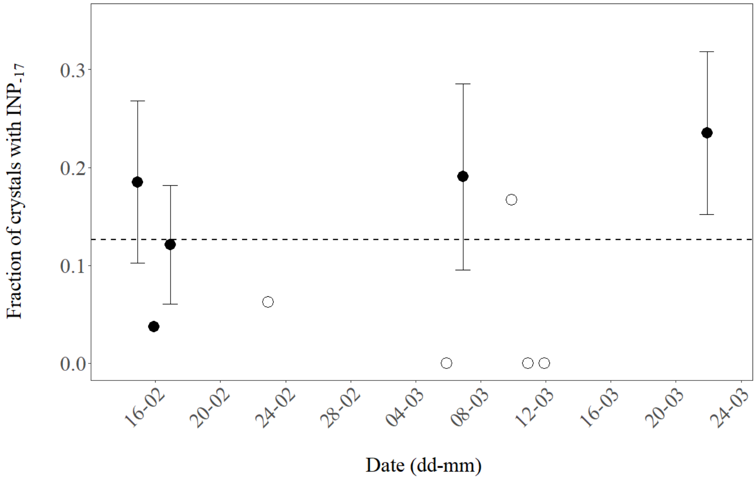


Figure 3. Daily fraction of ~~snow~~ice crystals with ~~INP~~INPs active at -17 °C or warmer (INP_{-17}) observed for 10 days during February and March 2018. The number of crystals analysed per day was between 21 and 34 (closed symbols) or less (3 to 16, open symbols). Error bars indicate an estimate of the standard deviation (proportional to $\sqrt{INP_{-17}}$) for days when at least four crystals with INP_{-17} were found. The dashed line shows the mean value of the pooled data (190 analysed crystals).

Supplement

~~Direct~~ New type of evidence for secondary ice crystals formed around -15 °C in mixed-phase clouds

by Claudia Mignani et al.

Further details of the custom-built stage

Cooling (and heating) of the cold stage is achieved with a Peltier element (13 mm x 12 mm x 2.75 mm, -40 °C to +80 °C; model TE-65-0.6-1.5P, TE Technology Inc., Traverse City, MI, USA). Temperature is measured with a thermistor (0.9 mm diameter, 5 kOhm at 25 °C; model MP-3176, TE Technology Inc., Traverse City, MI, USA) located in the centre of the cylinder just below the surface. Surface temperature can be adjusted within a range from +10 °C to -30 °C. It is set via a single-board microcontroller (Arduino, https://www.arduino.cc/) with a touchpad and a LCD display (control unit). The display shows the actual temperature of the stage, the set-point temperature, cooling rate, and other instrumental parameters. The heat formed during cooling is discharged through a ventilated heat-sink (Figure S1). Power is supplied to the stage and the control unit from a 12 V, 4.5 Ah LiFePO4 battery (model V-LFP-12-5, Vision Group, Shenzhen, China) lasting about four hours at ambient temperatures a few degrees below 0 °C. The cold stage, control unit, and other items necessary for the analysis of single crystals fit onto a small area (approximately 30 cm x 30 cm; Figure S2). Together with the macro camera used to document the crystals, the equipment fits into case the size of a piece of hand luggage allowed inside an aircraft. Its total weight is roughly 10 kg.

We validated the temperature of the cold stage by detecting the melting point of ice. For that purpose, a thin frost layer was grown on the cold stage surface. We then increased the temperature of the cold stage in 0.1 °C steps, starting from -0.2 °C. Melting of the frost layer occurred between the temperature readings of 0.0 °C and 0.1 °C. In addition, we conducted a surface temperature test with a commercial thermometer (model RDXL4SD, sensor type K, Pt100 Ohm, Omega Engineering Inc., Norwalk, CT, USA) in the temperature range of interest from -12 °C to -25 °C with a cooling rate of 3 K min^{-1}. For this test we greased the sensor of the thermometer with petrol jelly and pressed it with Styrofoam onto the surface of the cold stage. When the control unit of the cold stage indicated -12 °C the thermometer indicated -12.1 °C. When the cold stage gave a reading of -17.0 °C the thermometer indicated -16.4 °C. At -25.0 °C the offset of the thermometer had increased to 0.9 °C. This difference might be due to an imperfect contact between sensor of the thermometer, which is a bead of about 1 mm diameter, and cold stage surface. Or, it could be due to heat diffusion through the wires of the temperature sensor. Overall, the difference is too small to matter in the context of our study.

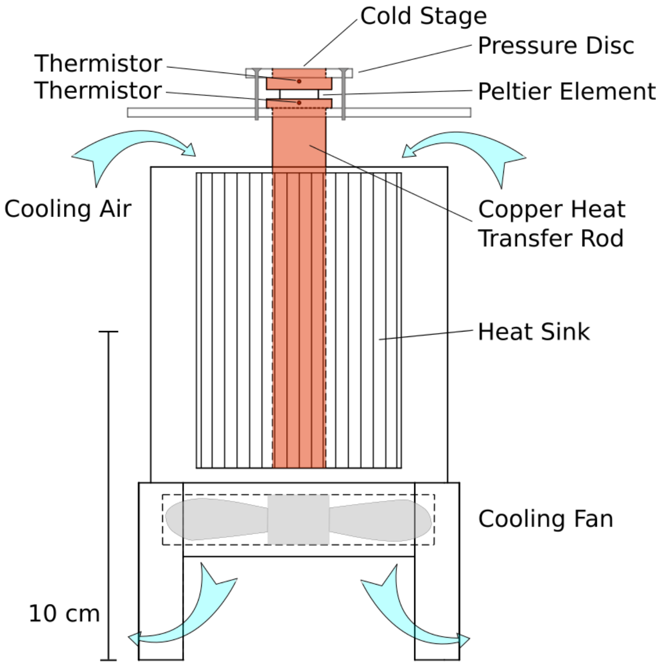
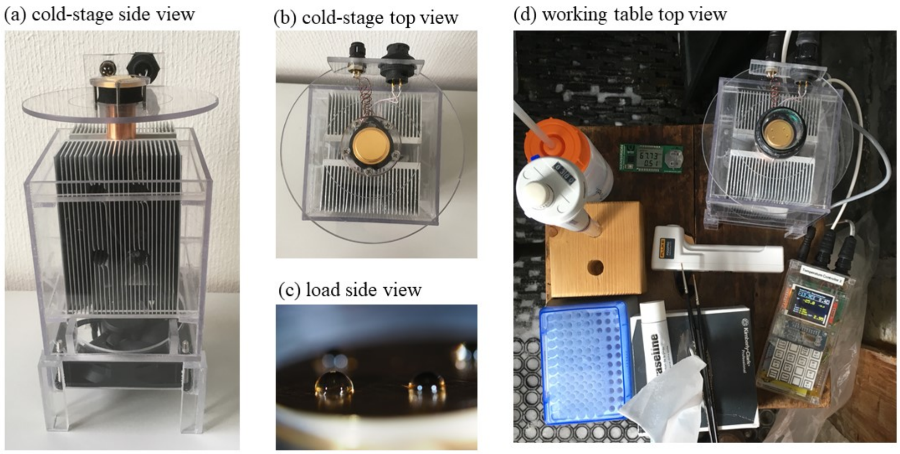


Figure S1. Technical drawing of the cold stage apparatus.


(a) cold-stage side view

(b) cold-stage top view

(c) load side view

(d) working table top view

Figure S2. Photographs of the cold-stage **(a)** from the side and; **(b)** from the top; **(c)** a close-up view of the stage loaded with droplets; (d) view from the top onto the working table during operations on Jungfraujoch.

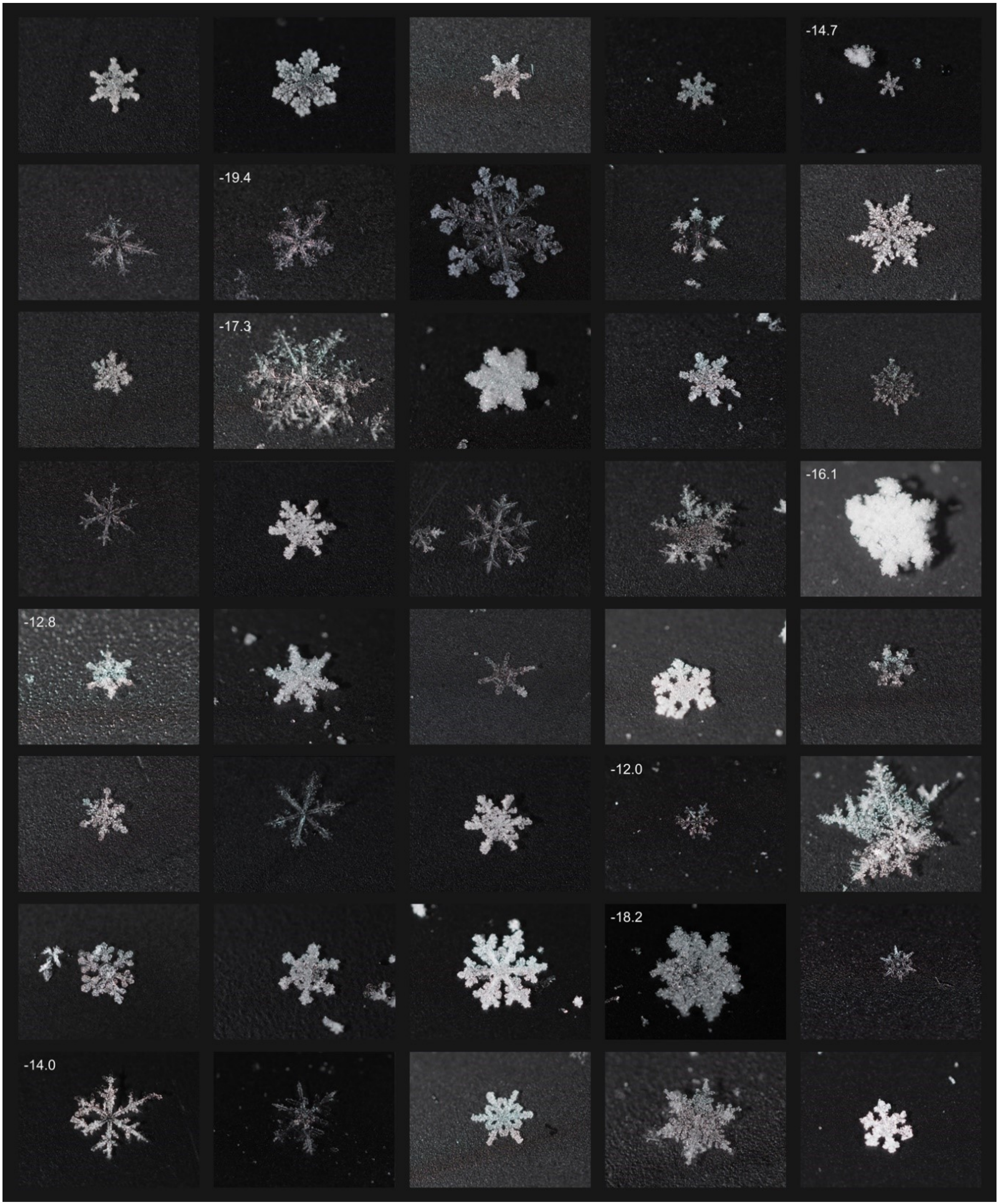


Figure S3. Examples of images of the analysed dendrites taken by macro (1:1) photography. Crystals of which the residues immersed in a water droplet froze above -20 °C have this freezing temperature added in the upper left corner of their image. Each image shows an area of 8.6 mm x 6.4 on the black surface where the crystals had been collected.