Response to Anonymous Referee #1

First of all, we thank the referee for submitting their helpful and productive annotations, which lead to improvements and clarifications within the manuscript.

We prepared a revised manuscript that addresses the questions and comments of the referees. Furthermore, below we explicitly respond to each of the items raised in the comments of anonymous referee #1. These comments are indicated in *italics,* whereas the author's response is presented in blue. Changes in the manuscript are given in green; changes to the supplement are given in purple. A response with "Okay." means we accepted the reviewers' suggestion and implemented it in the manuscript. The differences are also highlighted in separate PDFs using latexdiff. All line and page numbers refer to the ACPD manuscript version, not the revised manuscript.

Review of "Ice nucleating particle concentrations of the past: Insights from a 600 year old Greenland ice core" by Schrod et al.

General comments:

This reviewer supports publication of this manuscript in ACP. The research topic - researching INPs in the pristine past conditions - is an important addition to ACP for many reasons; e.g., providing a constraint to climate simulations/projections etc. In spite of many potential artifacts addressed throughout the manuscript, the authors conducted careful and dedicated offline lab experiments, and their findings warrant future follow up studies. Unfortunately, such care was not taken in the preparation of the manuscript (esp. after Sect. 2.2), with the manuscript containing a number of unusual word choices and non-intuitive statements. The reviewer has numerous revisions as listed below. Though most of them are minor, the reviewer would urge the authors of the manuscript to thoroughly proof read their manuscript for improving readability, as this list gets too long.

> We thank the reviewer for their careful reading of the manuscript. The long list of language edits, additional ideas and suggested literature are greatly appreciated. We agree that the suggested changes will improve the readability of the manuscript. We will go through the comments listed below one by one.

Specific and technical comments:

- *P1L13: The reviewer suggests the authors to specify dp is in a spherical diameter metric here.*

  > Okay.

- *P1L20-21: The reviewer appreciates the authors to be honest scientists extensively addressing some potential artifacts throughout the manuscript. However, the statement*

of "or some post-corning..." seems unnecessary to conclude the abstract. The reviewer suggests removing this part in the abstract.

Okay.

- *P2L6-7: Does the authors mean – "Unfortunately, heterogeneous ice nucleation, which is of primary importance of atmospheric ice formation, has not received..."?*

  The sentence was phrased this way to illustrate that although ice nucleation is very relevant to precipitation processes in the atmosphere and by extension to snow accumulation in the Arctic, ironically ice nucleation experiments on ice cores have not been sought out by researchers frequently. We rephrased the sentence to make this more clear:

  "Unfortunately, heterogeneous ice nucleation, which is of primary importance to atmospheric ice formation and therefore very relevant to Polar snow accumulation, has not received much attention in ice core sciences."

- *P2L7: As of today → Until now or To date (better word choice)*

  Okay.

- *P2L21: defines → constrains (this seems better fitting here)*

  Okay.

- *P2L27: Although...straightforward, → Evidently,*

  Okay.

- *P2L27: seen → implied*

  Okay.

- *P2L30: The reviewer finds the discussion of anthropogenic INP to be a very important part of the current manuscript and, therefore, wishes that the authors can extend the discussion a bit further? A suggestion for reading is Zhao et al. (2019, Nature Geosci.; https://www.nature.com/articles/s41561-019-0389-4?proof=trueMay) and references therein. Currently, the discussion of anthropogenic INPs is controversial, and the authors can help the community by including an extended discussion here. Doing such may reinforce the paper.*

  We agree with the referee about the importance of discussing the relevance of anthropogenic INPs for the manuscript. We thank the referee for pointing the suggested reading out to us. We added additional text to the manuscript to emphasize the discussion:

  "[...] Yet, the significance of anthropogenic pollution particles to atmospheric ice nucleation is still in question. Recently, Zhao et al. (2019) investigated the effects of pollution aerosol to the ice phase in moderate and strong convective systems in a top-down approach using a combination of satellite observations and model simulations. They present evidence that in the moderate convection case, where heterogeneous ice nucleation is more relevant, the ice particle effective radius is increased, indicating that continental pollution aerosol may in fact contain a considerable fraction of INPs. On the other hand, further experimental studies suggest that most anthropogenic aerosol particles are typically poor INPs. For example, Chen et al. (2018) found that the heavy air

pollution of Beijing did not affect the INP concentration in this urban setting in the investigated temperature range from -6 °C to -25 °C. Overall, there are still few studies available on the ice nucleation efficiency of anthropogenic aerosol and some of the presented evidence is conflicting. Although pure pollution aerosols are considered rather inactive INPs, this does not per se mean that the INP population as a whole has not changed at all over the last centuries. On the contrary, it seems rather likely that certain particles with ice nucleating potential may in fact be more abundant in today's atmosphere. [...]"

- *P2L34: Biomass burning aerosol is...least potential contributor to anthropogenic INP.*
  Okay.

- *P3L13: Indeed, soil dust, in part derived from agricultural systems/practices,... Is this what the authors meant? Feel free to modify it.*
  Yes, that's what we meant. Okay.

- *P3L17: ...global land area, of which approx. 9% were identifies...*
  Okay.

- *P3L20-23: Please clarify what "anthropogenic increase in mineral dust concentration" means. Also, a bit more discussion of aerosol particle episodes to Greenland would strengthen the paper.*
  There are several instances throughout the manuscript, where the dust transport patterns to Greenland are discussed. Therefore, we chose not to overly go into details in the introduction. We rephrased the sentence:
  "[...] however a recent increase in mineral dust concentration from these areas due to anthropogenic impacts is not documented."

- *P3L25-26: write out LINA and INDA? They appear once only, so it seems no abbreviations are necessary.*
  Okay. The line now reads:
  "[...] Leipzig Ice Nucleation Array (LINA, 90 x 1 µL) and Ice Nucleation Droplet Array (INDA, 96 x 50 µL)."

- *P3L30 INP analysis is...* → *Cumulative INP data is presented at temperatures of ...*
  Okay.

- *P3L30-31: Hartmann et al. (2019) observed...* → *The authors observed no alternation in the INP concentration over long-term period.*
  We chose to keep our phrasing, as it is more concise.

- *P3L31: Furthermore,* → *Instead,*
  We chose to keep our phrasing. "Instead" would indicate an opposite finding, but we feel the high short-term variability is an independent finding from the non-existing long-term trends.

- *P3L32: Please clarify what "dominate the total variability of the complete data set" means to the readers here. One may be able to guess, but the clarification would be appreciated.*

  We rephrased the sentence:
  "Furthermore, they found the "short-term" variability of INP concentrations from adjacent sub-year samples to be as large as or even larger than the total variability of the complete data set."

- *P3L32-35: this sentence runs too long. The reviewer suggests separating this sentence into two. For example - ... INP concentrations for the last few centuries. Their suggestion was to include...*

  Okay.

- *P4L3: write out FRIDGE.*

  Okay.

- *P4L22: B30. Complementary chemical profiles of...*

  Okay.

- *P4L25: Merge this sentence to the previous paragraph.*

  We are not quite sure what the reviewer meant by the comment.
  We deleted the line break.

- *P5L2-3: ... then split for the online chemical analysis and offline ion chromatography (IC) measurements, where discrete aliquots in vials were used (section 2.4).*

  We chose to keep our phrasing. In the suggested sentences the reader might think that IC measurements were performed right away, when in fact they were performed sometime later.

- *P5L4: thus covering → translating to*

  Okay.

- *P5L4: Further, depending on the exact...*

  Okay.

- *P5L5-6: Subsequently, the vials were refrozen and shipped to AWI to measure the concentration of major ions in order to complement the CFA measurements. Keep it simple!*

  Okay.

- *P5L7-8: Some of these samples → Some remained samples*

  We chose to keep our phrasing.

- *P5L11: The reviewer suggests deleting "Temperature variability ranged...15 hours."*

  Okay.

- *P5L13-14: ...were refrozen. (once again is repetitive of re:).*

  Okay.

- *P5L17: longitudinal pertains to vertical sections?*

  Yes.

  We deleted "longitudinal" for clarity.

- *P5L19: The reviewer suggests deleting "absolutely" – the sentence is good and makes sense without this accessory word, so not adding any value to the sentence. Perhaps let the readers decide on their own.*

  Okay.

- *P5L23: purpose-built*

  Okay.

- *P5L24-26: The reviewer suggests deleting "Additionally, trace-elemental...for this manuscript". If the data was not used in this study, then there is no need to report/mention in the reviewer's opinion.*

  Okay.

- *P5L31: are → were*

  Okay.

- *P6L2: are → were*

  Okay.

- *P6L2: The IC provides → In this study, the IC provided*

  Okay.

- *Comment: While the reviewer understands that everyone has their own style on how they use tenses in writing, the use of past/present etc. seems not consistent in this manuscript. The reviewer suggests the authors to improve the consistency on the tenses usage throughout the manuscript. Perhaps, the following site could help the authors: https://services.unimelb.edu.au/__data/assets/pdf_file/0009/471294/Using_tenses_in_scientific_writing_Update_051112.pdf*

  We thank the reviewer for noticing the inconsistencies in tense usage. We will carefully proof-read the manuscript again in this regard.

- *P6L6-: We placed a strong emphasis on having a data set with quasi-consistent time intervals for our samples (approximately decadal interval). Furthermore, our sample selection strategy was intended to consider the pre-industrial INP concentration vs. the INP concentration of the recent past (1960-1990).*

  Okay. "We considered these time intervals to be both meaningful and feasible." was added in between the suggested sentences.

- *P6L9:... in the latter time period to rightly match up sub-total sample numbers for each set.*

  We added the following clause to the sentence:
  "[...] in the latter time period to potentially enhance the statistical significance."

- *P6L12: ...as well as a couple of samples collected before and after it.*

  Okay.

- *P6L12-14: Please clarify what is meant by "Due to..." to the readers. Not intuitive to this reviewer.*

  We selected a subgroup of samples to be analyzed in FRIDGE according to the high-resolution CFA data. Some samples were selected, because there was a peak in the high-resolution dust or conductivity signal. However, the discrete INP samples are random means over several months around this peak, which means that a sample with a CFA peak does not necessarily have to have a high mean value. We will rephrase the sentence:

  "Due to the episodic nature of such an event and the fact that the INP samples were automatically collected as multi-month means, the sample containing the high-resolution peak signal does not necessarily need to have an extraordinarily high average value itself."

- *P6L15: ...were selected. These samples were typically...*

  We rephrase the sentence to:

  "Similarly, peak samples in the high-resolution signal of conductivity were selected. Large peaks in the electrolytic conductivity record are most often derived from high sulfuric acid deposition in the ice after volcanic eruptions."

- *P6L23-25: A majority (63%) of the analyzed samples averaged over a time period of 6 ± 2 months. The rest averaged over a shorter (26%) and longer (11%) time. Reads better this way?*

  We rephrase the sentence to:

  "The majority (63%) of the analyzed samples averaged over a time period of 6 ± 2 months. About a quarter of the samples (26%) averaged over a shorter time and 11% over a longer time."

- *P6L28: ...aerosol particles are activated to ice crystals by ...*

  Okay.

- *P6L30: The reviewer suggests the authors to briefly address the importance of droplet freezing. The question here is that - why was the droplet freezing mode selected and used rather than another? The readers would appreciate a justification.*

  We thank the reviewer for pointing this question out. First and foremost, immersion freezing is considered to be the most atmospherically relevant mechanism in heterogeneous ice nucleation for mixed-phase clouds (e.g Murray et al. (2012)). Moreover, using a droplet freezing assay (DFA) feels like the natural choice to study the ice nucleation ability of particles that are already immersed within ice core meltwater, especially considering that a DFA needs only few microliters of water. All other methods would require additional steps of particle generation (e.g. atomizer), which may introduce further contamination sources and would likely require more sample water. We added a few sentences to the manuscript:

  "We focused on the droplet freezing assay (DFA), because 1) immersion freezing is considered to be the most atmospherically relevant process in heterogeneous ice nucleation for mixed-phase clouds (e.g. Murray et al. 2012), 2) the use of a DFA seems to be the natural choice considering that the aerosol particles are already immersed within the ice core meltwater, 3) the technique requires only

a few mL of sample water, and 4) other methods would likely introduce further contamination sources through the particle generation setup (e.g. atomizer)."

- *P7L4-6: are → were (x3)*
  Okay.

- *P7L7: is decreased quickly → was quickly decreased*
  Okay.

- *P7L8: slowly lowered at...until all droplets were frozen.*
  Okay.

- *P7L10: is controlled → was measured (or was it really controlled?)*
  Okay.

- *P7L12: limit → minimize*
  Okay.

- *P7L13-16: Did the authors observe any half-or-less frozen droplets at given Ts? If so, how did the authors systematically judge the freezing moment/T?*
  The moment of freezing was registered automatically by the LabView software as freezing causes a significant change in brightness. However, sometimes the freezing of a droplet begins just as the images is saved. In these cases the software sometimes misses it, and would count the frozen droplet one image later. But we checked every image manually to account for this. However, it is possible that a droplet froze between two measurement images (which are 10 seconds apart). Therefore, the freezing temperature has an uncertainty of 1/6 °C at the freezing rate of 1 °C/min due to this effect.

- *P7L24-31: The reviewer thinks all future tenses should be changed to present.*
  Okay.

- *P7L30: Please provide an overall uncertainties in numeric terms, and discuss these here. The words "substantially" and "higher" seem too abstract.*
  We find it difficult to provide a general numeric uncertainty here, as individual freezing curves are substantially different from one another. Moreover, we cannot concisely predict how the cumulative INP concentration of a freezing curve would extrapolate at lower temperatures. Further, as stated in the text the underestimation is dependent on the temperature were the last droplet froze. For example, if sample a. was completely frozen at -24°C and sample b. at -28°C, the extrapolated cumulative INP concentration at -30°C would likely be much higher at sample a.

- *P8L2: The authors may want to recap the unique importance of 1977, 1680 & 1630 and provide the readers a brief justification of why they were picked for SEM analysis.*
  Unfortunately, as this was a novel measurement approach for us, the labor intensive SEM analysis was limited to a small number of samples in this study. We plan to increase the number of SEM samples future studies.

The three samples were selected for different reasons. The 1977 sample was selected as example for an IN active modern-era sample. The 1680 sample was selected, because it had an average INP concentration at -25°C and was in the middle of the time series. The 1630 sample was selected, because it showed extraordinarily high INP activity and we were interested to find out if we could identify the underlying reasons in the chemical aerosol signature of the sample.
We will add a short paragraph to the manuscript:
"The 1977 sample was selected exemplarily as an active modern-era sample. The 1680 sample was chosen for its average INP concentration at -25 °C, as well as being in the middle of the time series. The 1630 sample was analyzed with SEM, because it had an extraordinarily high INP activity at comparably warm temperatures."

- *Sect. 2.7: Briefly describe the operation conditions of SEM-EDX – beam intensity, WD, SS etc. Were these experimental variables all consistent for all analyses?*

  Yes, experimental variables were consistent for all three samples. We expanded the method description, which now reads:
  "For SEM-EDX analysis on each filter some 100 rectangular fields of about 100 µm x 100µm in the center of the filter were scanned and for all detected particles the size was determined and an EDX analysis (acceleration voltage: 20 kV, spot size: 4, acquisition time: 10 s, working distance: 10 mm) was performed. Using this procedure, particles down to approximately 250 nm were detected. Smaller particles will often be overlooked. This is also true for larger carbonaceous particles, because of their poor contrast on the polycarbonate filter."

- *P8L11-12: The reviewer suggests excluding "Smaller particles will...". Adding not much value to the section.*

  As reviewer 3 seemed to be confused which particles were collected for SEM analysis and which were likely lost during filtering, we think we should keep this sentence.

- *P8L16: review the state of the art of → reviewed several*

  Okay.

- *Sect. 2.8: In general, this section can be much more concise. Especially, P8L30-P9L2 seems containing repetitive information and, thus, could be excluded. Three most important sentences in this section are: P9L6 However,...; P9L7 Unfortunately,...; and P9L15 Therefore,... The reviewer suggests the authors to summarize the section by putting simple emphasis on these, and reduce the # of words. The reviewer defers to the point addressed in P9L18-21. No worries. The authors' method sounds.*

  We agree with the reviewer that the highlighted text passages are the most important sentences in this section. We understand that the presented approach of listing and addressing potential factors influencing the background signal is not strictly necessary and it may take the reader some time to find the most relevant bits concerning the actual measurement data. But we feel in that these uncertainties and measurement routines are often not clearly addressed in many publications. Also, this is the first first-author publication concerning the FRIDGE droplet freezing method, and we would like to be able to refer to this

method paper in our future publications. Therefore, we chose to be rather detail-oriented.

- *P10L19-20: This means as well... → This implies that INP concentrations may be higher in ice core samples than ambient INP concentrations at any given time. Or something similar?*

  We rephrase the sentence to:

  "This implies that INPs may be overrepresented in ice core samples compared to non-INPs or the ambient atmosphere at any given time."

- *P10L26-27: The reviewers agrees about INPs being preserved. The authors may add discussion of Beall et al. (Beall, C. M., Lucero, D., Hill, T. C., DeMott, P. J., Stokes, M. D., and Prather, K. A.: Best practices for precipitation sample storage for offline studies of ice nucleation, Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2020-183, in review, 2020.).*

  We thank to reviewer for the suggested literature, which we were not aware of. Thanks to this note and a concern shared by reviewer 2 and 3, we now feel that we need to highlight possible losses of (high temperature) INP activity due to storage effects. Although we ensured a frozen storage at our laboratory, the samples needed to be melted and refrozen several times prior to the IN measurements, possibly deactivating warm INPs and thus lowering the cumulative INP concentration. Text passages were added to:

  Page 9, line 30: "However, recent studies indicate that sample storage (i.e. storage temperature) significantly affects the ice nucleation activity of fresh precipitation samples in the range of -7 C to -19 °C (Beall et al., 2020). For example, samples stored at room temperature lost on average 72% of their INPs compared to the freshly analyzed samples. An average INP loss of 25% was still observed, even when samples were stored at -20 °C. Storage time did only weakly affect the INP concentrations. Therefore, based on this study a loss of INP activity on the order of a factor of 2 – 5 is possible, if not likely for the ice core measurements presented here. Furthermore, it is likely that the warmer end of INPs were disproportionally affected by these disturbances, while cold-temperature INPs were likely more robust. However, as all the samples experienced the same sample history, relative changes within the ice core can still be interpreted."

  Page 10, line 27: "However, as previously stated, storage conditions may have affected the INP activation."

- *P10L31-34: Not adding much value to the section. The reviewer suggests removing this part from the manuscript.*

  We recognize that the quote does not add much to the manuscript. Although, we like the quote, we deleted the sentence from the manuscript.

- *P11L3: Where does this 'an order-mag.' come from? Please clarify in the text for the readers.*

  We think we give ample explanations in sections 2.9 and 2.10 why the conversion to atmospheric concentrations is uncertain. The phrase signaling that the conversion "should be interpreted only as an order-of-magnitude estimation", is added to the text to highlight these uncertainties and to sensitize other researchers, which might want to use the data for atmospheric modelling, etc.

- *P13L3: The reviewer accepts the idea of conversion. If the authors are confident it is only +/- 50%, the reviewer suggests massively cut # of texts/words in this section. In general, this section is hard to follow. Spending full 2 pages to derive seems a simple sub-conclusion (i.e., P13L6-7) seems overwhelming. You may list the typical value of each variable (A, v_dry, and epsilon) +/- 'reasonable' upper/lower ranges (that correspond to shape a blue square in Fig. 4) in a table format to reduce # of total words. For that matter, the reviewer wonders if Fig. 4 is really needed and meaningful. A different presentation (again, tabular format) may be considered.*

  We shortened the text substantially and moved the extended version into the Supplement. However, we feel that a visual representation of the conversion factor depending on dry and wet deposition gives the reader a good idea about the sensitivity of those uncertain parameters. Therefore, we prefer Fig. 4 to a table and chose to keep it.

- *P13L13-15: This paragraph seems not fitting here.*

  Okay.

- *P13L28: very steep freezing → local maximum in – or something similar*

  We chose to keep the phrasing.

- *P13L29-30: → We verified a reproducibility of our results by confirming two separate measurements agreed each other. This verification eliminated the contamination during our FRIDGE measurements. Does this what the authors mean?*

  We rephrased the sentence. The manuscript now reads:

  "We verified our results by reproducing the measurement of this sample. The separate second measurement confirmed the strikingly different freezing characteristics, thus eliminating a contamination during the FRIDGE measurements themselves."

- *P14L4: → they showed a frozen fraction of only 0.7% on average.*

  Okay.

- *P14L7: average in ice concentration → average* N_{INPice}

  Okay.

- *P14L9: Here → At this temperature,*

  Okay.

- *P14L10: From here onward,... → Next, our characterization of INPs at -25°C is specifically discussed.*

  We rephrased the sentence. The manuscript now reads:
  "Henceforth, the discussion of results is focused on the characterization of INPs at -25°C specifically."

- *P14L11-12: ...every single sample... → all samples showed some droplet freezing events at this T.*

  Okay.

- *P14L14: , so the reader can see → in order to clarify*

  We rephrased the sentence. The manuscript now reads:
  "[...] in order to illustrate the typical variation in the INP concentration, while still allowing for easy identification of differences in the absolute INP concentration level."

- *P14L15: The reviewer suggests deleting ", but is still..." – not much value added.*

  See above.

- *P14L16: arise from → can be inferred from*

  Okay.

- *P14L17: delete "somewhat" and specify/clarify what include "more recent samples" in the main text.*

  Okay. The manuscript now reads:
  "We find on average higher and more variable INP concentrations for the last couple of decades as compared to the rest of the time series."

- *P14L22: Yet, → Nevertheless,*

  Okay.

- *P14L30 moderate yet significant → notable*

  We kept the phrasing as is, because we think our phrasing is more precise.

- *P14L34-P15L2: Delete 'however' and re-write the sentence to clarify what the authors mean to the readers.*

  We rephrased the sentence and moved Tab. 2 to the Supplement:
  "When the data is grouped into subsets according to Fig. 1, we find that the correlation weakens for the 10 year samples and the modern day samples, but increases for special event and seasonal samples (Tab. S2)."

- *P15L6: We like to point out here → It is noteworthy*

  Okay.

- *P15L11: That being said, going forward → Regardless,*

  Okay.

- *P15L12-14: "The four..." – the reviewer could not understand what it meant. Please rephrase and clarify the sentence.*

  The sentence was added to clarify that samples with the years 1960, 1970, 1980 and 1990 originally belonged to both subgroups (10 years and 1960 to 1990), but in the analysis presented they are only included in the 1960 to 1990 subgroup. We now see that the sentence is redundant and confuses the reader more than it helps, so we removed the sentence from the manuscript.

- *P15L14—16: → The observed difference between pre- and post-1960 samples is based on Subramanian (2019), which defines the 20th century as the beginning of the Anthropocene. Keep it simple, and delete "Note, however,..." – not much adding in.*

  The above cited literature is an article from the News Feature from Nature and does only report about the scientific debate about when to start the Anthropocene. We now added a solid reference. The manuscript now reads:
  "The observed difference between pre- and post-1960 samples is based on Zalasiewicz et al. (2011), who propose to define the middle of the 20th century as the beginning of the Anthropocene."

- *P15L17-19: But, then, excluding it also biases the authors' data... It is an important outlier, correct? It can be still excluded, but the reviewer suggests the authors to provide a better (and more constructive) justification to exclude it in the text.*

  We changed the text to:
  "Furthermore, we excluded the sample from 1630 in most of the following analysis in favor of more consistent freezing spectra. The statistical outlier is certainly important, as it was the only sample that was completely frozen before reaching -22 °C. At this state, however, we cannot explain what caused its high IN activity (cf. section 3.2). Moreover, as stated previously a contamination prior to the INP analysis cannot be excluded completely for this sample. Including the outlier does not change the general results."

- *P16L1: delete "seem to"*

  Okay.

- *P16L7: Only 36 particles for 1977. Please provide a justification for this small #.*

  On this filter only a very small number of particles were detected during the SEM analysis in the analyzed filter center region. The border regions were not analyzed, because of a higher risk of artefacts. The reason for the very low number is not known.
  Page 16, line 15 now reads:
  "For example, only a very small number of particles were detected on the 1977 sample in the analyzed center region of the filter. Generally, the border regions were not analyzed due to a higher risk of artefacts."

- *P16L11-13: Please provide reference(s). "will be feldspars" sound awkward. Please rephrase it.*

  Although EDX analysis does not allow an unambiguously mineralogical phase assignment, the typical elemental ratios (e.g. Al/Si ratio) and the content of minor elements in the alumosilicate particles allow at least an appraisal of the present silicate classes. In this case most of the detected alumosilicates are most

likely feldspars (sodium and potassium feldspars), amphiboles and pyroxenes. Besides this, some quartz and clay minerals are also present. For a more profound and detailed phase classification Transmission electron microscopic (TEM) investigations could be performed. Such kind of investigations require a specific sample preparation and are very time intensive.
We rephrased the mentioned sentence to:
"[...] most of the detected alumosilicates are most likely feldspars (and here more sodium and potassium feldspars), amphiboles and pyroxenes."

- *P16L16: How did the authors define "fly ash" through SEM-EDX? Reference(s)?*
  The fly ash definition in SEM analysis is strictly following the morphological analysis. If "perfect" melting spheres of refractive particles are detected the particles will be classified as fly ashes. For particle types with high melting points (silicates, metal oxides) no other particles source (as the high temperature process producing fly ashes) is known producing "perfect" spherical particles beside volcanic activities. But even when particles from volcanic activity can also show "spherical-like" morphologies, they differ strongly in morphology and mixing-state from fly ashes.
  However, not all fly ashes are spherical, therefore not all fly ashes, but only the spherical ones, can be classified/identified in SEM analysis.

- *P16L17: No notable difference found here might be due to limited # of particles analyzed, correct? If so, it should be stated in the text.*
  Correct. The manuscript now reads:
  "Otherwise there was no obvious distinction between the modern-era sample and the other two samples with regards to their chemical composition, which might be due to the limited number of particles analyzed."

- *P16L27-28: does seem to follow → shows*
  Okay.

- *P16L33-P17L7: The reviewer suggests the authors to soften the tone regarding the annual cycle. Yes. It is nice to see the seasonal cycle exists in this subset of samples, but the authors might need to be careful on not generalizing it as a bold conclusion here. The authors need to make it clear in the text in this particular section that this applies to only what they have analyzed for. Otherwise, please provide a proper justification why the authors believe the seasonal cycle could persist for other eras.*
  Okay. The manuscript now reads:
  "These findings suggest that the INP concentration in this year was subject to the annual dust input in Greenland. As the seasonal variability in particulate dust number can be clearly detected throughout the entire core, we expect that such a seasonal INP variability will hold for the entire record. Future high-resolution studies will have to test this assumption. Bory et al. (2002) show that the main dust source in Northern Greenland is the Taklamakan Desert in Northern China. At the beginning of the monsoon season, the dust particles are transported to Greenland within a few days via the jet stream and cause the annual maximum dust input for Greenland in spring."

- *P17L1: How about an episode of dust along with Atlantic Monsoon? How about Iceland etc.? Suggested reading: Iceland is an episodic source of atmospheric ice-nucleating particles relevant for mixed-phase clouds, Sanchez-Marroquin, https://advances.sciencemag.org/content/6/26/eaba8137.abstract*

  We thank the reviewer for suggesting the interesting article. We agree that both Saharan and Icelandic dust are possible (episodic) contributors to atmospheric INPs reaching the Arctic. However, the literature consensus suggests that the listed East Asian deserts and the described mechanism are largely responsible for the dust input in Greenland. Nevertheless, we added a sentence to the manuscript:

  "Furthermore, episodic dust transport from the Sahara desert (Lupker et al., 2010) and Iceland (Sanchez-Marroquin et al., 2020) may have contributed as well."

- *P17L30-P18L4: The reviewer appreciates the authors being careful, honest scientists by these statements here and elsewhere in the manuscript. Nonetheless, this part (right before the conclusion!) may give a very negative impression about the authors' study to the readers. Scattered concern statements throughout the manuscript bothers this reviewer, at the least. The authors may compile their concerns here and there regarding all uncertainties in Sect. 2.9 in a brief manner. The readers would understand that the results come with uncertainties, and the authors do not need to be too sensitive to sound.*

  We did not want to overly interpret the data as there are a number of uncertainties. Therefore, we were cautious when stating and discussing the findings in the manuscript. However, we understand the point the reviewer is trying to make.

  Regarding the issue of a potential post-coring contamination, we now reanalyzed some existing Abakus (particle diameter >1 µm) and SPES (single particle extinction and scattering instrument, particle diameter <1 µm) ice core data, which we like to share. The Abakus was used on the B17 and the EGRIP S6 ice core. On the S6 core we also used the SPES instrument, which was not yet available, when B17 was measured:

  Abakus: Analyzing the Abakus data of those two independent ice cores we find an average twofold increase of the mean background concentration of particles larger than 1 µm (but also in Ca^{2+}) in the top 8 m, which roughly corresponds to the time interval of 1960 – 1990, compared to deeper / older data. Already at 20 – 30 m (around 1900), where the firn is still porous, we do not see such an increase. The seasonality in the top 8 m is not as clean as in deeper intervals, which is to be expected as there are lots of breaks and wicking effects within the top 8 m. However, the seasonality is still detectable and comparable in amplitude to intervals below 20 m or even below 60 m (solid ice). Obviously, we cannot rule out contamination effects with absolute certainty, but the existence of a distinct seasonal variation is a valid argument that the observed increase in the dust concentration may be atmospheric.
  We will try to resolve the seasonality of the porous firn in future INP studies.

SPES: The SPES data from the S6 ice core looks quite different. For particles smaller than 1 µm we observed the average background concentration to increase by a factor of 4 – 5 within the top meters of the ice core. Furthermore, there was no seasonal signal within the top 100 years of the S6 ice core. Therefore, we conclude that for these smaller particles the post-coring contamination of the porous firn is severe. At this state, we do not know what kind of particles they are, but the mean diameter of the number size distribution is about 0.6 µm.

In conclusion, the INP results seem to agree sufficiently to the observations made by the Abakus, which sees an average twofold increase for the 1960 – 1990 interval in B17 (and S6). One could cautiously argue that therefore the INPs seem to reflect the mineral dust input of particles larger than 1 µm. However, as we have seen by the SPES data (from another ice core), a contamination effect is likely for particles smaller than 1 µm (and cannot be excluded completely for larger particles). As we did not observe the 4 – 5 times increase in INP concentrations as the SPES did for particles smaller than 1 µm, we expect that these contamination particles are no particularly active INPs in the investigated temperature regime, either due to their size, which might be substantially lower than 1 µm, or their surface structure, morphology or chemical composition, etc.
Regardless, we carefully read the manuscript again and removed some repetitious sections that mentioned a possible post-coring contamination, while adding to other text passages. Below we now list each instance, where the possible effect was mentioned, and describe if the passage was kept, removed or changed.

Abstract: "[...] or some post-coring contamination of the topmost, very porous firn."
We removed the text passage from this section.

Section 2.9: The effect was not yet mentioned.
We now introduce the effect in Section 2.9 (Other uncertainties).
Page 10, Line 4 now reads: "Specifically, we like to emphasize that the topmost part of the ice core is made up of relatively porous firn, which is more prone to post-coring contamination of dust during storage as compared to the rest of the ice core. Preliminary results of two particle counters (Abakus: spherical diameter > 1 µm, SPES: spherical diameter < 1 µm) from the B17 ice core (only Abakus) and the EGRIP S6 ice core (Abakus and SPES, 75.62° N, 35.97° W, 2702 m asl, C. Zeppenfeld, personal communication) suggest that a contamination effect is likely for particles < 1 µm and rather unlikely for particles > 1 µm. However, post-coring contamination still cannot be fully excluded for the latter measurements."

The effect was introduced in Section: 3.1: "It is noteworthy that the topmost part of the ice core is made up of relatively porous firn, which is more prone to post-coring contamination of dust as compared to the rest of the ice core. Unfortunately, we cannot entirely exclude the possibility that differences emerged or are enhanced due to post-coring contamination of the firn, as the ice core was stored for some time, despite the CFA decontamination technique."

We now only mention the effect shortly here.
Page 15, Line 7 now reads: "Unfortunately, despite the CFA decontamination technique we cannot entirely exclude the possibility that differences emerged or are enhanced due to post-coring contamination of the porous firn, as the ice core was stored for some time. Preliminary measurements (cf. section 2.9) found a twofold increase of particles larger 1 µm in the top 8 m (roughly the time interval of 1960 – 1990) compared to older intervals, which does seem to match the results observed by the INP measurements. Further, a distinct seasonality could be established for the dust measurements of the top layers, which argues against a strong contamination effect."

Later in 3.1 (after the revision): "If there was, however, only little influence by post-coring contamination and the latter two listed effects, the findings suggest that certain particles that are ice nucleation active in a mid-supercooled temperature regime may be more abundant in today's atmosphere."
We kept the mention of the effect here to transition to the next topic (i.e. which INPs could be enhanced in today's atmosphere).

Section 3.4: "However, we cannot fully rule out post-coring contamination as the cause for the observed differences."
We removed the text passage from this section.

Conclusions: "Alternatively, differences may have been caused by post-coring contamination, which is likely more relevant for these samples as they stem from the more porous firn layer."
We removed the text passage from this section.

- *P17L23: Fig. 11 tells the reviewer that the diversity may derive from the concentration and size of dry & wet deposited particles rather than the listed differences? The variability due to composition is ruled out in Sect. 3.2, correct? Please clarify.*

  The stated line gives possible explanations why our range and means of absolute INP concentrations are different from what Hartmann et al. (2019) observed in two Arctic ice cores. After reading the comments of all reviewers, we added storage effects to the list. Then, as we understand the reviewer refers in the comment to the diversity of INP concentrations that is observed in our data set specifically, which is another matter. We agree that the concentration and size of deposited particles are likely a driver of the INP concentration in the ice core. However, we don't think that the results of section 3.2 definitely rule the chemical composition of particles out here. We explicitly say that "[...] due to the low number of analyzed particles, we were unable to determine significant differences in particulate composition of the particles and size distribution in the three samples." The sentence now reads:
  "This disparity may arise from experimental (droplet volume, etc.), methodological (e.g. sample storage conditions) and or geographical differences, which may affect the deposition mechanisms and efficiency"

- *P18L11: particularly → significantly or substantially?*

  We chose the keep the phrasing.

- *P18L12: group → selected subset*

  Okay.

- *P18L14: recap and specify "certain aerosol species" here for the readers.*

  Okay. The manuscript now reads:

  "Furthermore, we found significant correlations between concentrations of INPs and the insoluble particle concentration > 1.2 µm, Ca2+ concentration and the conductivity for a broad range of temperatures."

- *P18L20: Delete "several mechanisms can be considered by which". The sentence makes sense without it.*

  Okay.

- *P18L31: The reviewer strongly agrees ☺*

- *P19: Perhaps, one of top priorities for the future ice core INP research includes the assessment of particle size distributions in liquid samples by DLS etc. The authors may elaborate it as an outlook? Connecting INP properties to aerosol propensities may resolve some raised concerns?*

  We agree with the reviewer that the proposed method of dynamic light scattering to gain information about the particle size distribution in liquid aerosol samples is certainly very interesting and promising. However, as far as we know, this method has not yet been tested in ice core studies. Furthermore, the low number of particles might be challenging for the instrument. We added a sentence to the manuscript:

  "[...] Furthermore, we plan to expand our ice core analysis to include a more rigorous, systematic study analyzing the chemical and morphological composition of insoluble aerosol particles as well as their size distribution by scanning electron microscopy. Particle size distributions of liquid samples may also be attainable by the dynamic light scattering and the single particle scattering and extinction method."

- *Tables 1 & 2: Add "Temperature (°C)" as the first column header, and delete °C from the send row.*

  Okay.

- *Table 2: What are "dust, volcanic and seasonal"? Please clarify within the table caption.*

  We added a reference to Fig. 1 (and moved Tab. 2 to the Supplement).

- *Fig. 1 caption: → Time coverage of the samples selected for assessing IN properties.*

  Okay.

- *Fig. 1 caption: longer → long*

  Okay.

- *Fig. 2: Adding the least active spectrum from the core sample (P9L14) may increase the visual importance of this figure.*

  Okay.

- *Fig. 3: The authors may superpose the 1:1 ratio line on top of the fit line. Doing such reinforce the authors' point in a visible manner.*

  Okay.

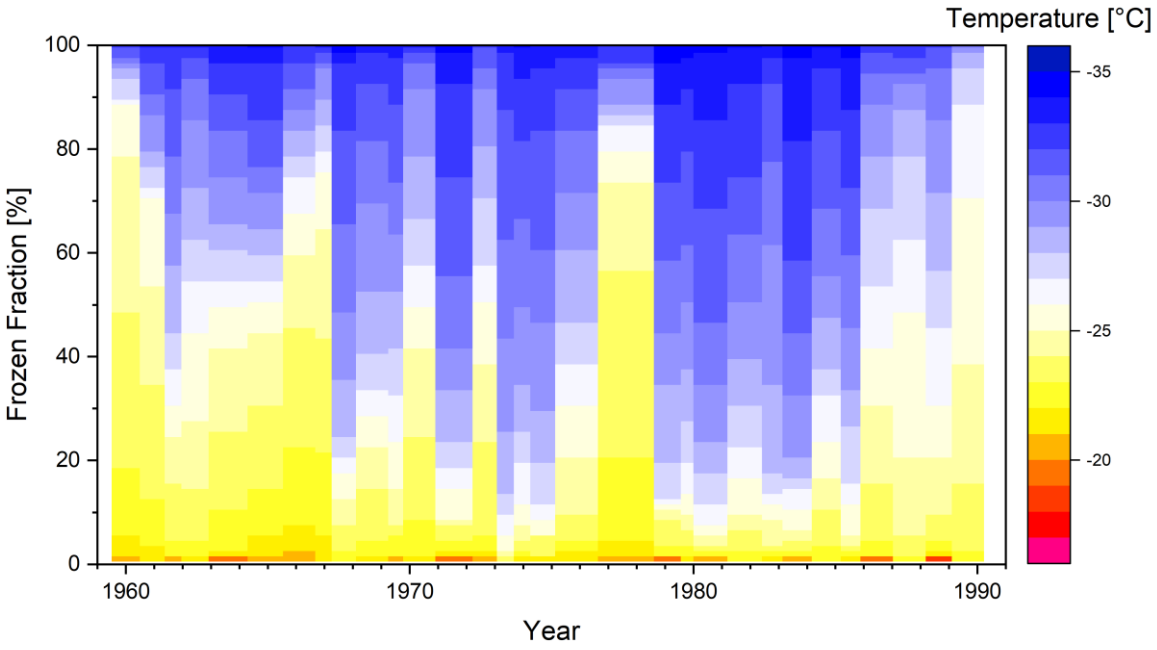
- *Fig. 6: INP /L ^-1_ atm/ or N_ INP_ atm? Perhaps, the authors may choose one way to improve the consistency throughout the manuscript.*

  Okay.

- *Fig. 7 caption: "However, data..." – the reviewer did not understand this. Please clarify.*

  The sentence points out that the underlying data (i.e. 31 samples that averaged over time periods of 0.24 years to 1.96 years, average 0.58 years, see Fig. 1b) was interpolated in time to create visually regular yearly columns of frozen fraction data, similar to what is presented in Fig. 5. After the interpolation 30 yearly columns are shown with the same width. We added the original (non-interpolated) data here and in the supplement (Fig S.2) for clarification. The caption of Figure 7 now reads:

  "However, data points are interpolated in time to generate yearly columns of regular width. The non-interpolated data is presented in Fig. S2."



- *Fig. 7 caption: Delete "Note, that".*

  Okay.

- *The reviewer enjoyed reading it. Hope some of suggestions/comments made here help the authors.*

  We are glad that the reviewer liked the manuscript. Again, we thank the reviewer for their valuable suggestions, which will definitely improve the paper.

Literature

Beall, C. M., Lucero, D., Hill, T. C., DeMott, P. J., Stokes, M. D., and Prather, K. A.: Best practices for precipitation sample storage for offline studies of ice nucleation, Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2020-183, in review, 2020.

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Response to Anonymous Referee #2

First of all, we thank the referee for submitting their helpful and productive annotations, which lead to improvements and clarifications within the manuscript.

We prepared a revised manuscript that addresses the questions and comments of the referees. Furthermore, below we explicitly respond to each of the items raised in the comments of anonymous referee #2. These comments are indicated in *italics,* whereas the author's response is presented in blue. Changes in the manuscript are given in green; changes to the supplement are given in purple. A response with "Okay." means we accepted the reviewers' suggestion and implemented it in the manuscript. The differences are also highlighted in separate PDFs using latexdiff. All line and page numbers refer to the ACPD manuscript version, not the revised manuscript.

Interactive comment on "Ice nucleating particle concentrations of the past: Insights from a 600 year old Greenland ice core" by Jann Schrod et al.

The authors have made a great effort in trying to reconstruct from the analysis of an ice core the atmospheric concentration of ice nucleating particles (INPs) in the atmosphere over Central Greenland between the years 1370 and 1990. It is only the second such attempt, after a similar but less comprehensive study published last year by another group. Overall, the manuscript is clearly written. Everything is well explained. The text is easy to follow. Data are arranged in a meaningful way in Tables and Figures. Half of the main text is description of methods. Interpretation of results is cautious, if not hesitant. It is here that I see some room for improvement, apart from a few other, minor issues.

The most surprising outcome of this study, from my point of view, is the narrow range of INP concentrations in ice and atmosphere during a period in which Earth has seen a tenfold increase in land area used for agriculture (Pongratz et al., 2008). Ploughing of the North American prairies and the Russian steppes during the past two centuries has greatly accelerated wind erosion with drastic consequences, like the harvest failure of 1891 in the Russian steppes (Moon, 2005) and the Dust Bowl situation in the USA during the 1930s. Also intensive grazing by exploding numbers of domesticated animals has had its share in fostering wind erosion during that time (Neff et al., 2008). Other than desert dust, soil dust from more fertile land carries INPs active at moderate supercooling (O'Sullivan et al., 2014). Therefore, I would have expected to see growing number concentrations of INP active at temperatures at around -15 °C or warmer in samples deposited over the last two centuries. However, this does not seem to be the case. Only 3% of all samples, each consisting of 0.5 mL of melted ice, contained INPs active at -15 °C. There are at least two plausible explanations for this observation. First, it could be that anthropogenically caused dust in the midlatitudes was not transported in detectable quantities to the Arctic and deposited in Central Greenland. The overwhelming majority of dust and INPs deposited in the Arctic probably originates from regions north of 60 °N in America and Eurasia, latitudes not much affected by landuse change in the past. Regions in North America located south of 60 °N probably contribute less than one percent to the total surface dust concentration in the Arctic (Groot Zwaaftink et al., 2016, Table 3 therein). Thus,

large-scale landuse change and increased wind erosion of fertile soils in the midlatitudes following the colonisation of North America by settlers mainly from Europe may indeed not have had a marked effect on INPs deposited in Central Greenland, although it clearly increased dust deposition in the midlatitudes (Neff et al., 2008).

We greatly appreciate the interesting and well-presented, detailed remarks, and suggested literature by the reviewer regarding the potential anthropogenically enhanced source of soil dust INPs. We fully agree to the statements made by the referee. We also list soil and desert dust due to desertification, land-use change, the expansion of agriculture and related practices, and consequently higher erosion rates as one of our main candidates for anthropogenic INPs (Page 3, lines 6 – 24). We added a paragraph to the discussion in section 3.1 (see following answer).

Another explanation for landuse change over the past centuries not being reflected in the INP record of the analysed ice core could be a loss of IN-activity, in particular the loss of biological INPs that dominate the spectrum at temperatures warmer -15 °C in ice or during sample preparation, in particular during melting of the core and while the samples were in liquid form. Since Hartmann et al. (2019) found clearly enhanced INP activity between -5 °C and -15 °C even in some older sample (year 1484), sample preparation may be the more relevant issue. It would be interesting to know the temperature on the hot side of the instrument in which the ice core was melted. Further, for how long, in total, were samples in liquid form between the first melting of the core and INP analysis? Evidence pointing at a partial loss of INPs is in Figure 9 of the manuscript in discussion. It shows from -30 °C to -24 °C increasingly larger INP concentrations in the modern, as compared to the older samples. The relative difference between modern and older samples collapses quickly towards the warmer end of the temperatures scale. I would have expected this difference to continue increasing further until the warmest temperature is reached at which INPs are detectable. Maybe there is no difference at warmer temperatures detectable today because INPs active above -22 °C had lost their activity before INP analysis? In my experience, any challenge put to a population of INPs, such as warming or storage in water, always leads first and foremost to a loss of those INPs that are active at the warmest temperature. The warm temperature "bulge" in a cumulative INP spectrum disappears with increasing severity or duration of a challenge, resulting in the cumulative spectrum approaching a linear shape on a log-scale. The same applies to certain mineral INPs (Harrison et al., 2016, their Figure 4a, top panel). Partial deactivation most likely results in the remaining part of the INP population becoming increasingly homogenous, a guess supported by Figure 8 in the discussed manuscript: the distribution of frozen fractions at a specific temperature was much narrower for the older samples (pre- 1960) as compared to the modern samples (1960 to 1990). The majority of fragile INPs, which may have been present at the time of deposition, and still are to some extent in the samples from 1960 onwards, may have been lost, leaving behind a relatively homogenous population of very stable INPs. To summarise, very limited dust transport from the midlatitudes, where most landuse change has happened in past centuries, and deactivation of INPs active at temperatures warmer than -20 °C may explain why the concentration of INPs (Murray et al., 2012). Deactivation might have happened during decades and centuries in the ice core is confined to a narrow range and does not reflect the growing human impact on land over the past few centuries. These considerations are of cause speculative, but I hope they encourage the authors to push their interpretation a bit further.

We thank the referee for their interesting and inspiring thoughts, and the encouragement to deepen our interpretation of the data. Both ideas presented by the reviewer appear probable to us. The reviewer's argument for a partial deactivation of

the warmer end of INPs from the interpretation of the freezing spectra and INP concentrations in Figs. 8 and 9 are convincingly portrayed. As a consequence we retraced the conditions of storage and melting of the samples as well as possible. In fact, we come to the conclusion that the suggested partial deactivation of INPs is at least possible. Although care was taken during and before INP measurements were made in our laboratory, sample vials may have been subject to temperatures between 0°C and room temperature for up to some tens of hours in total (during repeated cycles of melting and refreezing, supporting measurement, and transport). For example, during the CFA decontamination step the ice core is melted in the typically temperature range from 12 – 25 °C depending on the density of the ice and the desired meltspeed. Unfortunately, the exact times and temperature conditions during storage, etc. are difficult to assess in retrospect. We recognize the need to decrease the time samples were in an unfrozen state in future studies.

We added the following text passages to the manuscript:

Page 5, line 11: "Hence, it was ensured that samples remained frozen at all times in our laboratory. However, sample vials may have been subject to temperatures between 0 °C and room temperature for up to some tens of hours in total (during repeated cycles of melting, storage and refreezing, non-INP measurements, and transport, etc.)."

Page 9, line 30: "However, recent studies indicate that sample storage (i.e. storage temperature) significantly affects the ice nucleation activity of fresh precipitation samples in the range of -7 °C to -19 °C (Beall et al., 2020). For example, samples stored at room temperature lost on average 72% of their INPs compared to the freshly analyzed samples. An average INP loss of 25% was still observed, even when samples were stored at -20 °C. Storage time did only weakly affect the INP concentrations. Therefore, based on this study a loss of INP activity on the order of a factor of 2 – 5 is possible, if not likely for the ice core measurements presented here. Furthermore, it is likely that the warmer end of INPs were disproportionally affected by these disturbances, while cold-temperature INPs were likely more robust. However, as all the samples experienced the same sample history, relative changes within the ice core can still be interpreted."

Page 10, line 26: "Hartmann et al. (2019) come to the same conclusion that INPs are well preserved in an ice core and a reconstruction of their concentration for past climates is possible. However, as previously stated, storage conditions may have affected the INP activation."

Page 16, line 5: "Considering that the total global agricultural land area is estimated to have increased by a factor of 10 from 1400 to 1992 (Pongratz et al., 2008) combined with the fact that wind erosion has immensely accelerated within the last two centuries (Neff et al., 2008), partly due to intensive grazing by the heavily increasing number of domesticated animals, one could even have expected larger differences between the two data groups. Especially in the temperature range around -15 °C, at which soil dust INPs from fertile agricultural regions are known to be active (O'Sullivan et al., 2015). We can only speculate why we generally did not observe many INPs in this temperature range, and why the significant differences between the two data groups were only observed for temperatures below -22 °C. First, it is possible that dust from anthropogenic practices was not transported to Central Greenland in a detectable

amount. According to Groot Zwaaftink et al. (2016), most of the dust input contributing to the dust surface concentration of the Arctic is from Eurasia north of 60° N, North America north of 60° N and Asia south of 60° N. In contrast, North America and Europe south of 60° N, where land-use change and the agricultural expansion are most prominent, contribute only little to the Arctic dust input (below 1%). Moreover, Asian agricultural dust sources may not exhibit the necessary high wind speeds to inject mineral dust into the upper troposphere as required for long-range transport to Greenland. In contrast, mineral dust from the Taklamakan desert is intrinsically linked to dust storms in this area.

Second, the more fragile (biological) INPs may have been deteriorated during sample storage (Beall et al., 2020). As a result, the warm-end of INPs might have been largely lost, leaving only a homogeneous fraction of very stable INPs behind. Figures 8 and 9 present some evidence for this hypothesis. As seen in Fig. 8, we find a much narrower range of frozen fractions for the 10 year samples, hinting at a rather homogenous population of INPs. On the other hand, the variability is much higher for the modern-day samples, possibly because some of the more fragile INPs were still active. However, as both sample groups experienced the same sample history after coring, this hypothesis would only be reflected by deterioration effects related to the time elapsed since the particles were deposited in the ice. Furthermore, Fig. 9 depicts increasingly greater relative differences in the INP concentration from -30 °C to -24 °C until the warmer end of the data is reached, at which only few samples show ice nucleation activity. This observation could possibly be explained by assuming that the warmer INPs were largely deactivated due to storage effects."

Minor issues

- *Page 9, lines 19-20: I am always at a loss when told that results "...should be interpreted with care." Is not every interpretation or conclusion based on empirical evidence a preliminary one and absolutely true statements only to be found within closed systems (mathematics, logic)?*

  The reviewer is obviously right with their remark. The phrase in question is only added to sensitize the reader about the lower temperature part of the data, because we did not subtract a background as is otherwise common practice (Page 9, lines 6 – 17).

- *Page 9, line 32: Why use the number of frozen droplets and not the number of INPs in the assay (INPs in 195 droplets) as the criterion from which to estimate uncertainty?*

  We believe both phrasings mean the same thing. The most active INP within a droplet will initiate the freezing of said droplet. Therefore, the number of frozen droplets is related to the number of active INPs. The uncertainty specifies an upper and lower range in the number of droplets that are expected to freeze within a 95% confidence interval at a certain temperature.

- *Page 15, line 26: The data has a lognormal distribution. Was it log-transformed before the t-test?*

  The data was not log-transformed in the reviewed version of the manuscript. Transforming data yields similar results: We observed significant differences in

the average (log-transformed) INP concentration for -23 °C ($p < 0.00011$), -24 °C ($p < 0.000002$), -25 °C ($p < 0.00005$), -26 °C ($p < 0.0011$) and -27 °C ($p < 0.02$).

- *Conclusions section: Effects of INPs on cloud radiative properties are mentioned and I wonder whether the very small number concentrations found in the ice core, and the difference between 1960 to 1990 or before, are indeed in a range where they might lead to differences in radiative properties?*

  Answering this interesting question is beyond the scope of this paper. However, we believe it is worth exploring in future studies, e.g. by atmospheric modelling (page 19, line 13 – 15).

- *Regional sources and geographical differences in INPs may not only be accessible through the analyses of ice cores but also through modelling approaches making use of historical records of land cover.*

  We agree with the reviewer and refer to the very last sentence of our manuscript (Page 19, lines 13 – 15). The addition of modelling studies based on historical records of land cover definitely seems like an interesting approach, which we did not consider before. We modified the manuscript, which now reads:

  "Finally, a modeling study could help identify (possibly anthropogenically altered) INP source regions (e.g. based on historical records of land use cover) and estimate the potential atmospheric impact that could be expected from a threefold increase of INPs at −24 °C since the mid of the twentieth century, as it was seen in this study."

- *Figure 1b: Would it be possible to indicate the season for samples with time coverage below one year?*

  Unfortunately, the dating of the ice core is not precise enough to establish this information in an absolute sense. Furthermore, the seasonal distribution of snow fall is not known. See also the responses to reviewer 3 and the new Tab. S1 that entails the detailed sampling list (including the best estimate for the year and the sample averaging time).

- *Figure 2: I would like to see more than one background measurement.*

  We added more background freezing spectra to Fig. 2 (as well as the least active ice core freezing spectrum, as suggested by reviewer 1).

Literature

Beall, C. M., Lucero, D., Hill, T. C., DeMott, P. J., Stokes, M. D., and Prather, K. A.: Best practices for precipitation sample storage for offline studies of ice nucleation, Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2020-183, in review, 2020.

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Response to Anonymous Referee #3

First of all, we thank the referee for submitting their helpful and productive annotations, which lead to improvements and clarifications within the manuscript.

We prepared a revised manuscript that addresses the questions and comments of the referees. Furthermore, below we explicitly respond to each of the items raised in the comments of anonymous referee #3. These comments are indicated in *italics,* whereas the author's response is presented in blue. Changes in the manuscript are given in green; changes to the supplement are given in purple. A response with "Okay." means we accepted the reviewers' suggestion and implemented it in the manuscript. The differences are also highlighted in separate PDFs using latexdiff. All line and page numbers refer to the ACPD manuscript version, not the revised manuscript.

Interactive comment on "Ice nucleating particle concentrations of the past: Insights from a 600 year old Greenland ice core" by Jann Schrod et al.

Review of Ice nucleating particle concentrations of the past: Insights from a 600 year old Greenland ice core

In this study Schrod et al, present the ice nucleating particle (INP) concentrations from a Greenland ice core spanning the past 600 years. The collected data set shows that the concentration of INPs has been rather consistent over the past 600 years. However, since 1960, the concentration and variability in INPs has increased. This has led the authors to suggest that human activities may be influencing INP concentrations, which could have significant impacts on future cloud radiative forcing. I appreciate that the authors are very careful in not over interpreting their results and are very thorough in addressing potential issues with conversions and contamination. I support the publication of this manuscript and provide some minor technical revisions. Additionally, I think it would be very interesting to extend the analysis to investigate the role of changing atmospheric circulation and rising arctic temperatures may have on the observed changes in INP concentration in this ice core sample.

General comments:

Although all layers of the ice core were treated the same and likely experienced similar temperature variabilities while accumulating on the ice sheet, it would be worthwhile to mention the recently found impacts of the storage on INPs relative to freshly collected samples. For example see Beall et al., (2020) and Stopelli et al., (2014). As the long term storage of the INPs in the ice may contribute to the observed difference between the ice core samples and precipitation samples shown in (Petters and Wright, 2015).

> We thank the referee for directing our attention to potential storage effects. In fact, all reviewers agree that sample storage may have an important impact to the INP activity of the ice core samples. We now address this effect on several instances throughout the manuscript:

Page 5, line 11: "Hence, it was ensured that samples remained frozen at all times in our laboratory. However, sample vials may have been subject to temperatures between 0 °C and room temperature for up to some tens of hours in total (during repeated cycles of melting, storage and refreezing, non-INP measurements, and transport, etc.)."

Page 9, line 30: "However, recent studies indicate that sample storage (i.e. storage temperature) significantly affects the ice nucleation activity of fresh precipitation samples in the range of -7 °C to -19 °C (Beall et al., 2020). For example, samples stored at room temperature lost on average 72% of their INPs compared to the freshly analyzed samples. An average INP loss of 25% was still observed, even when samples were stored at -20 °C. Storage time did only weakly affect the INP concentrations. Therefore, based on this study a loss of INP activity on the order of a factor of 2 – 5 is possible, if not likely for the ice core measurements presented here. Furthermore, it is likely that the warmer end of INPs were disproportionally affected by these disturbances, while cold-temperature INPs were likely more robust. However, as all the samples experienced the same sample history, relative changes within the ice core can still be interpreted."

Page 10, line 26: "Hartmann et al. (2019) come to the same conclusion that INPs are well preserved in an ice core and a reconstruction of their concentration for past climates is possible. However, as previously stated, storage conditions may have affected the INP activation."

Page 16, line 5: "Considering that the total global agricultural land area is estimated to have increased by a factor of 10 from 1400 to 1992 (Pongratz et al., 2008) combined with the fact that wind erosion has immensely accelerated within the last two centuries (Neff et al., 2008), partly due to intensive grazing by the heavily increasing number of domesticated animals, one could even have expected larger differences between the two data groups. Especially in the temperature range around -15 °C, at which soil dust INPs from fertile agricultural regions are known to be active (O'Sullivan et al., 2015). We can only speculate why we generally did not observe many INPs in this temperature range, and why the significant differences between the two data groups were only observed for temperatures below -22 °C. First, it is possible that dust from anthropogenic practices was not transported to Central Greenland in a detectable amount. According to Groot Zwaaftink et al. (2016), most of the dust input contributing to the dust surface concentration of the Arctic is from Eurasia north of 60° N, North America north of 60° N and Asia south of 60° N. In contrast, North America and Europe south of 60° N, where land-use change and the agricultural expansion are most prominent, contribute only little to the Arctic dust input (below 1%). Moreover, Asian agricultural dust sources may not exhibit the necessary high wind speeds to inject mineral dust into the upper troposphere as required for long-range transport to Greenland. In contrast, mineral dust from the Taklamakan desert is intrinsically linked to dust storms in this area.

Second, the more fragile (biological) INPs may have been deteriorated during sample storage (Beall et al., 2020). As a result, the warm-end of INPs might have been largely lost, leaving only a homogeneous fraction of very stable INPs behind. Figures 8 and 9 present some evidence for this hypothesis. As seen in Fig. 8, we find a much narrower range of frozen fractions for the 10 year samples, hinting at a rather homogenous population of INPs. On the other hand, the variability is much higher for the modern-

day samples, possibly because some of the more fragile INPs were still active. However, as both sample groups experienced the same sample history after coring, this hypothesis would only be reflected by deterioration effects related to the time elapsed since the particles were deposited in the ice. Furthermore, Fig. 9 depicts increasingly greater relative differences in the INP concentration from -30 °C to -24 °C until the warmer end of the data is reached, at which only few samples show ice nucleation activity. This observation could possibly be explained by assuming that the warmer INPs were largely deactivated due to storage effects."

As each of the samples used to probe the concentration of INPs every 10 years only covers a period of 6 months, is the 6 month period roughly the same for each of the 10 yr samples? Based on Fig. 6, the variability over a year (monthly sample from 1463-64) looks to be about an order of magnitude. Therefore, if the 6 months covered by a 10 yr sample differs, some of the variability between the 10 yr samples, albeit a small amount, could be explained.

Theoretically, we selected the sample vials for the 10 year time series, whose midpoints were closest to the same season of a year (e.g. 1950.0). However, the uncertainty in the dating of the ice core effectively does not allow to assume that each sample corresponds to the same season (also the "sample resolution" varies to some degree, see Fig. 1b). Therefore, we agree to the referee that some part of the overall variability can be explained by possibly comparing different times of a year. We added a table to the supplement entailing the sample list (Tab. S1; sample number, depth, estimated year, representative time average, data subset). Also see the following answer. We added a sentence to page 6, line 9:

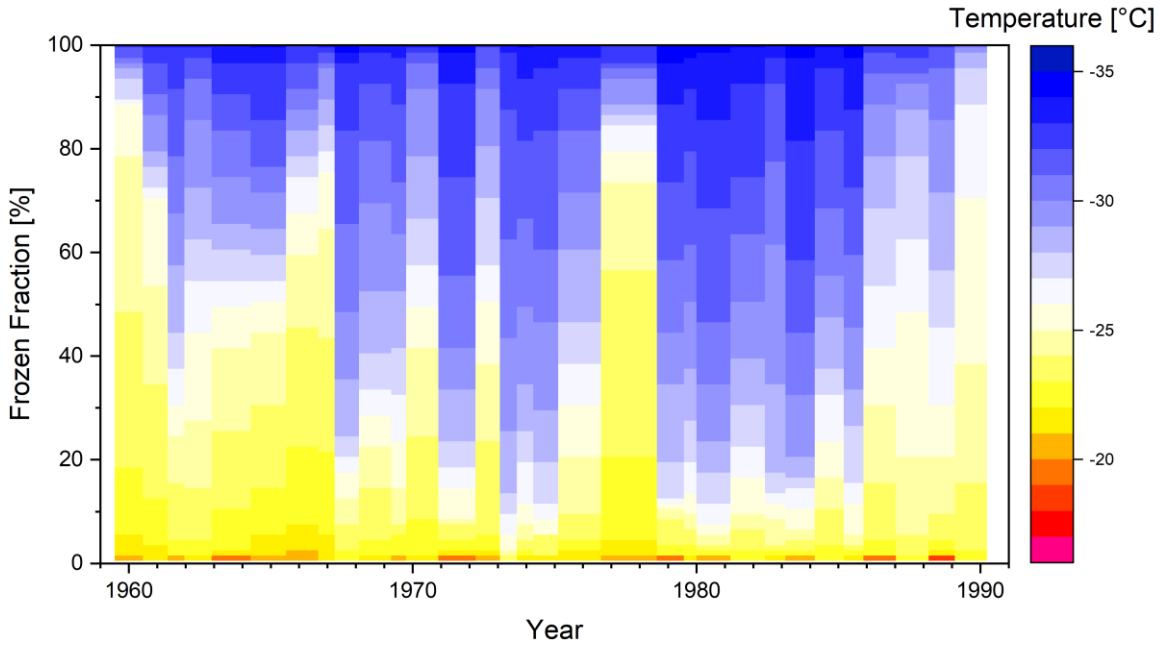
"Whenever possible, we selected samples that theoretically represented the same season(s). However, due to the uncertainty in the ice core dating some of the variability in the INP concentration may be attributed to seasonal differences."

The same question is also relevant for the modern day samples (Fig. 7) where there are some years with higher activity than others. It would be important to know if the yearly samples (actually only 6 months) cover the same 6 month period for each year.

The same procedure was applied to the modern day samples. However, due to the higher sampling frequency of the modern day samples the number of samples to choose from was lower. Accordingly, there is somewhat more diversity to be expected for this group with regards of the averaged seasons. We added a few words to page 15, line 10:

"Furthermore, the results could potentially be intrinsically influenced to some degree by differences in sampling frequency and time coverage, as well as samples representing different seasons of the year."

On a related matter we now added an alternative figure to the Supplement (Fig. S2), similar to Fig. 7, but with the original (non-interpolated) time coverage:



Here it is shown that the Anthropocene samples are significantly different from the preindustrial samples. This is a very interesting finding and something that the authors suggest may be due to a change in the dust due to desertification, and other anthropogenic related aerosols that reach the Greenland ice sheet. Although these seem like possibilities, it would be interesting to discuss the potential influence from changes in atmospheric circulation patterns such as the NAO (Pinto and Raible, 2012).

> We regard changes in the emission strength much more likely than changes to atmospheric circulation patterns. To our knowledge, there is no clear evidence from aerosol tracers or models suggesting that there were strong anthropogenic circulation changes in Greenland yet. However, some changes in transport patterns cannot be entirely disregarded. In fact, we address this on page 10, line 4 – 8. Related effects on dry and wet deposition, which may be caused by a change in atmospheric transport patterns, and the relevance to the interpretation of the INP results are described on page 11, line 20 – 24. Also see following answer.

Additionally, it has been shown that precipitation effectively removes precipitation (Stopelli et al., 2015) and as the ice core site is at a high altitude arctic site, it may be extremely sensitive to the temperature and amount of precipitation that falls (removal of INPs) upstream of the site. The fact that an overall increase in IN activity has been observed in more recent, warmer years may be consistent with warmer air masses precipitating over the ice sheet where fewer INPs have been removed upstream compared to previous (colder) years. Therefore, it may be worthwhile to compare the INP concentrations with the reconstructed temperature record over the same period from the ice core.

> We assume the first sentence was meant to read: "it has been shown that precipitation effectively removes INPs" (?). We recognize that temperature and precipitation are two dominant factors determining the deposition efficiency and therefore the amount of INPs in the accumulated snow (see sections 2.9 and 2.10). The suggested idea to compare the warming climate via a reconstructed temperature record to the INP concentration is definitely an interesting thought. Yet, we feel it is beyond the scope of this manuscript and could be explored further in a follow-up study, which might include a modelling aspect.

We added a paragraph to the discussion in section 3.1 including the last two points of the referee:

"Now the question arises, what factors may have caused these significant differences in INP concentrations. Several hypothetical explanations come to mind. First, the changing climate may have influenced both the deposition pathways and their efficiencies (cf. sections 2.9 and 2.10). But, at least locally, the accumulation rate at B17 does not show a change between modern and pre-industrial times. Further, changes to relevant large-scale atmospheric circulation patterns are essentially unknown for the investigated time period. [...]"

Minor comments:

- *Page 3, line 3: Consider adding the following references: Grawe et al., (2016, 2018); Kanji et al., (2020); Ullrich et al., (2016)*

  Okay.

- *Page 3 line 14: Consider adding the following references: Hill et al., (2016); Steinke et al., (2016)*

  Okay.

- *Page 3 line 20: It is highlighted here that the dominant dust sources in Greenland ice cores come from Chinese deserts and the Taklamakan. Therefore, it would be worthwhile to discuss the observed ability of these mineral dusts to act as INPs. Do they match in terms of INA with the observed INPs found in the ice cores (it seems like they do)? Consider mentioning previous studies on INPs from this region such as Boose et al., (2016); Field et al., (2006); Paramonov et al., (2018); Ullrich et al., (2016).*

  We agree that a short discussion about the ice nucleation activity of the mineral dust from the relevant desert regions is an interesting addition. We thank the reviewer for the suggested literature. The manuscript now reads:

  "Mineral dust from China, and the Taklamakan desert in particular, has been characterized in several laboratory ice nucleation studies (Field et al., 2006; Niemand et al., 2012; Boose et al., 2016; Ullrich et al., 2017; Paramonov et al., 2018), which revealed a relatively high ice active site density in the temperature range below -25 °C, comparable to other natural deserts such as the Sahara (e.g. Niemand et al., 2012; Boose et al., 2016)."

  It is, however, difficult to assess how well these laboratory measurements with pure dust from the Chinese deserts match to the observed INP spectra in the ice core. Most times, laboratory studies provide the active site density n_s as their metric for ice nucleation activity. We don't have a good enough characterization of aerosol particles within the ice core samples to estimate a reliable n_s value, which makes the comparison difficult. Assuming that all particles counted by the CFA measurements have a spherical diameter of 1.2 µm we can estimate the active site density to be on average $1.5 \pm 6.1 \times 10^{10}$ m^{-2} (range: $1.4 \times 10^{8} - 6.3 \times 10^{11}$ m^{-2}) at -25 °C and $8.4 \pm 13.3 \times 10^{10}$ m^{-2} (range: $4.4 \times 10^{9} - 1.0 \times 10^{12}$ m^{-2}) at -30 °C. Obviously, this assumption is flawed, as there will be smaller particles that could not be counted by the CFA measurements, which would add to the total aerosol surface area, as well as

particles that were larger than 1.2 µm, which were here assumed to have this lower size. However, the estimated n_s values are indeed in the range of those presented in the literature for the Taklamakan desert and other Chinese deserts. We added a paragraph to section 3.4:

"Moreover, evidence presented in section 3.3 and Tab. 1 indicated that the long-range transported dust from East Asian deserts influenced the freezing characteristics of the ice core samples. Laboratory studies characterizing the ice nucleation activity of mineral dust from the Taklamakan desert and other Chinese deserts report active site densities ns at -25 °C of approximately 1 x 10^{10} m^{-2} (Niemand et al., 2012; Ullrich et al., 2017) and between 1 x 10^{10} to 1 x 10^{11} m^{-2} at -30 °C (Niemand et al., 2012; Boose et al., 2016; Ullrich et al., 2017; Paramonov et al., 2018). We can only roughly calculate n_s from the CFA particle measurements. Lacking a solid particle size distribution measurement, we assumed all counted particles to have a spherical diameter of 1.2 µm. This assumption is obviously flawed, as particles smaller than 1.2 µm were not counted by the CFA measurements, and larger particles were assumed to have this lower size. With this rough assumption, we find an average n_s of 2 ± 6 x 10^{10} m^{-2} at -25 °C and 8 ± 13 x 10^{10} m^{-2} at -30 °C, which is in surprisingly good agreement with the literature."

- *Page 6 line 14: change "must" to "does"*

  Okay.

- *Page 6 line 20-21: why was the seasonal variability explored in the 1463? Is there a reason for choosing this period? Wouldn't a more recent year make it easier to identify the months of the year as the ice is less compact?*

  There was no particular reason why the year 1463 was explored specifically other than opportunity. The INP analysis was done after CFA and IC measurements were already performed. Particularly, the CFA decontamination step determined the resolution of the samples. There were only two periods with samples of near monthly resolution (average: approx. 10 samples per year) from which seasonal cycles could be established: 1744 – 1763 and 1454 – 1468). The latter period was chosen for being unaffected by the industrial revolution. The exact samples were chosen more or less at random. (The chosen samples were in the center of the period and preliminary CFA data showed a clear annual signal.) But we agree with the reviewer that it would be very interesting to investigate the seasonal resolution of more recent years in future studies (also see page 19, lines 2 – 4). We added a sentence to page 16, line 3:

  "There was no particular reason why this year was explored specifically. As the CFA decontamination step determined the resolution of samples, there were two periods with samples of near monthly resolution from which seasonal cycles could be established (1744 – 1763 and 1454 – 1468). The latter period was chosen for being unaffected by the industrial revolution."

- *Page 6 line 28: "hast" should be "has"*

  Okay.

- *Page 7 line 5: consider rephrasing "picked up" to "pipetted"*

  Okay.

- *Page 7 line 7-8: Why is FRIDGE kept at 14 C initially? Based on what was stated earlier, the samples were defrosted at 6 C, so why wasn't FRDIGE set to 6 C to minimize the temperature range a sample was exposed to. Granted, all of the samples experienced the same treatment so this likely has no impact on the overall comparison between samples.*

  The initial temperature was set to 14 °C for practical reasons and is based on the experience of the operators. While pipetting the droplets, the chamber needs to be partially opened. When the chamber is open the flow of dry synthetic air did sometimes not suffice to prevent condensation on the surface of the wafer substrate if the temperature was set to a cooler temperature (depending on ambient conditions). Overall, we don't think that the short amount of time during pipetting altered the freezing spectra substantially. (However, other storage effects may be more relevant, see other responses and specifically the comments of reviewer 2.)

- *Page 7 line 8-10: Do you mean that the Lauda cryostat was used to dissipate heat from the Peltier element. Please rephrase this sentence to make that clearer.*

  Yes. The manuscript now reads:
  "The temperature ramp was implemented by a PID-controlled Peltier element. A cryostat (Lauda, Ecoline Staredition RE110; ethanol coolant) was used to dissipate the heat from the Peltier element."

- *Page 7 line 11: Does the synthetic air flush change the size of the droplets during the experiment via evaporation? If yes, would this be significant enough to increase the concentration of solutes in a droplet such that it may lead to a freezing point depression in the samples? In theory, the colder the cell gets (the longer the experiment lasts) the more concentrated these solutes would become.*

  Judging from measurement images we can't say for sure if or how much of the droplet size is shrinking due to evaporation. As for freezing point depression, CFA and IC measurements indicate that solutes such as Na^+ and Ca^{2+} are on the order of 10 to 100 ng/mL, which is very low. We agree to the referee that the possible effect of a freezing point depression will increase with shrinking droplet size, however we don't think this will have a significant effect on the overall results.

- *Page 7 line 18: Here you mention mL of meltwater but then use mLice when reporting INP concentrations. Consider making the terminology consistent.*

  Okay.

- *Page 8 line 6: Why was the SEM analysis conducted on the samples after being filtered (400 nm pore size) when the highest correlation between INP concentration and particles concentrations was for particles larger than 1.2 microns? Do these large particles make it through the filter?*

  We believe, the reviewer misunderstood the SEM preparation procedures: The sample water was pumped through a 400 nm pore size filter using a water jet vacuum. Then these filters were then analyzed with SEM. Large particles will therefore be present during the SEM analysis, whereas smaller particles will be lost.

- *Page 8 line 27: Check if "microscopical" should be "microscopic" in this case.*

  Okay.

- *Page 9 line 29: Here it is mentioned that the freezing and melting of the same droplets does not influence the ice nucleating ability of the samples. As previously mentioned in the general comments, it might be worthwhile to mention other studies where it was shown that over longer periods, the storage and repeated melting and freezing of samples influenced the ice nucleating ability of samples.*

  We thank the reviewer for pointing out the possible deactivation of INPs by storage, etc. We will add to the manuscript at the suggested lines (and elsewhere):

  "However, recent studies indicate that sample storage (i.e. storage temperature) significantly affects the ice nucleation activity of fresh precipitation samples in the range of -7 °C to -19 °C (Beall et al., 2020). For example, samples stored at room temperature lost on average 72% of their INPs compared to the freshly analyzed samples. An average INP loss of 25% was still observed, even when samples were stored at -20 °C. Storage time did only weakly affect the INP concentrations. Therefore, based on this study a loss of INP activity on the order of a factor of 2 – 5 is possible, if not likely for the ice core measurements presented here. Furthermore, it is likely that the warmer end of INPs were disproportionally affected by these disturbances, while cold-temperature INPs were likely more robust. However, as all the samples experienced the same sample history, relative changes within the ice core can still be interpreted."

- *Page 12 line 22: Remove extra "/" after gprecip in first term of equation*

  Okay.

- *Page 14 line 8: please specify that this is the concentration at -20 C as mention of -20C comes two sentences earlier.*

  Actually, page 14, line 8 gives the INP concentration at -25°C, which is mentioned two sentences earlier. We believe the structure of the paragraph is clear without repeating the temperature in every sentence.

- *Page 16 line 10-11: How do these large particles make it through the 400 nm pore sized filters described in the methods?*

  See comments above.

- *Page 16 line 27: Here it is mentioned that there is a seasonal cycle in INP and although the variability is significantly less than the over the entire period of the study, it may be worth mentioning if the 6 month samples are taken to over the same 6 months in every time point (as said in the general comments).*

  See comments above.

- *Page 17 line 15-25: Could some of the differences in the INP concentrations be due to the droplet size used in the studies? Perhaps the small droplet volume in this study makes the measurement of rarer INPs less quantifiable. Additionally, could location differences between sampling sites, lead to differences in the number and efficiency of INPs removed upstream of the sites (Stopelli et al., 2015). For example, Svalbard often experiences periods of relatively warm air masses laden with INPs that would*

precipitate out before reaching the high altitude location of this core. These points, although briefly mentioned, could be expanded on.

Drop size used in Hartmann et al. (2019) was 1 µL (LINA) and 50 µL (INDA). Our droplet size of 2.5 µL was therefore somewhere in the middle of those. We therefore think that the droplet size should not have biased the comparison greatly. Of course, the droplet size determines the effectively observed freezing range, but in the Vali (1971) equation of the cumulative concentration it is accounted for. However, generally speaking we agree to the reviewer that a small droplet volume might make it less likely for rare INPs to be quantifiable.

Geographical differences on the INP number and deposition efficiency between the core sites are well within the realm of possibility. Additionally, we now add possible storage effects as a further possible reason for the different concentration range observed. We expanded upon the lines, which now read:

"This disparity may arise from experimental (droplet volume, etc.), methodological (e.g. sample storage conditions) and or geographical differences, which may affect the deposition mechanisms and efficiency."

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Ice nucleating particle concentrations of the past: Insights from a 600 year old Greenland ice core

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Abstract.

Ice nucleating particles (INPs) affect the microphysics in cloud and precipitation processes. Hence, they modulate the radiative properties of clouds. However, atmospheric INP concentrations of the past are basically unknown. Here, we present INP measurements from an ice core in Greenland, which dates back to the year 1370. In total 135 samples were analyzed with the FRIDGE droplet freezing assay in the temperature range from $-14\,^{\circ}\mathrm{C}$ to $-35\,^{\circ}\mathrm{C}$. The sampling frequency was set to 1 in 10 years from 1370 to 1960. From 1960 to 1990 the frequency was increased to 1 sample per year. Additionally, a ~~number of~~ few special events were probed, including volcanic episodes. The typical time coverage of a sample was on the order of a few months. Historical atmospheric INP concentrations were estimated with a conversion factor, which depends on the snow accumulation rate of the ice core, particle dry deposition velocity and the wet scavenging ratio. Typical atmospheric INP concentrations were on the order of $0.1\,\mathrm{L}^{-1}$ at $-25\,^{\circ}\mathrm{C}$. The INP variability was found to be about $1-2$ orders of magnitude. Yet, the short-term variability from samples over a seasonal cycle was considerably lower. INP concentrations were significantly correlated to some chemical tracers derived from continuous flow analysis (CFA) and ion chromatography (IC) over a broad range of nucleation temperatures. The highest correlation coefficients were found for the particle concentration (spherical diameter $d_p > 1.2\,\mu\mathrm{m}$). The correlation is higher for ~~the~~ a time period of seasonal samples, where INP concentrations follow a clear annual pattern, highlighting the importance of the annual dust input in Greenland from East Asian deserts during spring. Scanning electron microscopy (SEM) ~~of single particles retrieved from~~ analysis of selected samples found ~~particles of soil origin~~ mineral dust to be the dominant particle fraction, verifying ~~the significance of mineral dust particles~~ their significance as INPs. Overall, the concentrations compare reasonably well to present day INP concentrations, albeit they are on the lower side. However, we found that the INP concentration at medium supercooled temperatures differed before and after 1960. Average INP concentrations at $-23\,^{\circ}\mathrm{C}$, $-24\,^{\circ}\mathrm{C}$, $-25\,^{\circ}\mathrm{C}$, $-26\,^{\circ}\mathrm{C}$ and $-28\,^{\circ}\mathrm{C}$ were significantly higher (and more variable) in the modern day period, which could indicate a potential anthropogenic impact~~or some post-coring contamination of the topmost, very porous firn.~~, e.g. from land-use change.

1 Introduction

Ice cores offer an unparalleled opportunity to study atmospheric conditions of the past. The physico-chemical state of the atmosphere is recorded and preserved for many atmospheric constituents in the form of entrained gas bubbles and aerosol particles. Fittingly, ice core archives have been dubbed *a window into the past* by scientists and media alike. Over the past decades, many different parameters and proxies have been measured in ice cores using a diverse set of techniques from a variety of scientific fields. Unfortunately, ~~the very property that enables most of~~ heterogeneous ice nucleation, which is of primary importance to atmospheric ice formation ~~in the first place, i.e. heterogeneous ice nucleation,~~ and therefore very relevant to Polar snow accumulation, has not received much attention ~~with regards to ice core studies. As of today~~in ice core sciences. To date, there has been only a single study to analyze the concentration of ice nucleating particles (INPs) from ice cores (Hartmann et al., 2019). Yet, this parameter is vitally important from an atmospheric science and climate-modelling perspective, since it strongly influences cloud formation and modulates precipitation processes. Mülmenstädt et al. (2015) confirmed that the majority of global precipitation is produced in clouds involving the ice phase. Moreover, INPs influence the phase of a cloud and in turn interact with radiation processes (Lohmann, 2015).

There is a number of open questions regarding the nature of INPs: their geographical and vertical distribution, seasonal variation, as well as the types of aerosol particles that contribute to their population even in today's atmosphere. Hence, it is hardly surprising that very little knowledge exists about the pre-industrial concentrations and sources of INPs. Carslaw et al. (2017) reviewed the state of aerosols in the pre-industrial atmosphere. However, they did not discuss this specific matter in depth, because "our understanding of global ice-nucleating particles in terms of particular aerosol components is only just emerging" (Carslaw et al., 2017). They conclude that a potential change in INP concentrations since the pre-industrial period remains entirely ~~open~~possible, as are related impacts on cloud formation, precipitation processes and the radiation budget. ~~Albeit~~Also, knowledge about the pre-industrial baseline of cloud-active aerosols is essential for climate modelers, as – together with the scattering and absorption properties of the aerosol – it ~~defines~~ constrains the baseline upon which the current radiative forcing by anthropogenic aerosols is calculated. In fact, climate models are highly sensitive to the pre-industrial aerosol conditions (Andreae et al., 2005; Carslaw et al., 2013). As a consequence, a lack of knowledge of the pre-industrial aerosol state leads to large uncertainties when radiative forcings are estimated.

Many modeling studies exist, which suggest that general aerosol characteristics have changed significantly since pre-industrial times, such as aerosol composition, number concentration, size distribution and mixing state (e.g. Stier et al., 2006; Tsigaridis et al., 2006; Hamilton et al. , 2014). ~~Although usually not as straightforward~~Evidently, this trend ~~can be seen~~ is implied in ice core observational data for black carbon (McConnell et al., 2007; Kaspari et al., 2011) and various other trace elements and aerosols (Kaspari et al., 2009; Carslaw et al., 2017, and references therein). Yet, the ~~literature consensus indicates that~~ significance of anthropogenic pollution particles to atmospheric ice nucleation is still in question. Recently, Zhao et al. (2019) investigated the effects of pollution aerosol to the ice phase in moderate and strong convective systems in a top-down approach using a combination of satellite observations and model simulations. They present evidence that in the moderate convection case, where heterogeneous ice nucleation is more relevant, the ice particle effective radius

is increased, indicating that continental pollution aerosol may in fact contain a considerable fraction of INPs. On the other hand, further experimental studies suggest that most anthropogenic aerosol particles are typically poor INPs. For example, Chen et al. (2018) found that the heavy air pollution of Beijing did not affect the INP concentration in this urban setting in the investigated temperature range from −6 °C to −25 °C. ~~However,~~ Overall, there are still few studies available on the ice nucleation efficiency of anthropogenic aerosol and some of the presented evidence is conflicting. Although pure pollution aerosols are considered rather inactive INPs, this does not per se mean that the INP population as a whole has not changed at all over the last centuries. On the contrary, it seems rather likely that certain particles with ice nucleating potential may in fact be more abundant in today's atmosphere. Biomass burning aerosol is probably the most uncertain and least likely contributor ~~here~~to anthropogenic INPs. Both the magnitude and sign of a potential anthropogenic change in global fire emissions since the pre-industrial period is the subject of active scientific debate (Hamilton et al., 2018, and references therein). Moreover, the literature is still ~~split~~ divided about the ice nucleating capability of aerosol particles from biomass burning ~~(Twohy et al., 2010; McCluskey et al., 2014; Umo et al., 2015; Levin et al., 2016)~~(or soot in general) (Twohy et al., 2010; McCluskey et al. . Anthropogenic metal enriched particles from industrial processes (e.g. from coal combustion, mining, smelting, etc.) have been consistently found in the Arctic during Arctic Haze events (e.g. Shaw, 1995). Such heavy metals appear regularly as a small fraction of ice residuals in field experiments (Ebert et al. , 2011; Eriksen Hammer et al. , 2018). The most likely candidate for INPs, however, may actually be soil or desert dust particles from areas that may have been subject to land-use change and desertification since the pre-industrial times. The IPCC Special Report Climate Change and Land (IPCC, 2019) estimates that 12 – 14 % of today's global ice-free land surface are croplands. Intensive and extensive pasture land as well as savannahs and shrublands used for livestock farming make up another 30 – 47 %. Due to the expansion of these agricultural areas as well as the practices themselves, the erosion of these agricultural soils is increasing. In fact, it is estimated that soil erosion is currently between 10 – 100 times higher (depending on tillage) than the natural soil formation rate (IPCC, 2019). Eroded soil particles may enter the atmosphere and potentially affect micro-physical cloud formation processes. Indeed, ~~(agricultural) soil dust~~soil dust, in part derived from agricultural areas/practices, has been proven to be an active INP in many studies ~~(Conen et al., 2011; Tobo et al., 2014; O'Sullivan et al., 2015)~~(Conen et al., 2011; Tobo et al., 2014; O'Sullivan et al., 2015; Hill et al., 20 . Furthermore, the range and intensity of desertification, which is defined as the land degradation of arid, semi-arid and dry subhumid areas (i.e. drylands), has increased in the past several decades (Shukla et al., 2019). According to the IPCC Special Report, drylands currently cover about 46% of the global land area, ~~about~~ of which approximately 9~~% of which~~ % were identified as hotspots of desertification. Especially during droughts such areas are susceptible to higher dust storm activity, which may introduce more mineral dust to the atmosphere. For example, Ganor et al. (2010) found the number of events ~~with transport of~~ that transport African dust over the Eastern Mediterranean to increase significantly over the years 1958 – 2006. Concerning Greenland, isotopic studies showed that the main sources of mineral dust aerosol in both glacial times and during the Holocene are natural Chinese desert areas, and in particular the Taklamakan desert (Svensson et al., 2000; Bory et al., 2003), however a recent ~~anthropogenic~~ increase in mineral dust concentration ~~has not been found~~from these areas due to anthropogenic impacts is not documented. Mineral dust from China, and the Taklamakan desert in particular, has been characterized in several laboratory ice nucleation studies (Field et al., 2006; Niemand et al., 2012; Boose et al., 2016; Ullrich et al., 2017; Paramonov et al., 2018), which

revealed a relatively high ice active site density in the temperature range below −25 °C, comparable to other natural deserts such as the Sahara (e.g. Niemand et al., 2012; Boose et al., 2016).

Hartmann et al. (2019) were the first to estimate the concentration of INPs from two Arctic ice cores from Lomonosovfonna, Svalbard (78.82° N, 17.43° E) and Summit, Greenland (72.58° N, 37.64° W) using the droplet freezing devices ~~LINA and INDA~~Leipzig Ice Nucleation Array (LINA, 90 x 1 µL) and Ice Nucleation Droplet Array (INDA, 96 x 50 µL). They analyzed 69 samples in total (42 from Svalbard and 27 from Greenland). Svalbard samples were subdivided into multi-year samples (6 samples in 2 – 6 year resolution) and sub-year samples (36 samples with a resolution of some months), which covered the same time periods as the multi-year samples. The investigated time periods were approximately 1480, 1720, 1780, 1800 and 1950. Greenland samples covered the time from 1735 to 1989 with a resolution of about 2 – 5 years per sample. ~~INP analysis~~ Cumulative INP data is presented mainly ~~for T =~~ at temperatures of −10 °C, −15 °C and −20 °C. Hartmann et al. (2019) observed no long-term trend in the INP concentration. Furthermore, they found the "short-term" variability of INP concentrations from adjacent sub-year samples to ~~dominate~~ be as large as or even larger than the total variability of the complete data set. In their closing remarks, they recommend future studies to focus on creating a continuous record of ice core INP concentrations for the last few centuries~~,~~. Further, they suggest to include a simultaneous analysis of INP-related chemical and biological substances, and to analyze ice cores from other Arctic locations to gain knowledge about the spatial distribution of INP concentrations over time.

Here, we present INP data from an ice core from north eastern central Greenland (B17, 72.25° N, 37.62° W) that dates back to about 1370 (Weißbach et al., 2016). The ice core was drilled in the framework of the North Greenland Traverse (NGT, 1993 – 1995) and reaches a depth of about 100 m. In total 135 samples were measured with the FRIDGE instrument ~~(Klein et al., 2010; Schrod et al., 2016)~~ (FRankfurt Ice Nuclei Deposition FreezinG Experiment, Klein et al., 2010; Schrod et al., 2016) in its droplet freezing mode (Hiranuma et al., 2015; DeMott et al., 2018; Hiranuma et al., 2019). Samples were selected in regular intervals of 10 years to cover the whole period of the ice core. Most of these discrete samples typically integrate over a time period of half a year. Furthermore, sampling frequency was increased to 1 sample per year between 1960 – 1990 to establish a statistically sound "modern day" reference period. Moreover, certain samples were selected based on extraordinarily high concentrations in their "dust" concentration and/or peaks in the ~~signal of conductivity, which is a measure of the acidity of the atmosphere (i.e.~~ electrolytic conductivity, where these peaks are most often caused by H_2SO_4 (from volcanic eruptions). Prior to our ice nucleation measurements, the ice core was analyzed for dust, conductivity, and soluble particle concentrations of Ca^{2+}, Na^+, NH_4^+ and NO_3^- using continuous flow analysis (CFA) (Kaufmann et al., 2008) at the University of Bern and for Ca^{2+}, Na^+, NH_4^+, NO_3^-, K^+, Mg^{2+}, F^-, MSA^-, Cl^-, Br^- and SO_4^{2-} using ion chromatography (IC) at the ~~Alfred-Wegener Institute~~ Alfred-Wegener-Institute for Polar and Marine Research (AWI), Bremerhaven. Finally, we analyzed a ~~high resolution~~ high-resolution period with almost monthly resolution (1463 – 1464, N = 12) to investigate a potential seasonal variation in the INP concentrations.

2 Methods

2.1 Ice core NGT B17

The ice core B17 was drilled during the NGT in 1993 – 1995 by the Alfred-Wegener-Institute as one of 13 ice cores along the traverse. The drill site is located east of the main ice divide in Central Greenland (72.25° N, 37.62° W, 2820 m asl). The ice core has a total depth of 100.8 m, a depth which corresponds to the year 1363 CE. More information about the characteristics of B17 and the other NGT ice cores can be found in Weißbach et al. (2016). Weißbach et al. (2016) presents and discusses the density profile, the water accumulation rate, and the ratio of stable water isotopes ($\delta^{18}O$) of the ice cores B16 – B23 and B26 – B30~~, while~~ . Complementary chemical profiles of selected NGT ice cores are presented in Fischer et al. (1998) and Bigler et al. (2002). Recently, Burgay et al. (2019) introduced Fe^{2+} as a potential new proxy to identify volcanic events by presenting B17 measurements ~~of~~ using a chemiluminescence method.

The ice core was dated on the basis of identified volcanic layers (Weißbach et al., 2016), interpolating between these tie points, supported by measurements of stable water isotopes.

2.2 Sample preparations and overview of measurements

After the B17 core was drilled in the early 1990s, it was cut into pieces of 1 m each and stored at −25 °C in a cold storage at ~~the Alfred Wegener Institute for Polar and Marine Research (AWI) in Bremerhaven~~AWI. In 2018, a longitudinal subsection of the ice core with a cross section of 35 mm x 35 mm was cut from the whole length of the core. The pieces of the ice core were transported in frozen state to the University of Bern, where they were continuously melted using a well-established decontamination technique, which is the first step in the continuous flow analysis (CFA) (Kaufmann et al., 2008) (section 2.3). The decontaminated meltwater flow was then split between the online chemical analysis ~~,~~ and a fraction, which was sampled directly into numbered clean vials of discrete aliquots for offline ion chromatography (IC) measurements (section 2.4). Each vial was filled with approximately 1.5 – 8 mL of sample water, ~~thus covering~~ translating to 4 – 20 cm of core depth. ~~Depending~~ Further, depending on the exact sampling resolution this corresponds to a time resolution of about 1 – 10 data points per year. ~~The~~ Subsequently, the vials were refrozen ~~,~~ and shipped to AWI ~~and subsequently measured for~~ to measure the concentration of ~~a large number of major ions , expanding on~~ major ions in order to complement the CFA measurements. As the IC analysis required a few µL only, the vials still contained most of the sample water after the measurements. ~~Some~~ A part of these samples were later selected for the ice nucleation analysis in this study (section 2.5). These samples were transported from Bremerhaven to Frankfurt in a small insulated PP-foam cooling box with additional cold packs~~to guarantee that the temperature of the samples was always well below 0~~ . Then, samples were stored inside a freezer (WAECO Coolmatic CF-40) at about −17 °C. ~~Temperature variability ranged from −16.1 to −17.9 over a period of 15 hours.~~ Hence, it was ensured that samples remained frozen at all times ~~.~~ in our laboratory. However, sample vials may have been subject to temperatures between 0 °C and room temperature for up to some tens of hours in total (during repeated cycles of melting, storage and refreezing, non-INP measurements, and transport, etc.). Prior to the ice nucleation measurement (section 2.6), ~~the respective~~ each sample was slowly melted over night in a refrigerator at about 6 °C. After the ice nucleation analysis the samples were refrozen~~once again~~.

Selected samples that were previously analyzed for their INP activity, were transported to TU Darmstadt for chemical and morphological single particle analysis using a scanning electron microscope (SEM) (section 2.7).

2.3 Online chemical analysis

~~The longitudinal~~ For the CFA analysis the subsections of the ice core were melted continuously in a way that ~~separates~~ separated meltwater from the potentially contaminated outside of the ice from the clean meltwater from the inside~~during the CFA analysis~~. This decontamination technique is ~~absolutely~~ effective and even gastight for solid ice (density > 0.82 $\mathrm{kgL^{-1}}$). However, we cannot completely exclude some minor contamination for the relatively porous firn, which is found at the top of the ice core, as it is possible that melt water is drawn upwards by capillary forces and that surface contaminants may be mixed in here.

~~The~~ A fraction of the clean meltwater stream ~~is~~ was used to feed a range of detectors to determine the concentrations of ~~major~~ ions in the water using ~~purpose-build~~ purpose-built spectrophotometric methods (Ca^{2+}, Na^{+}, NH_4^{+} and NO_3^{-}), electrolytic conductivity and the concentration of insoluble particles (> 1.2 µm) as detailed in Kaufmann et al. (2008) and references therein. ~~Additionally, trace-elemental concentrations in the meltwater where determined using online ICP-TOF-MS (?), which were, however, not used for this manuscript.~~ All of these measurements ~~are~~ were performed continuously during the melting of the ice-core section to produce continuous high-resolution record. Typical analytically limited resolutions ~~are~~ were in the range of 0.5 – 1.0 cm governed by the smoothing of the individual detection methods.

2.4 Ion chromatography

The vials containing the discrete decontaminated aliquots of the ice core were melted at room temperature prior to the IC analysis. The vials ~~are~~ were then placed into an autosampler to be measured. Simultaneous analysis of anions and cations was performed using a 2 channel Dionex ICS 5000+ Reagent-free HPIC system (Thermo Fischer). For the anion (cation) determination the Dionex IonPac AG18-Fast-4 µm guard column (IonPac CG12A-5 µm column) and the Dionex IonPac As18-Fast-4 µm analytical column (IonPac CS12A-5 µm column) were used. The measurements were calibrated with 7 internal standards, prepared from available anion and cation standards. Pre-mixed external standards ~~are~~ were used for quality control. ~~The IC provides~~ In this study, the IC provided a quantitative analysis of the concentration of Ca^{2+}, Na^{+}, NH_4^{+}, NO_3^{-}, K^{+}, Mg^{2+}, F^{-}, MSA^{-}, Cl^{-}, Br^{-} and SO_4^{2-}.

2.5 Sample selection

Figure 1a shows the temporal distribution of the selected samples for the ice nucleation experiment (total N = 135, 7% of all samples) throughout the ice core ~~.~~ (the complete list of samples is presented in Tab. S1). We placed a strong emphasis on having a ~~consistent~~ data set with ~~samples in regular time intervals . Time steps of 10 years were decided~~ quasi-consistent time intervals for our samples (approximately decadal interval). We considered these time intervals to be both meaningful and feasible. Furthermore, ~~we were interested in investigating the question whether the~~ our sample selection strategy was intended to consider the pre-industrial INP concentration ~~is different from~~ vs. the INP concentration of the recent past (1960 – 1990).

Therefore, the sample frequency was increased to about 1 sample per year in the latter time period ~~.~~ to potentially enhance the statistical significance. Whenever possible, we selected samples that theoretically represented the same season(s). However, due to the uncertainty in the ice core dating some of the variability in the INP concentration may be attributed to seasonal differences.

Moreover, we selected some samples according to peak values in the ~~high resolution~~ high-resolution CFA measurements. Samples labeled "dust event" include a respective sample that featured a peak in the ~~high resolution~~ high-resolution signal of particles with spherical diameters larger than 1.2 µm, as well as a couple samples collected before and after it. Due to the episodic nature of such an event and the ~~automatic collection of sample water into the vials, which averages over peak-independent periods of time,~~ fact that the INP samples were automatically collected as multi-month means, the sample containing the ~~high resolution peak signal must not necessarily~~ high-resolution peak signal does not necessarily need to have an extraordinarily high average value itself. Similarly, peak samples in the ~~high resolution~~ high-resolution signal of conductivity were selected~~that are typically~~ . Large peaks in the electrolytic conductivity record are most often derived from high sulfuric acid deposition in the ice after volcanic eruptions. ~~One~~ For example, one group of these "volcanic event" samples can be unequivocally ascribed to the Laki eruption in 1783/84. The eruption of Grímsvötn (Laki) is the best-characterized historical large volume basaltic fissure eruption in Iceland. The 8-month lasting Laki eruption occurred from a 27 km long volcanic fissure in the Grímsvötn volcanic system. It emitted $\approx 15\,\mathrm{km}^3$ of lava, $0.4\,\mathrm{km}^3$ of tephra, an estimated 122 Tg of SO_2, and other gases and trace metals (Thordarson and Self, 1993, 2003; Sigl et al., 2018). Lastly, 12 adjacent samples with a near monthly resolution were measured in order to estimate the "short-term" variability of the data set and to check for a possible seasonal variation of the INPs (1463 – 1464).

Figure 1b gives the temporal coverage of each individual analyzed sample. The representative time of a certain sample is given by its lengths, which is estimated by calculating the average time difference between the sample before and after it. The majority (63%) of the analyzed samples ~~average~~ averaged over a time period of 6 ± 2 months. ~~26%~~ About a quarter of the samples ~~average~~ (26%) averaged over a shorter time and 11% over a longer time~~period~~.

2.6 Ice nucleation analysis

The ice nucleation measurements were performed with the FRIDGE instrument (Klein et al., 2010; Schrod et al., 2016). FRIDGE ~~hast~~ has two operational modes. In its "standard mode" aerosol particles ~~activate ice crystal growth~~ are activated to ice crystals by diffusion of water vapor at supercooled temperatures and near vacuum conditions (Schrod et al., 2017; DeMott et al., 2018; Thomson et al., 2018; Marinou et al., 2019). In this manuscript however, we solely used FRIDGE in the droplet freezing mode ~~(Hiranuma et al., 2015; DeMott et al., 2018; Hiranuma et al., 2019).~~ (Hiranuma et al., 2015; Boose et al., 2016; DeMott et al., 2018; . We focused on the droplet freezing assay (DFA), because 1) immersion freezing is considered to be the most atmospherically relevant process in heterogeneous ice nucleation for mixed-phase clouds (e.g. Murray et al., 2012), 2) the use of a DFA seems to be the natural choice considering that the aerosol particles are already immersed within the ice core meltwater, 3) the technique requires only a few mL of sample water, and 4) other methods would likely introduce further contamination sources through the particle generation setup (e.g. atomizer).

The performance of the FRIDGE instrument was tested during the Fifth International Workshop on Ice Nucleation – part 2 (FIN-02, DeMott et al., 2018). In this large-scale laboratory campaign 21 different INP counters were intercompared at the Aerosol Interaction and Dynamics in the Atmosphere (AIDA) facility of the Karlsruhe Institute for Technology (KIT). FRIDGE agreed generally very well with the other instruments (especially for the immersion freezing method) for the various investigated aerosol types (including natural mineral dusts, dust components and a biological material).

During a measurement of an ice core sample 65 droplets of 2.5 µL ± 5% each ~~are~~ were placed homogeneously at random onto a clean silanized Si-substrate of 47 mm diameter on the cold table in the FRIDGE chamber. The droplets ~~are picked up~~ were pipetted directly from the sample vial and ~~are~~ were semi-automatically dispensed using an Eppendorf Multipipette E3 with fresh Eppendorf tips of the highest level of purity (Combotips advanced, biopur grade, 0.1 mL). Temperature ~~is decreased quickly~~ was quickly decreased at first in the range from 14 °C to 0 °C and then slowly lowered at a constant cooling rate of 1 °C per minute until ~~every droplet is~~ all droplets were frozen. The temperature ramp ~~is~~ was implemented by a PID-controlled Peltier element~~that is supported by a~~ . A cryostat (Lauda, Ecoline Staredition RE110; ethanol coolant) ~~dissipating the heat . Temperature is controlled~~ was used to dissipate the heat from the Peltier element. Temperature was measured by a PT-100 sensor (precision ± 0.2 °C), which ~~is~~ was attached to the surface of the wafer. The measurement cell ~~is~~ was continuously flushed with synthetic air at a flow of 1 L min^{-1} to prevent condensation and riming and to ~~limit~~ minimize contamination from the laboratory environment during the measurement. The freezing of droplets ~~is~~ was observed by a CCD-camera (AVT Oscar F-510C 2/3″). A droplet changes its brightness significantly during the freezing event: droplets are nearly translucent when liquid but are opaque when frozen. LabView software automatically ~~detects~~ detected the moment of freezing, ~~records~~ recorded the corresponding temperature and ~~saves~~ saved the images every ten seconds. The final results ~~are~~ were always double-checked by the operator. After all droplets ~~are~~ were frozen, the substrate ~~is~~ was heated up, cleaned and the process ~~is~~ was repeated twice with new droplets. In total, the freezing temperatures of 195 individual droplets ~~are~~ were determined for each ice core sample (3 runs with 65 droplets). The cumulative INP concentration per mL of ~~meltwater~~ ice as a function of temperature ($N_{\mathrm{INPice}}(T)$) ~~is~~ was calculated by the well-established Vali (1971) equation:

$$N_{\mathrm{INPice}}(T) = \frac{1}{V_{\mathrm{d}}} \cdot \left[\ln\left(n_{\mathrm{total}}\right) - \ln\left(n_{\mathrm{total}} - n_{\mathrm{frozen}}\right)\right] . \quad (1)$$

Here, V_{d} is the volume of each droplet, n_{frozen} is the number of droplets that are frozen at temperature T and n_{total} is the total number of droplets of each freezing experiment. With the aforementioned experimental values for these variables we are typically able to resolve INP concentrations between 2 and 2000 $\mathrm{mL_{ice}}^{-1}$.

Due to the nature of the experiment, droplets ~~will~~ freeze in a different temperature range, leading to a slightly inconsistent data set. This means that while some samples ~~will~~ have measurement data at a warm temperature, others will not. ~~In terms of calculating~~ When we calculate average concentrations etc., we set the concentration of those non-active samples to zero, knowing that the actual concentrations is somewhere between zero and the lowest resolvable concentration (2 per $\mathrm{mL_{ice}}$). The same issue arises at lower temperatures. For some samples all droplets ~~will be~~ are frozen before reaching a certain temperature. In those cases the concentration was set to the highest resolvable concentration (2000 per $\mathrm{mL_{ice}}$). It should be noted that for

some cases the real INP concentration might actually be substantially higher due to the exponential behavior in ice nucleation. The presented average concentrations (section 3) should therefore be considered as a lower estimate.

2.7 Scanning Electron Microscopy

We selected three individual samples (years: 1977, 1680 and 1630) to be analyzed with scanning electron microscopy (SEM) to gain information about the chemical signature of deposited aerosol particles. The 1977 sample was selected exemplarily as an active modern-era sample. The 1680 sample was chosen for its average INP concentration at $-25\,^{\circ}\mathrm{C}$, as well as being in the middle of the time series. The 1630 sample was analyzed with SEM, because it had an extraordinarily high INP activity at comparably warm temperatures.

By use of a Quanta 200 FEG Environmental scanning electron microscope equipped with an EDAX Genesis energy dispersive X-ray microanalysis system (EDX) the elemental composition of individual aerosol particles as well as a rough size-distribution can be determined.

For this purpose, the samples were melted and subsequently filtered using a $25\,\mathrm{mm}$ Nucleopore membrane filter with $0.4\,\mu\mathrm{m}$ pore size and a filter flask at vacuum provided by a water jet. The area of filtration was about $5\,\mathrm{cm}^2$, ensuring that particles were concentrated on a relatively small area, which is advantageous to the SEM analysis.

For SEM-EDX analysis on each filter some 100 rectangular fields of about $100\,\mu\mathrm{m}$ x $100\,\mu\mathrm{m}$ in the center of the filter were scanned and for all detected particles the size was determined and an EDX analysis (acceleration voltage: $20\,\mathrm{kV}$, spot size: 4, acquisition time: $10\,\mathrm{s}$, working distance: $10\,\mathrm{mm}$) was performed. Using this procedure, particles down to approximately $250\,\mathrm{nm}$ ~~will be~~ were detected. Smaller particles will often be overlooked~~, what will be~~. This is also true for ~~even~~ larger carbonaceous particles, ~~which have a bad~~ because of their poor contrast on the polycarbonate filter.

2.8 Background freezing and uncertainties related to the INP measurements

There are numerous possible sources of contamination in a typical droplet freezing assay, which may cause a droplet to freeze before the homogenous limit. The potential contamination due to the analytical procedure may be evaluated by establishing a "background" from the freezing of "pure" water droplets. Polen et al. (2018) ~~review the state of the art of~~ reviewed several droplet freezing techniques, ~~summarize~~ summarized potential contamination sources, and ~~advise~~ advised on how to report background freezing. In general, contamination may arise from particles in the "pure" water itself, substrate interferences, or the environment that is in contact with the droplets. However, it is rather difficult to assess how much each of these categories contributes to the freezing spectrum of a specific background sample (Polen et al., 2018). We will now look at each of these factors and describe how exactly they relate to the actual ice nucleation experiment of this manuscript.

First, the surface of the substrate onto which the droplets are placed can induce freezing. It is well known that the contact angle of the droplets influences the freezing process. Furthermore, microscopical cavities, scratches, cracks or other surface defects, as well as actual particles on the surface of the substrate may affect the freezing temperature of the droplets. In our setup, we use custom-cut silicon wafer as substrates. The wafers were regularly coated with dichlorodimethylsilane in a vacuum desiccator to create a thin hydrophobic layer on the surface of the substrate. The silanization has several positive effects. First,

it "seals off" ~~microscopical~~ microscopic surface defects on the wafer. Second, the hydrophobic layer prevents condensation and rime formation and thereby limits the effects of a possible Wegener-Bergeron-Findeisen process. The Si-substrates are stored in PetriSlide containers before use. Finally, the surface of a wafer is cleaned thoroughly by hand with pure non-denatured ethanol (Rotipuran, >99.8%, Carl Roth) immediately before and after each measurement run.

Obviously, the environment surrounding the sample may affect its freezing temperature. Specifically, the vials in which the water is stored and the tips of the pipette may introduce contamination. Furthermore, the droplets can collect particles from laboratory air during a measurement, which may nucleate ice artificially. Our measurement cell is continuously flushed with particle-free, dehumidified synthetic air at a constant flow rate of 1 $\mathrm{L\,min^{-1}}$. This largely prevents the droplets to come in contact with aerosols from the laboratory and inhibits water condensation and growth of frost.

Lastly, we consider the pure water itself, which is used as a medium to establish the background signal, as a source for contamination. No matter how "pure" a manufacturer certifies its water to be, at very cold temperatures even a single contaminant particle inside a droplet might initiate the ice nucleation process and ~~causes~~ cause the droplet to freeze. For purposes of background measurements we used the "pure" water Rotipuran ultra (Carl Roth). However, in the analysis of droplets from the ice core the samples are not in contact with the "pure" water. Unfortunately, this results in an intrinsic problem of the background evaluation of our ice core measurements. Depending on the relative importance of the role of the reference water in the background measurement, our background freezing spectrum is more or less representative for the ice core freezing spectra. In other words, if non-water contamination effects dominate the freezing in the background measurement, the respective freezing spectrum could be adapted for the ice core measurements. If the majority of droplets in a background measurement freeze, however, due to contaminants in the reference water, the background freezing curve only serves as an upper limit, meaning that the ice core measurements have an unspecified better background than what the background freezing spectrum would suggest. In fact, we observed some samples from the ice core to freeze ~~even later than~~ as late as our typical background measurements (e.g. purple line in Fig. 2), which suggests that at least some contamination is introduced by the ultrapure water itself. Therefore, we chose not to subtract the background freezing spectrum from our measurements as is common practice, but give a range of temperatures, where no or only little interference is expected due to background contamination. Figure 2 shows ~~a~~ typical background freezing ~~spectrum~~ spectra compared to the average freezing spectrum of the ice core measurements. Accordingly, results of freezing temperatures colder than -31~~30~~ °C are likely to be influenced by a reasonable amount of background freezing (frozen fraction ~~≥ 25~~24 ± 10 %) and should be interpreted with care. Only little background influence is expected, however, for temperatures warmer than −28 °C (frozen fraction ~~≤ 10~~9 ± 5 %).

Moreover, we tested whether the freezing temperature of an individual droplet can be reproduced. For 120 (4 x 30) droplets the freezing temperatures T_1 and T_2 were individually measured during two subsequent freezing cycles (Fig. 3). Overall, we found that over a wide range of temperatures the freezing temperature is a property of each individual droplet and can be reproduced fairly accurately. The temperature difference between two subsequent freezing cycles of the same droplet was below ± 0.5 °C for 79% of the cases. Half of the droplets showed a temperature difference of ≤ 0.23 °C. Only 5 of 120 droplets differed by more than ± 1 °C in their nucleation temperature. Furthermore, the resulting slope of the data was close to unity (1.016) with a strong linear correlation (R^2 = 0.96). These results suggest that a) temperature uncertainty in FRIDGE

is relatively low, b) repeated cycles of freezing and defreezing of an ice core sample do not greatly affect its ice nucleation properties in the presented temperature range and c) this test sample showed a mostly deterministic ice nucleation behavior. However, recent studies indicate that sample storage (i.e. storage temperature) significantly affects the ice nucleation activity of fresh precipitation samples in the range of $-7\,^{\circ}\mathrm{C}$ to $-19\,^{\circ}\mathrm{C}$ (Beall et al., 2020). For example, samples stored at room temperature lost on average 72% of their INPs compared to the freshly analyzed samples. An average INP loss of 25% was still observed, even when samples were stored at $-20\,^{\circ}\mathrm{C}$. Storage time did only weakly affect the INP concentrations. Therefore, based on this study a loss of INP activity on the order of a factor of $2-5$ is possible, if not likely for the ice core measurements presented here. Furthermore, it is likely that the warmer end of INPs were disproportionally affected by these disturbances, while cold-temperature INPs were likely more robust. However, as all the samples experienced the same sample history, relative changes within the ice core can still be interpreted.

In this manuscript, we specify the uncertainty of the INP concentration as the 95% confidence interval, which is derived from the freezing statistics alone (i.e. number of frozen droplets at a certain temperature). The uncertainty of the INP concentration is high for the very first few drops (i.e. often as high or higher than $\pm\,100\%$) and levels out usually below $\pm\,20\%$ at lower temperatures, depending on the specific freezing spectrum.

2.9 Other uncertainties

There are undoubtedly many difficulties and uncertainties associated with estimating (atmospheric) INP concentrations from an ice core. First of all, high standards of precaution need to be met in order to prevent contamination effects (e.g. when cutting the ice, when handling and storing the samples, or during the INP analysis itself). Specifically, we like to emphasize that the topmost part of the ice core is made up of relatively porous firn, which is more prone to post-coring contamination of dust during storage as compared to the rest of the ice core. Preliminary results of two particle counters (Abakus: spherical diameter $> 1\,\mu\mathrm{m}$), SPES: spherical diameter $< 1\,\mu\mathrm{m}$) from the B17 ice core (only Abakus) and the EGRIP S6 ice core (Abakus and SPES, 75.62° N, 35.97° W, 2702 m asl, C. Zeppenfeld personal communication) suggest that a contamination effect is likely for particles $< 1\,\mu\mathrm{m}$ and rather unlikely for particles $> 1\,\mu\mathrm{m}$. However, post-coring contamination still cannot be fully excluded for the latter measurements.

Second, the overarching question is whether general source conditions, transport patterns and dry and wet deposition efficiencies, which directly influence the number of particles inside the ice as well as their possible source attribution, can be assumed not to have changed substantially over the time scale covered by the ice core. It is likely that for the time scale of a few centuries, when climate conditions were similar to today, this assumption holds ~~up~~ (Wolff, 1996), although there is obviously some uncertainty and unknown variability.

Moreover, it is often implicitly assumed that aerosol particles in ice core archives perfectly resemble the actual atmospheric situation at the time the particles entered the ice sheet. Yet, there is a number of possible biases to consider for the case of INPs. There are several routes an aerosol particle could have taken to end up in an Arctic ice core: a) The aerosol particle may have simply been transported to the ground by dry deposition, b) it was activated as a cloud nucleus (either INP or CCN) and was subsequently removed from the atmosphere via precipitation or c) it was removed either by in cloud or below cloud

scavenging. This means that aerosol particles with good ice nucleation activity may actually be preferably deposited in an ice core as compared to particles that are not as ice active (Dibb, 1996). The relative importance of riming processes determines how significant this potential bias is (i.e. the bias is low if most of the particles are transferred to the surface of the ice sheet by riming or dry deposition). Furthermore, INPs are typically large in diameter ($> 0.5\,\mu m$, DeMott et al. (2010)). Dry deposition is generally more efficient for larger particles ~~(gravitational settling)~~ and for very small particles (~~Brown~~ Brownian diffusion) than for ~ 100 nm particles, which represent the largest fraction the aerosol population. This ~~means as well~~ implies that INPs may be overrepresented in ~~an ice core as compared to non-ice-nucleating particles or to the surrounding atmosphere~~ ice core samples compared to non-INPs or the ambient atmosphere at any given time.

The next question is whether aerosol particles irreversibly remain inside of an ice sheet and if so, whether these particles stay physically and chemically inert while being preserved in the ice or if they experience modifications. Indeed, non-volatile atmospheric particles are considered to be essentially chemically inert and physically immobile once they are transferred to the ice. Yet, it is basically unknown if or how surface properties (e.g. active sites) of a particle are modified in the ice. Aerosol particles seem to remain at a given layer throughout the firnification (Bales and Choi, 1996). Aggregation of dust particles has ~~been only~~ only been observed close to the bottom of the Antarctic ice sheet (Tison et al., 2015). Hartmann et al. (2019) come to the same conclusion that INPs are well preserved in an ice core and a reconstruction of their concentration for past climates is possible.

~~However,~~ However, as previously stated, storage conditions may have affected the INP activation.

In contrast, it is likely that aerosol particles will alter physically and chemically during the atmospheric transport from their source region to the Arctic. This includes, but is not limited to, changes in size distribution, mixing state or coatings. We will therefore not try to speculate about potential atmospheric INP concentrations at a possible source location in the past.

In summary, one should be wary when interpreting results based on aerosol data from an ice core. Statements based on these findings should be assessed carefully. ~~Or in the words of Albrecht Neftel: "The reconstruction of an atmospheric record from the concentration versus depth profile gained from ice cores is similar to an odyssey through a labyrinth with many pitfalls ready to slur over enthusiastic students and researchers" (?).~~

In the light of these uncertainties associated with the transfer processes of INPs between the atmosphere and the ice sheet, the conversion factor from in-ice-concentrations to (Arctic) atmospheric concentrations, which will be introduced in the following chapter, should therefore be interpreted only as an order-of-magnitude estimation.

2.10 Conversion to atmospheric concentrations

To convert the cumulative INP concentration per volume of meltwater to an atmospheric concentration, we follow the theoretical considerations presented in Fischer et al. (2007). As for any aerosol particle, an INP can be transferred from the air to the surface of the ice sheet either by dry deposition ~~(predominantly gravitational settling and turbulent transport) and wet deposition(cloud particle activation or riming and subsequent removal by precipitation, or below-cloud scavenging)~~and wet deposition. Fischer et al. (2007) states that in a simplified model the total deposition flux J_{ice} (i.e. the sum of the flux of dry and wet deposition, J_{dry} and J_{wet}, respectively) to the ice surface is defined by the product of the snow accumulation rate A

and the average concentration of the investigated species (i.e. here for INPs: N_{INPice}) in the ice core sample. Over long periods of time the deposition flux can be written as:

$$J_{\mathrm{ice}} = A \cdot N_{\mathrm{INPice}} = J_{\mathrm{dry}} + J_{\mathrm{wet}} = v_{\mathrm{dry}} \cdot N_{\mathrm{INPatm}} + A \cdot \varepsilon \cdot N_{\mathrm{INPatm}}\,, \tag{2}$$

where N_{INPatm} is the atmospheric INP concentration (or any other investigated species of interest), v_{dry} is the dry deposition velocity and ε is the effective scavenging efficiency including in-cloud and below-cloud scavenging. Experimentally, ε is often defined as particle concentration in cloud water or in precipitation (snow/ice/rain) divided by the airborne particle concentration. Rearranging Eq. 2 leads to:

$$N_{\mathrm{INPatm}} = \frac{N_{\mathrm{INPice}}}{\frac{v_{\mathrm{dry}}}{A} + \varepsilon}\,. \tag{3}$$

Thus, it is possible to calculate the (Arctic) atmospheric INP concentration, when realistic values for the variables A, v_{dry} and ε are estimated. However, Eq. ~~2~~ 3 implies that if deposition fluxes change over the time span of the ice core (in particular the wet deposition, which is directly related to changes in the precipitation rate), the concentration of the investigated species in the ice will change as well. This means that not all potential changes seen in the ice core INP concentration, are necessarily caused by actual changes in the atmospheric concentration. Henceforth, we will, however, treat these variables as constants due to the lack of a better knowledge and because climate conditions changed only little over the last centuries. In particular, the average snow accumulation of the B17 ice core has been determined by Weißbach et al. (2016) and shows little variation over time ($A = 11.4 \pm 0.1\,\mathrm{cm\ water\ equivalent\ a^{-1}}$, N = 630). Unfortunately, the other deposition parameters are not as well-known.

In general, v_{dry} heavily depends on the particle diameter, shape, density and physical properties of the particle. The typical range is between 10^{-2} $\mathrm{cm\,s^{-1}}$ and 10 $\mathrm{cm\,s^{-1}}$ (Seinfeld and Pandis, 2006). Smaller particles ($d_{\mathrm{p}} < 0.1$ µm) and larger particles ($d_{\mathrm{p}} > 1$ µm) usually have higher dry deposition velocities than medium sized particles, where Brownian diffusion and gravitational settling are low (Davidson et al., 1996). Moreover, the nature of the surface itself (e.g. surface type and smoothness) and the level of atmospheric turbulence at the nearest layer to the ground have a major influence on v_{dry} (Seinfeld and Pandis, 2006). Moreover, over the ice sheet, the dry deposition is strongly influenced by snow ventilation effects induced by surface roughness (Cunningham and Waddington, 1993). ~~? evaluated five different dry deposition parametrizations with respect to their ability to accurately explain field observations from five land use categories (snow/ice: 8 studies). The parametrization by Zhang and He (2014) performed best overall, and best for snow/ice covered surfaces in particular. Therefore, we used the parametrization by Zhang and He (2014)(Eq. 4) to estimate the dry deposition velocity for $PM_{2.5}$ aerosol particles. The parametrization is predominantly dependent on the so-called friction velocity u_* and the particle diameter d_{p}. ? use a value $u_* = 0.12$ for snow/ice surfaces in their observation based accuracy test evaluation. We decided to set d_{p} in the parametrization to 0.5 , since particles of this size and larger are typically considered to be "good" INPs (DeMott et al., 2010; ?). ? analyzed *modern day* samples from two ice cores from west-central Greenland with a time-of-flight single-particle mass spectrometer to determine the size and composition of insoluble particles. The median particle diameter of insoluble particles within the detectable aerodynamic size range of 0.2 – 3 was about 520 (mean 595 ± 360 , N = 8021), which agrees well with our assumption. Filling in the other variables given in Zhang and He (2014) and ?, we find~~ For the purpose of this manuscript

we use a dry deposition velocity of $v_{\mathrm{dry}} = 0.05\ \mathrm{cm\,s^{-1}}$. This value agrees well with the dry deposition velocity of 0.03 , which is used for all aerosols over snow and ice surfaces in the GEOS-chem model (**?**), which we derived from a parametrization by Zhang and He (2014).

The scavenging efficiency ε (also known as scavenging ratio or washout ratio) is even less well known than the dry deposition velocity. The scavenging ratio is a very complex parameter that is controlled by the particle's size, its physical shape and chemical composition, as well as by cloud properties such as droplet size, cloud temperature and cloud type, and by the vertical extent of rain and the cloud (Duce et al., 1991; Shao, 2008). Hence, accurate predictions of ε are very difficult (Shao, 2008). Duce et al. (1991) warns that experimentally determined concentrations at the ground do not necessarily have to reflect the conditions near the cloud, where the particles are mainly scavenged. Furthermore, ε can vary greatly for different particle species and should therefore be assessed carefully (Duce et al., 1991). Attention should also be paid to the fact that ε is reported in the literature either in a mass- or volume-based dimension $((_{\mathrm{species}}/_{\mathrm{precip}})/(_{\mathrm{species}}/_{\mathrm{air}})$ vs. $((_{\mathrm{species}}/_{\mathrm{precip}})/(_{\mathrm{species}}/_{\mathrm{air}}))$. These two definitions differ by the factor $\rho_{\mathrm{precip}}/\rho_{\mathrm{air}}$ ($\varepsilon_{\mathrm{vol}}$ is about 1000 times higher than $\varepsilon_{\mathrm{mass}}$). Usually, ε is calculated by measuring the airborne concentration of a species and its concentration in a precipitation sample simultaneously at the ground. The volume-based scavenging ratio is typically in the range of 10^5 to 10^6 (**?**). Mass-based scavenging ratios for mineral aerosols are typically somewhere between 100 and 2000 (Duce et al., 1991). Davidson et al. (1996) reported Arctic $\varepsilon_{\mathrm{mass}}$ for Ca to be 840 for Summit, Greenland. For the purpose of this manuscript we use a value for ε of $1.11 \cdot 10^6$ that is derived from long time observations by Cheng and Zhang (2017). They measured the scavenging ratio for various species at 13 Canadian stations for several years. They give a long-time average value for several species, each composed of individual means from months that experienced at least 15 days with more than 0.2 of precipitation. The combined measured concentrations of Ca^{2+}, Mg^{2+}, and Na^{+} can be taken as a proxy for coarse particulate aerosols (e.g. mineral dust). The long-time average of all 13 stations of these three species yields $\varepsilon_{\mathrm{mass}} \approx 1.12 \cdot 10^3$, which we will use for the scavenging ratio in this manuscript. Note, that the densities of air and water, which are part of the definition of ε, depend on temperature and altitude. Here, we assumed the densities of air ρ_{air} and water ρ_{water} to be 1.01 (-25 , 2820) and 1000 , respectively. This yields a $\varepsilon_{\mathrm{vol}}$ of $1.11 \cdot 10^6$. Moreover, technically $\varepsilon_{\mathrm{vol}}$ compares the mass and not the number of a certain species within a volume of water and air. INP concentrations, however, give the number of ice-active particles per volume. Considering the large uncertainties accompanied with the scavenging ratio, we disregard this inconsistency.

Following these assumptions, we obtain a factor derive a best-guess of about $8 \cdot 10^{-7}$ for converting from N_{INPice} to N_{INPatm} at the B17 drill site (Fig. 4, blue cross). Figure 4a displays the range of the possible conversion factors as a result of other combinations of v_{dry} and ε. Figure 4b shows the sensitivity of the chosen conversion factor associated with the uncertainties in dry and wet deposition efficiencies. Judging from the typical range of literature values of v_{dry} and ε, the uncertainty of the conversion factor is likely within $\pm 50\,\%$ of our best estimate. Likewise, our conversion factor is only about twice as high as the conversion factor proposed in Petters and Wright (2015), who compiled INP data from precipitation measurements and translated these to atmospheric INP concentrations at cloud level. Petters and Wright (2015) based their estimation on the assumption that cloud droplets of typically 1 pL (each containing no more than one INP) dispersed in $1\ \mathrm{m^3}$ of air weigh about

0.4 g (cloud water content (CWC) ranges between 0.2 and 0.8 $\mathrm{g\,m^{-3}}$). Depending on the exact CWC, the uncertainty of the Petters and Wright (2015) estimation is also a factor of 2.

~~Similar to what we propose here, Schüpbach et al. (2018) successfully implemented the assumptions described above into a trajectory based source apportionment study to translate ice core concentrations of Na^+, Ca^{2+}, NH_4^+, NO_3^- and SO_4^{2-} to atmospheric source concentrations for a 130k year record of Greenland ice core aerosol data.~~

3 Results and Discussion

Overall, the ice core samples show relatively low ice nucleation activity. Droplets freeze in the range of $-14\,^\circ\mathrm{C}$ to $-35\,^\circ\mathrm{C}$ (Fig. 2). On average, 1% of the droplets is frozen at $-21.27 \pm 1.43\,^\circ\mathrm{C}$, 10% at $-24.93 \pm 1.53\,^\circ\mathrm{C}$, 25% at $-26.62 \pm 1.87\,^\circ\mathrm{C}$, 50% at $-28.33 \pm 2.09\,^\circ\mathrm{C}$ and 90% at $-31.03 \pm 2.02\,^\circ\mathrm{C}$, respectively. Reiterating our statements from section 2.8, we find a reasonable amount of droplets freezing only at temperatures, where some influence from background freezing is expected ($T < -28\,^\circ\mathrm{C}$). Accordingly, the interpretation of the lower end of the data is difficult. Figure 5 shows a time series of the fraction of frozen droplets in samples with a regular time interval of 10 years between each sample. In general, this subset of the data (about half of all samples) reflects the basic characteristics of the ice core samples well (see also Fig. S1 in the Supplement), with a few distinct exceptions, which we we will discuss later. The freezing spectra show relatively little variation between individual samples overall, and from sample to sample. Some notable exceptions are samples that feature an early ice nucleation onset (e.g. 1400, 1430, 1630, 1740, 1950) or a freezing spectrum that is completely shifted to warmer freezing temperatures (e.g. 1450, 1550, 1620, 1630, 1930, 1960, 1990). Of these samples, the sample of 1630 stands out the most. Here, a very steep freezing spectrum was observed with a freezing range of only about 3.5 °C ($-18.27\,^\circ\mathrm{C}$ to $-21.74\,^\circ\mathrm{C}$). We ~~analyzed this samplea second time to test if our first measurement was caused by some sort of contamination, but the corresponding freezing spectrum was very similar~~verified our results by reproducing the measurement of this sample. The separate second measurement confirmed the strikingly different freezing characteristics, thus eliminating a contamination during the FRIDGE measurements themselves. This may point to a real atmospheric event. However, CFA and IC data of that sample do not indicate the presence of volcanic particles or exceptional concentrations in any other trace element. Unfortunately, the single particle analysis by SEM did not provide any additional explanation for the remarkable ice activity of this sample (see section 3.2). A contamination during the sampling generation step cannot be excluded altogether.

We turn the discussion now to 1 °C-binned average INP concentrations (± standard deviation) of all ice core samples. At $-15\,^\circ\mathrm{C}$ only 3% of the samples (4) showed ice nucleation with an average frozen fraction of only 0.02%. This translates to N_{INPice} of $0.06 \pm 0.35\,\mathrm{mL^{-1}}$ or N_{INPatm} of about $5 \cdot 10^{-5}\,\mathrm{L^{-1}}$, respectively. At $-20\,^\circ\mathrm{C}$ 61 samples (45%) were ice-active, yet still ~~only averaging~~ they showed a frozen fraction of only 0.7% on average. An average ~~in ice INP concentration~~ N_{INPice} of $3.06 \pm 18.76\,\mathrm{mL^{-1}}$ was observed, which corresponds to atmospheric concentrations of about $2 \cdot 10^{-3}\,\mathrm{L^{-1}}$. All samples displayed some freezing activity at $-25\,^\circ\mathrm{C}$. The previously mentioned sample from 1630 was the only sample that was completely frozen at this temperature. We found an average ~~in ice concentration~~ N_{INPice} of $113.92 \pm 272.01\,\mathrm{mL^{-1}}$, which corresponds to an atmospheric concentration of about $0.09\,\mathrm{L^{-1}}$. Only about 4% of all samples (6) were completely frozen before reaching $-30\,^\circ\mathrm{C}$. On

average, 69.3% of the droplets were frozen at −30 °C. ~~Here~~At this temperature, N_{INPice} was found to be $668.09 \pm 529.10\,\mathrm{mL^{-1}}$ on average, translating to a N_{INPatm} of $0.53\,\mathrm{L^{-1}}$.

~~From here onwards we will focus mainly on INP characteristics at $T = -$~~Henceforth, the discussion of results is focused on the characterization of INPs at −25 °C specifically. Although, usually only a relatively low percentage of droplets was frozen at this temperature (17 ± 20 %), ~~every single sample showed some amount of freezing here~~all samples showed some droplet freezing events at this temperature. Only one sample was completely frozen prior to reaching −25 °C. Furthermore, we do not expect much influence from background freezing at this temperature (Fig. 2). Figure 6 displays the INP concentrations of the ice core at −25 °C. We chose to show the data both on a linear (a) and logarithmic (b) scale, ~~so the reader can see the~~ in order to illustrate the typical variation in the INP ~~concentrations, but is still able to identify samples with higher than usual concentrations more easily~~concentration, while still allowing for easy identification of differences in the absolute INP concentration level. Several important findings ~~arise~~ can be inferred from the figure. The observed range of variability in the INP concentration is about 1 – 2 orders of magnitude. We find ~~somewhat~~ on average higher and more variable INP concentrations for the ~~more recent samples~~ last couple of decades as compared to the rest of the time series. ~~Yet~~Nevertheless, there is no obvious trend. Further, back-to-back samples that differ by less than a year (brown, black and green symbols) typically show a comparably low variability, with the exception of two samples from 1475. These two outliers correspond to samples, which show a peak in the particle number and conductivity signal from the CFA measurements. Currently, it is unclear if this corresponds to a volcanic eruption, which the data seem to suggest. The Laki eruption in 1783, however, did not increase the INP concentrations. Yet, this may have to do with the type of volcanic eruption of Laki, which is categorized as a mostly effusive eruption. In contrast to typical explosive eruptions, during which vast amounts of ash particles are blasted into the atmosphere, effusive mixed eruptions involve alternating mostly liquid lava fountains and flows. Moreover, the location of Greenland (and the ice core drilling site) situated upwind of the Laki eruption source may contribute to the lack of an increased INP burden over the Greenland ice-sheet in 1783. Cryptotephra from the Laki eruption were only detected at one ice core site (GISP2, Summit; Fiacco et al., 1994). The effusive nature of the eruption and the location away from the main wind direction appear to be reflected by the CFA and IC measurements, which do not find increased particle loads during the Laki eruption, but show the most pronounced peak in conductivity and the SO_4^{2-} concentration. Interestingly, other samples with a peak in the ~~dust signal~~ particle number concentration did not always translate to high INP concentrations. Overall, however, we did find a moderate yet significant correlation between particles larger 1.2 µm and the INP concentration over a wide range of temperatures (Tab. 1). This points to a terrestrial source of INPs. The dust signal in Greenlandic ice cores is mainly associated with long range transport from East Asian deserts (Bory et al., 2002; Schüpbach et al., 2018). For certain temperatures we find significant correlations between the INP concentration and Ca^{2+} and the conductivity as well. ~~If~~ When the data is grouped into subsets according to Fig. 1~~however~~, we find that the correlation ~~breaks down~~ weakens for the 10 year samples and the modern day samples, but increases for special ~~events~~ event and seasonal samples (Tab. ~~??~~S2). A complete correlation analysis can be found in the supplement (Tab. ~~S1~~S3).

3.1 Pre-Anthropocene vs. modern era INP concentrations

Figure 7 presents the frozen fraction vs. temperature spectrum of each sample between 1960 and ~~1990 in a contour plot.~~ 1990. Comparing Fig. 7 to Fig. 5, it is visible at first glance that more droplets froze at warmer temperatures (yellow colors) for the modern day samples than for the 10 year samples, which cover the complete time from 1370 to 1990. ~~We like to point out here that the topmost part of the ice core is made up of relatively porous firn, which is more prone to post-coring contamination of dust as compared to the rest of the ice core. Unfortunately,~~ Unfortunately, despite the CFA decontamination technique we cannot entirely exclude the possibility that differences emerged or are enhanced due to post-coring contamination of the porous firn, as the ice core was stored for some time~~, despite the CFA decontamination technique.~~ . Preliminary measurements (cf. section 2.9) found a twofold increase of particles larger than 1 µm in the top 8 m (roughly the time interval of 1960 – 1990) compared to older intervals, which does seem to match the results observed by the INP measurements. Further, a distinct seasonality could be established for the dust measurements of the top layers, which argues against a strong contamination effect. Furthermore, the results could ~~potentially~~ be intrinsically influenced to some degree by differences in sampling frequency and time coverage~~. That being said, going forward~~ , as well as samples representing different seasons of the year. Regardless, we will compare the ice nucleation characteristics of these two data sets in more detail (i.e. 31 samples from 1960 to 1990 and 59 samples from 1370 to 1950). The ~~four samples that originally overlapped with both data groups (1960, 1970, 1980 and 1990) will only be included in the modern day subset from now on. We believe this differentiation~~ observed difference between pre- and post-1960 samples ~~to be reasonable, as the mid of the 20th-century has been recently proposed to indicate~~ is based on Zalasiewicz et al. (2011), who propose to define the middle of the 20th century as the beginning of the Anthropocene~~(?)~~ ~~. Note, however, that this comparison differs from the commonly used pre-industrial vs. present day distinction mostly for practical reasons.~~ . Furthermore, we excluded the sample from 1630 in most of the following analysis ~~because~~ in favor of more consistent freezing spectra. The statistical outlier is certainly important, as it was the only sample that was completely frozen before reaching −22 °C~~and would have therefore introduced a bias at colder temperatures, at which it was not possible to specify an INP concentration.~~ . At this state, however, we cannot explain what caused its high IN activity (cf. section 3.2). Moreover, as stated previously a contamination prior to the INP analysis cannot be excluded completely for this sample. Including the outlier does not change the general results.

Figure 8 illustrates the statistical freezing properties of both data groups using a box-whisker diagram. The figure confirms the previously observed finding that the modern day samples generally show higher frozen fractions at the same temperature. Furthermore, they exhibit a higher variability than the pre-1960 samples for most nucleation temperatures. The differences intensify at a medium supercooled temperature range (−23 °C to −26 °C). On average, the INP concentration of the modern day samples are 1.85 to 3.35 times higher than the samples with 10 year ~~samples~~ intervals in this specific temperature range (Fig. 9). We tested the significance of these differences with a two-sided T-test. We found that the average INP concentrations of modern day and pre-Anthropocene samples are in fact significantly different from one another at −23 °C ($p < 0.0181$), −24 °C ($p < 0.0008$), −25 °C ($p < 0.0011$), −26 °C ($p < 0.0360$) and −28 °C ($p < 0.0463$). Figure 10 compares the relative frequencies of observed INP concentrations of the two groups at −25 °C. Modern day samples follow a relatively broad log-

normal probability distribution with a median ice INP concentration of about $100\,\mathrm{mL}^{-1}$. The INP frequency distribution of pre-1960 samples, on the other hand, is evidently different from the post-1960 samples. Here, we find INP concentrations below $100\,\mathrm{mL}^{-1}$ more frequently. The distribution is more narrow and seems to be right-skewed to some degree, although the log-normal shape is still matched relatively well. Similar results emerge from the INP distributions at $T = -23\,^{\circ}\mathrm{C}$, $-24\,^{\circ}\mathrm{C}$ and $-26\,^{\circ}\mathrm{C}$, which can be found in the Supplement (Figs. ~~S2,~~ S3~~and~~, S4 and S5).

~~If there was no influence of~~ Now the question arises, what factors may have caused these significant differences in INP concentrations. Several hypothetical explanations come to mind. First, the changing climate may have influenced both the deposition pathways and their efficiencies (cf. sections 2.9 and 2.10). But, at least locally, the accumulation rate at B17 does not show a change between modern and pre-industrial times. Further, changes to relevant large-scale atmospheric circulation patterns are essentially unknown for the investigated time period. Assuming there was only little influence by post-coring contamination ~~, these findings seem to~~ and no change in climate and circulation, the findings suggest that certain particles that are ice nucleation active in a mid-supercooled temperature regime may be more abundant in today's atmosphere. We already hypothesized about possible candidates in the introduction (e.g. enhanced mineral or soil dust particles due to desertification, land-use change and agriculture, metals from industrial processes and/or fire particles from biomass burning emissions). In this regard, we consider it fairly likely that enhanced concentrations of desert dust and soil dust have influenced the modern INP concentrations. Potential atmospheric implications of this ~~finding~~ hypothesis are discussed in the conclusions.

Considering that the total global agricultural land area is estimated to have increased by a factor of 10 from 1400 to 1992 (Pongratz et al., 2008) combined with the fact that wind erosion has immensely accelerated within the last two centuries (Neff et al., 2008), partly due to intensive grazing by the heavily increasing number of domesticated animals, one could even have expected larger differences between the two data groups. Especially in the temperature range around $-15\,^{\circ}\mathrm{C}$, at which soil dust INPs from fertile agricultural regions are known to be active (O'Sullivan et al., 2015). We can only speculate why we generally did not observe many INPs in this temperature range, and why the significant differences between the two data groups were only observed for temperatures below $-22\,^{\circ}\mathrm{C}$. First, it is possible that dust from anthropogenic practices was not transported to Central Greenland in a detectable amount. According to Groot Zwaaftink et al. (2016), most of the dust input contributing to the dust surface concentration of the Arctic is from Eurasia north of 60° N, North America north of 60° N and Asia south of 60° N. In contrast, North America and Europe south of 60° N, where land-use change and the agricultural expansion are most prominent, contribute only little to the Arctic dust input (below 1%). Moreover, Asian agricultural dust sources may not exhibit the necessary high wind speeds to inject mineral dust into the upper troposphere as required for long-range transport to Greenland. In contrast, mineral dust from the Taklamakan desert is intrinsically linked to dust storms in this area.

Second, the more fragile (biological) INPs may have been deteriorated during sample storage (Beall et al., 2020). As a result, the warm-end of INPs might have been largely lost, leaving only a homogeneous fraction of very stable INPs behind. Figures 8 and 9 present some evidence for this hypothesis. As seen in Fig. 8, we find a much narrower range of frozen fractions for the 10 year samples, hinting at a rather homogenous population of INPs. On the other hand, the variability is much higher for the modern-day samples, possibly because some of the more fragile INPs were still active. However, as both sample groups

experienced the same sample history after coring, this hypothesis would only be reflected by deterioration effects related to the time elapsed since the particles were deposited in the ice. Furthermore, Fig. 9 depicts increasingly greater relative differences in the INP concentration from −30 °C to −24 °C until the warmer end of the data is reached, at which only few samples show ice nucleation activity. This observation could possibly be explained by assuming that the warmer INPs were largely deactivated due to storage effects.

3.2 Chemical composition of single particles

In total 308 particles were analyzed by SEM in the three selected samples (1977: 36 particles, 1680: 188 particles, 1630: 84 particles). Overall, the chemical composition was very similar between the three samples. The dominant part (287 particles – 93%) were soil particles, i.e. alumosilicates and silicon oxides (Fig. S5a). Besides the soil particles, 19 iron-rich particles, 1 titanium-rich and one calcium carbonate particle were found. Most particles are detected in the size interval 1 – 2 µm (only 13 particles above 5 µm diameter). Looking at the minor elements in the alumosilicate particles and the typical elemental ratios, most of the detected alumosilicates ~~will be~~ are most likely feldspars (and here more sodium and potassium feldspars), amphiboles and pyroxenes. Besides this, some quartz and clay minerals were also found. Unfortunately, due to the low number of analyzed particles, we were unable to determine significant differences in ~~particulate composition of the particles~~ the particulate composition and size distribution ~~in~~ between the three samples. For example, only a very small number of particles were detected on the 1977 sample in the analyzed center region of the filter. Generally, the border regions were not analyzed due to a higher risk of artefacts.

Moreover, a few fly ash particles (8%) were found ~~on~~ in the most recent sample (1977), which indicates ~~a~~ an anthropogenic chemical signature (Fig. S5b). Otherwise there was no obvious distinction between the modern-era sample and the other two samples with regards to their chemical composition~~with the limited analysis presented here~~, which might be due to the limited number of particles analyzed.

3.3 Seasonal cycle of INPs during a ~~high resolution~~ high-resolution period

Here we present a case study of 12 samples with an improved time resolution (only 1 – 2 months each). These samples ~~represent~~ cover a period of about 1.5 years in 1463 – 1464 (ice core depth: 87.647 m to 87.848 m), thus ~~, covering~~ representing a continuous annual cycle. There was no particular reason why this year was explored specifically. As the CFA decontamination step determined the resolution of samples, there were two periods with samples of near monthly resolution from which seasonal cycles could be established (1744 – 1763 and 1454 – 1468). The latter period was chosen for being unaffected by the industrial revolution.

Figure 11 shows the temperature at which 50% of the droplets were frozen (T_{50}). The T_{50} temperature is a simple but meaningful metric, which indicates how ice active a sample is. For the 12 samples T_{50} ranged between −28.2 °C and −31.1 °C. The entire T_{50} range of the ice core is from −20.2 °C to −32.1 °C. Thus, with a span of only 2.9 °C the seasonal samples have a significantly smaller range in T_{50} (76% smaller) than all samples from the ice core. Hence, the long-term INP variation of the ice core is considerably larger than the short-term variation in that specific year.

The number of data points are too few for an in depth seasonal analysis, but the ice nucleation activity of the samples ~~does seem to follow~~ shows a clear annual cycle. Interestingly, we find a similar annual pattern for various other IC and CFA parameters (lower panel of Fig. 11). The best correlation is found between T_{50} and the log of the concentration of insoluble particles with spherical diameters larger than 1.2 µm (R = 0.87, N = 12, $p < 0.0003$). The minima and maxima of both parameters are largely the same. In addition, even small fluctuations in T_{50} are reflected in the particle concentration. The results indicate that a higher particle concentration triggers earlier freezing, which is intuitive. A higher number of particles in a droplet means that there is a greater probability of the droplet to contain an INP. These findings suggest that the INP concentration ~~is~~ in this year was subject to the annual dust input in Greenland. As the seasonal variability in particulate dust number can be clearly detected throughout the entire core, we expect that such a seasonal INP variability will hold for the entire record. Future high-resolution studies will have to test this assumption. Bory et al. (2002) show that the main dust source in ~~Northern~~ Greenland is the Taklamakan Desert in Northern China. At the beginning of the monsoon season, the dust particles are transported to Greenland within a few days via the jet stream and cause the annual maximum dust input for Greenland in spring. Furthermore, episodic dust transport from the Sahara desert (Lupker et al., 2010) and Iceland (Sanchez-Marroquin et al., 2020) may have contributed as well.

The clear existence of a seasonal cycle and the significant correlation of T_{50} with the particle concentration also shows that the INP background was chosen conservatively and thus confirms the reliability of the data up to this point (at least for the deeper, less porous firn section of the core). Furthermore, the data suggest that even at low temperatures the ice nucleation behavior of the ice core samples is induced by actual atmospheric perturbations.

3.4 Comparison with literature data

Hartmann et al. (2019) found no long-term INP trend in their recent study, in which they analyzed ice core samples from Greenland and Svalbard with two droplet freezing devices. They found the overall range of observed concentrations to be comparable to present day concentrations. INP concentrations did not seem to be influenced by either anthropogenic impacts or volcanic eruptions. Furthermore, sub-year samples showed a large variability, which was as high or even higher than the total range of the other samples from the ice cores. Hartmann et al. (2019) regularly observed an early nucleation onset, which they interpret as an influence from particles with biological origin.

In general, past atmospheric INP concentrations of this ice core study align reasonably well to the lower end of INP concentrations currently observed in the atmosphere (Fig. 12). INP concentrations in this figure comprise data from vastly different environments and range over 4 orders of magnitude at a certain temperature (Kanji et al., 2017). However, our INP concentrations are significantly lower than those presented in Hartmann et al. (2019). Note that the data is difficult to compare as the freezing spectra do not overlap very well. Ice nucleation in this study occurred largely below $-25\,^{\circ}\mathrm{C}$, when most droplets were already frozen in the study of Hartmann et al. (2019). At $T = -20\,^{\circ}\mathrm{C}$ Hartmann et al. (2019) found atmospheric INP concentrations from about 0.004 to about 2 L^{-1}, whereas we found INP concentrations between 0.002 and 0.2 L^{-1}. The conversion to atmospheric concentrations was handled differently in both studies, but this does not explain differences up to one order of magnitude. This disparity may arise from experimental ~~, methodological~~ (droplet volume, etc.), methodological (e.g. sample

storage conditions) and or geographical differences, which may affect the deposition mechanisms and efficiency. Unfortunately, large discrepancies between different INP counters are relatively common, even in controlled laboratory environments (Hiranuma et al., 2015; DeMott et al., 2018; Hiranuma et al., 2019), and can often not be fully explained. Furthermore, the "short-term" variability of adjacent seasonal, dust and volcano samples were usually lower than the overall variability of the total ice core samples in our study. Whether the INP concentration was influenced by volcanic eruptions or not cannot be assessed conclusively at this point. The Laki eruption of 1783 did not increase the INP concentration, however two samples from 1475 indicate volcanic dust particles with ice nucleation potential.

Similarly, we cannot fully exclude an anthropogenic impact on the Arctic INP population. In fact, some evidence indicates that the concentration of INP active at medium supercooled temperatures has changed significantly after 1960, where we found higher and more variable INP concentrations, compared to the rest of the ice core samples. ~~However, we cannot fully rule out post-coring contamination as the cause for the observed differences.~~ It is possible that this result could not be observed by Hartmann et al. (2019) for several reasons. First, Hartmann et al. (2019) mainly investigated the temperature regime from $-10\,^{\circ}\mathrm{C}$ to $-20\,^{\circ}\mathrm{C}$, while significant differences occurred in our study only below $-22\,^{\circ}\mathrm{C}$. Second, the overall temporal distribution of samples in Hartmann et al. (2019) was less regular, had a coarser time resolution and included only few samples prior to the year 1735. Moreover, we specifically designed our sample selection (regular time intervals of 10 years, increased sample frequency after 1960) with this scientific question in mind.

Moreover, evidence presented in section 3.3 and Tab. 1 indicated that the long-range transported dust from East Asian deserts influenced the freezing characteristics of the ice core samples. Laboratory studies characterizing the ice nucleation activity of mineral dust from the Taklamakan desert and other Chinese deserts report active site densities n_s at $-25\,^{\circ}\mathrm{C}$ of approximately $1 \cdot 10^{10}\,\mathrm{m}^{-2}$ (Niemand et al., 2012; Ullrich et al., 2017) and between $1 \cdot 10^{10}$ to $1 \cdot 10^{11}\,\mathrm{m}^{-2}$ at $-30\,^{\circ}\mathrm{C}$ (Niemand et al., 2012; Boose et al., . We can only roughly calculate n_s from the CFA particle measurements. Lacking a solid particle size distribution measurement, we assumed all counted particles to have a spherical diameter of $1.2\,\mu\mathrm{m}$. This assumption is obviously flawed, as particles smaller than $1.2\,\mu\mathrm{m}$ were not counted by the CFA measurements, and larger particles were assumed to have this lower size. With this rough assumption, we find an average n_s of $2 \pm 6 \cdot 10^{10}\,\mathrm{m}^{-2}$ at $-25\,^{\circ}\mathrm{C}$ and $8 \pm 13 \cdot 10^{10}\,\mathrm{m}^{-2}$ at $-30\,^{\circ}\mathrm{C}$, which is in surprisingly good agreement with the literature.

4 Conclusions

Ice nucleating particle concentrations of ice core samples were measured in the immersion freezing mode by the FRIDGE droplet freezing assay. This analysis provides valuable insights into atmospheric variables related to microphysical cloud processes of the past six centuries. A process-based approach was chosen to estimate order-of-magnitude atmospheric concentrations from the directly observed ice concentration. Ice samples were selected for INP analysis following a systematic protocol.

Overall, the samples were not particularly ice nucleation active, with freezing occurring predominantly below $-25\,^{\circ}\mathrm{C}$. However, a ~~group of high resolution~~ selected subset of high-resolution samples displayed meaningful and intuitive results

– following a seasonal cycle – even at comparably low temperatures, where some influence from background freezing would usually be expected. Furthermore, we found significant correlations between concentrations of INPs and ~~certain aerosol species~~ the insoluble particle concentration $> 1.2\,\mu m$, Ca^{2+} and the conductivity for a broad range of temperatures. We did not observe a clear trend over time in the INP concentration. Yet, it appears that the population of particles acting as INPs at medium supercooled temperatures has increased after 1960. It ~~cannot be ruled out~~ is possible that the observed results are caused by an enhanced fraction of particles originating from anthropogenic activity. ~~Alternatively, differences may have been caused by post-coring contamination, which is likely more relevant for these samples as they stem from the more porous firn layer.~~

~~Still, this~~ This prompts the question which atmospheric implications can be expected, if there were more INPs today than in a pre-industrial atmosphere. In general, ~~several mechanisms can be considered by which~~ an increased number of INPs would affect cloud formation processes and consequently radiation interactions (DeMott et al., 2010; Murray, 2017). First, it is ~~thought~~ generally expected that the lifetime of mixed-phase clouds is shortened in the presence of ~~ice nucleating particles~~INPs. Ice crystals will form more rapidly at the expense of cloud droplets and water vapor, leading to earlier precipitation. Since supercooled clouds (e.g. stratus or altocumulus) usually have a net cooling effect, more INPs will consequently decrease this cooling effect due to the shorter lifetime. Similarly, cirrus clouds are also expected to have a shortened lifetime in a high INP scenario. Compared to a cirrus cloud ~~at~~ in which cloud droplets predominantly freeze homogeneously in a narrow temperature range, cirrus clouds that formed by heterogeneous ice nucleation will have fewer but larger ice crystals. Since in this case ice crystals have formed earlier, they have had more time to grow and hence will sooner fall out of the cloud. These upper tropospheric clouds typically have a net warming effect. A reduced lifetime will decrease this effect. Furthermore, different proportions of water droplets to ice crystals obviously also alter the cloud albedo. Unfortunately, it is rather unclear which of these effects dominates overall.

The apparent finding presented in this study is not to be generalized easily. It investigates only one location in the Arctic, which is quite isolated from direct human influence. It is also possible that, for example, urban aerosols and/or coatings reduce the ice nucleation properties of the INP population as a whole under more direct anthropogenic influence. We stress that the observed differences in the average INP concentration at specific temperatures are statistically significant, but the implications are far from certain. We recommend that our measurements should be repeated and verified in other studies, where we recommend to obtain seasonal resolution of the data, as the existence of a clear seasonality represents an effective check for the quality of the INP results. INP analysis should also be performed immediately after the first melting of the ice core samples.

There is a strong need to investigate INP concentrations of the past, and ice cores provide an unique and feasible opportunity to do so. We suggest to analyze the freezing properties of ice core melt water at different locations worldwide – we feel that other Arctic, Antarctic and mid-latitude Alpine ice cores are equally of interest. Beyond researching a possible anthropogenic INP signal, a multitude of ice core studies could improve our understanding of regional sources and geographical differences of INPs over otherwise inaccessible time scales. Furthermore, we plan to expand our ice core analysis to include a more rigorous, systematic study analyzing the chemical and morphological composition of insoluble aerosol particles as well as their size distribution by scanning electron microscopy. Particle size distributions of liquid samples may also be attainable by

the dynamic light scattering and the single particle scattering and extinction method. Moreover, future studies would greatly benefit from more comprehensive and precise knowledge about the present day INP concentration (atmospheric and fresh snow) and its variance, as well as dry and wet deposition metrics at the actual ice core drilling site. Finally, a modeling study could help identify (possibly ~~antropogenically~~ anthropogenically altered) INP source regions (e.g. based on historical records of land use cover) and estimate the potential atmospheric impact that could be expected from a threefold increase of INPs at $-24\,^{\circ}\mathrm{C}$ since the mid of the twentieth century, as it was seen in this study.

Data availability. The INP data of this study is uploaded to the PANGAEA data repository: https://doi.pangaea.de/10.1594/PANGAEA.922047.

Author contributions. JS and HB designed the conceptional idea of the presented manuscript. DK, SR and JS performed the INP measurements. JS compiled and analyzed the INP data with support of DK and SR. JS created the figures. Authors affiliated with the Alfred Wegener Institute and the University of Bern were responsible for the drilling, handling and cutting of the ice core, performed IC and CFA measurements and generated the samples for the INP analysis. ME performed the SEM measurements. All authors took part in the discussion of the results. JS wrote the manuscript, receiving valuable input from HB, JC, HF, MH and TE.

Competing interests. The authors declare no competing interests.

Acknowledgements. The methods and instruments of the ice nucleation experiment of the University of Frankfurt were established through financial support of Deutsche Forschungsgemeinschaft under Research Cooperations SFB 641 and FOR 1525 (INUIT), which is gratefully acknowledged. Long-term financial support of ice core research at the University of Bern by the Swiss National Science Foundation (SNF) is gratefully acknowledged. Funding for the CFA analyses used in this study was provided by the SNF project iCEP (200020_172506). We thank Remi Dallmayr and Melanie Behrens, who prepared and set up the fraction collection for the the CFA campaign, and Chantal Zeppenfeld who analyzed the Abakus and SPES data.

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Table 1. Pearson correlation between the INP concentration and selected CFA parameters of the complete data set. Bold coefficients indicate a significant correlation ($p < 0.05$). The number of samples is given in parenthesis.

T [°C]	dust	conductivity	Ca^{2+}
-20	-0.11 (57)	-0.04 (58)	-0.16 (58)
-21	-0.06 (91)	-0.03 (92)	-0.10 (91)
-22	0.19 (111)	0.09 (112)	0.04 (111)
-23	**0.19** (121)	0.15 (122)	0.06 (121)
-24	**0.26** (125)	**0.20** (126)	0.12 (125)
-25	**0.27** (125)	**0.20** (126)	0.12 (125)
-26	**0.21** (125)	0.15 (126)	0.07 (125)
-27	**0.24** (124)	0.11 (125)	0.09 (124)
-28	**0.31** (123)	0.14 (124)	**0.18** (123)
-29	**0.30** (123)	0.09 (124)	**0.19** (123)
-30	**0.34** (120)	0.04 (121)	**0.20** (120)
-31	**0.27** (113)	-0.07 (114)	0.12 (113)

~~Pearson correlation between the INP concentration and selected CFA parameters of indicated subsets of the data ("events" include the groups dust, volcanic and seasonal). Bold coefficients indicate a significant correlation ($p < 0.05$). The number of samples is given in parenthesis. 10 years modern day events dust conductivity Ca^{2+} dust conductivity Ca^{2+} dust conductivity Ca^{2+} -20 -0.20 (18) 0.12 (19) -0.29 (19) -0.37 (11) -0.09 (11) -0.08 (11) -0.01 (25) -0.01 (25) -0.06 (25) -21 -0.13 (37) 0.04 (38) -0.19 (38) -0.25 (17) -0.35 (17) -0.44 (16) **0.35** (34) **0.44** (34) 0.29 (34) -22 -0.05 (46) -0.08 (47) -0.05 (47) -0.16 (23) -0.27 (23) -0.38 (22) 0.29 (39) 0.15 (39) 0.21 (39) -23 0.02 (53) -0.08 (54) -0.06 (54) -0.17 (23) -0.27 (23) - 0.40 (22) 0.23 (42) 0.18 (42) 0.16 (42) -24 0.00 (57) -0.04 (58) -0.06 (58) -0.12 (23) -0.21 (23) -0.35 (22) **0.34** (42) 0.22 (42) 0.25 (42) -25 0.01 (57) -0.08 (58) -0.11 (58) -0.09 (23) -0.21 (23) -0.37 (22) **0.35** (42) 0.22 (42) 0.26 (42) -26 -0.04 (57) -0.08 (58) -0.15 (58) -0.05 (23) -0.21 (23) -0.38 (22) **0.31** (42) 0.20 (42) 0.23 (42) -27 -0.05 (57) -0.09 (58) -0.16 (58) -0.02 (23) -0.20 (23) -0.38 (22) **0.55** (41) 0.26 (41) **0.47** (41) -28 0.05 (56) -0.10 (57) -0.03 (57) 0.01 (23) -0.18 (23) -0.34 (22) **0.50** (41) 0.23 (41) **0.46** (41) -29 0.03 (56) -0.09 (57) -0.02 (57) 0.01 (23) -0.19 (23) -0.32 (22) **0.45** (41) 0.18 (41) **0.45** (41) -30 0.05 (55) -0.01 (56) -0.07 (56) 0.04 (23) -0.16 (23) -0.26 (22) **0.58** (39) 0.08 (39) **0.55** (39) -31 0.14 (53) -0.17 (54) -0.07 (54) -0.01 (22) -0.21 (22) -0.31 (21) **0.38** (36) -0.06 (36) **0.39** (36)~

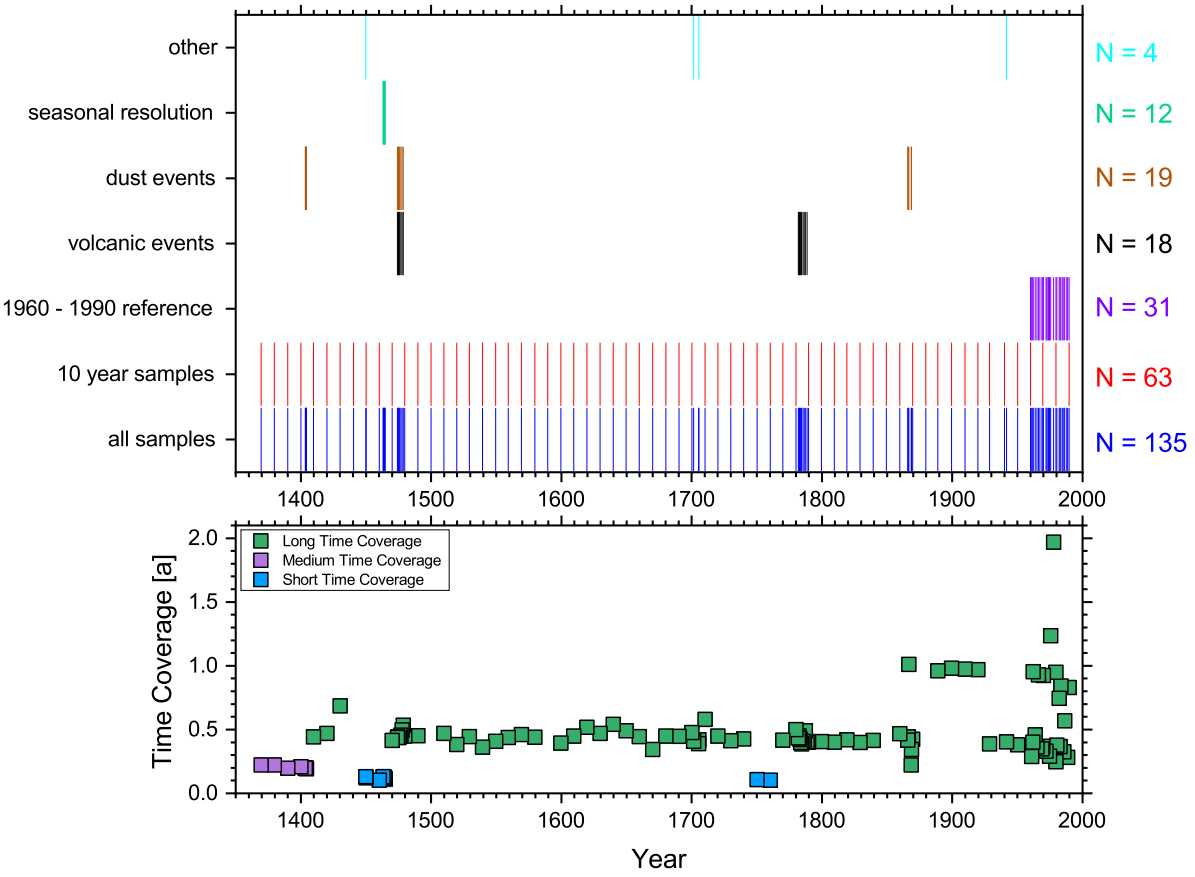

Figure 1. a) Temporal distribution and number of ice nucleation samples for different groups (colors). b) Time coverage of ~~ice nucleation~~ the samples selected for assessing IN properties. The different colors represent a broad grouping into samples averaging over short, medium and ~~longer~~ long time periods.

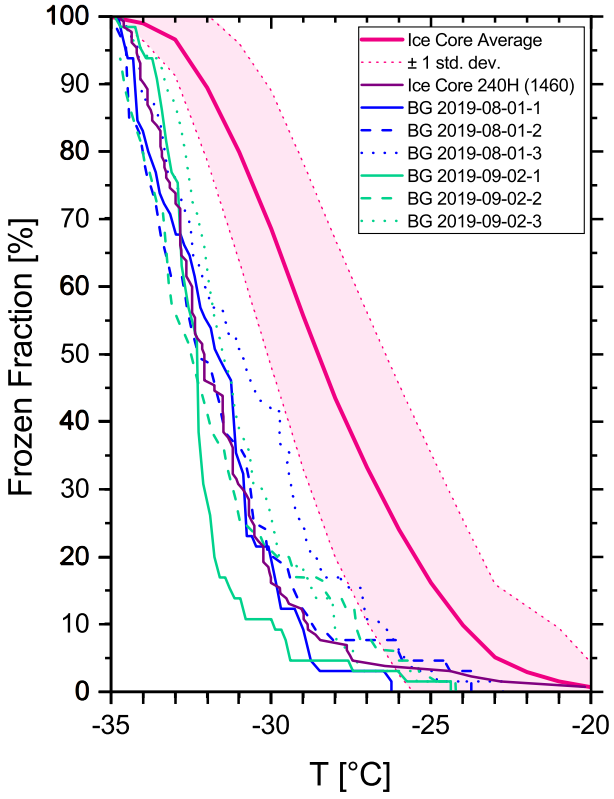

Figure 2. Freezing spectrum of ~~a typical~~ background ~~measurement~~ measurements (blue ~~line~~and green lines) compared to the average freezing spectrum from all ice core samples (pink line) ± one standard deviation (pink dotted lines). The ~~background freezing temperatures at~~ purple line shows the ~~frozen fractions of 10%, 20% and 25% are indicated~~least active ice core sample for comparison.

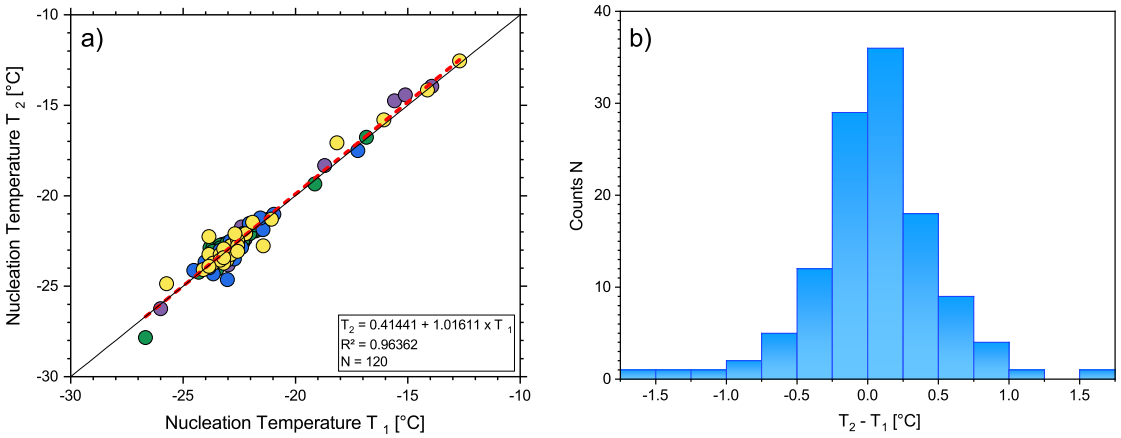

Figure 3. a) Freezing temperatures of individual droplets at two subsequent measurements. The different colors correspond to the four experimental runs of 30 droplets each. The linear regression is shown in a dashed red line, and the 1:1 line in a black line. b) Histogram of the individual droplet temperature difference between the two measurements.

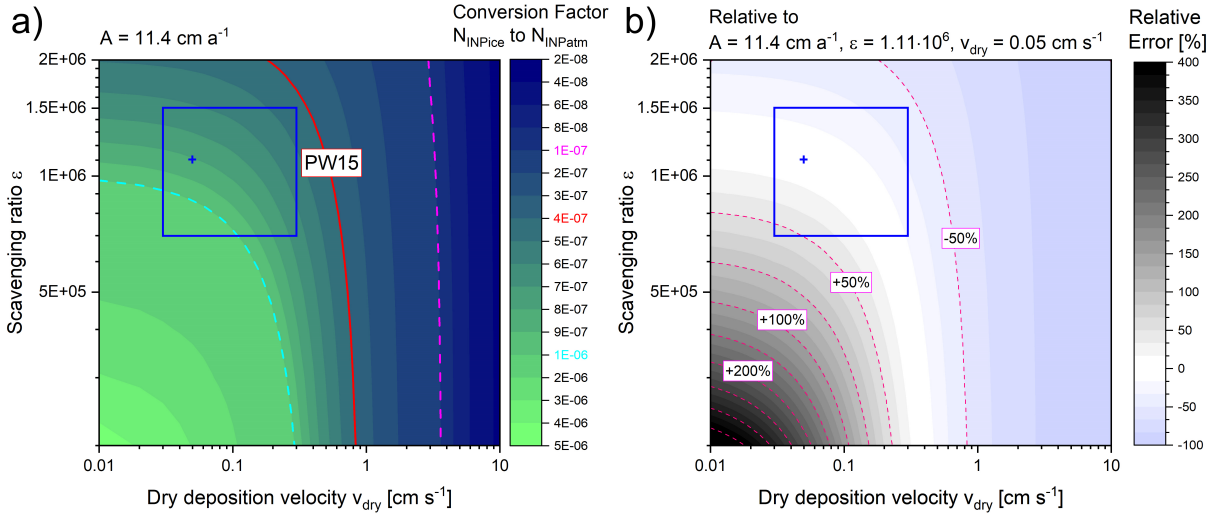

Figure 4. a) Conversion factor between the INP concentration per volume of ice and per volume of air depending on dry deposition velocity and scavenging ratio at a fixed accumulation rate. Our best estimate of $8 \cdot 10^{-7}$ is given by a blue cross. A likely range is indicated by a blue rectangle. The conversion factor introduced in Petters and Wright (2015) (PW15, red line) is added for reference. b) Potential errors relative to our best estimate due to uncertainties in v_{dry} and ε.

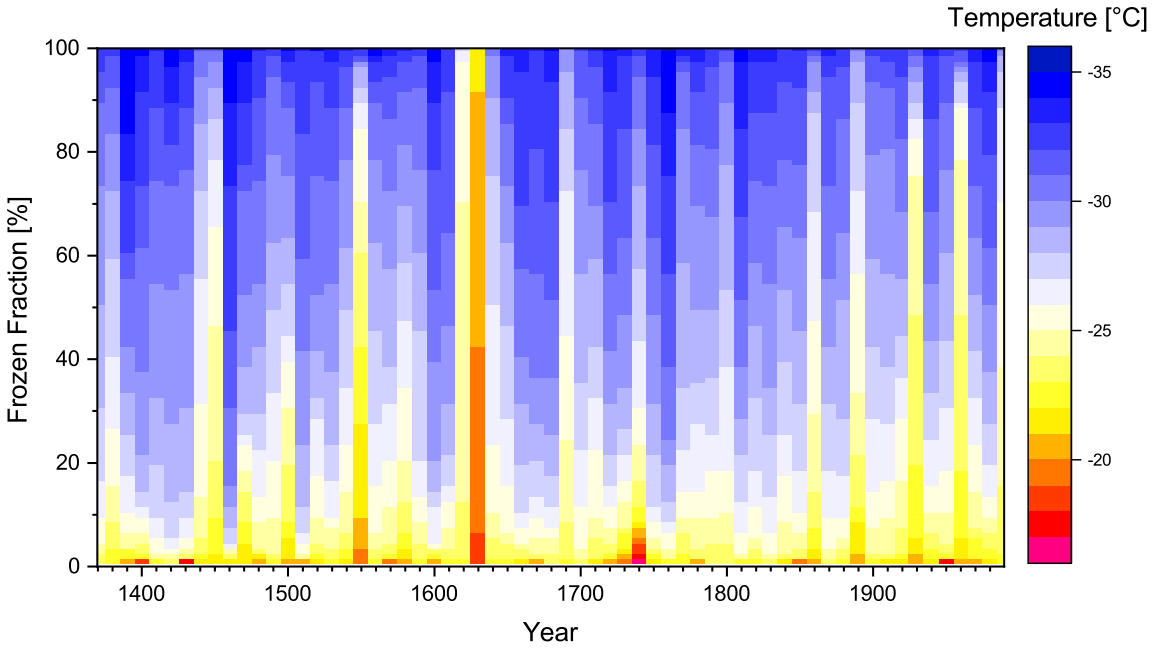

Figure 5. Frozen fractions of the samples with regular time intervals of 10 years depending on freezing temperature (colors). ~~Note, that the~~ The temporal coverage of an individual sample typically averages over about six month.

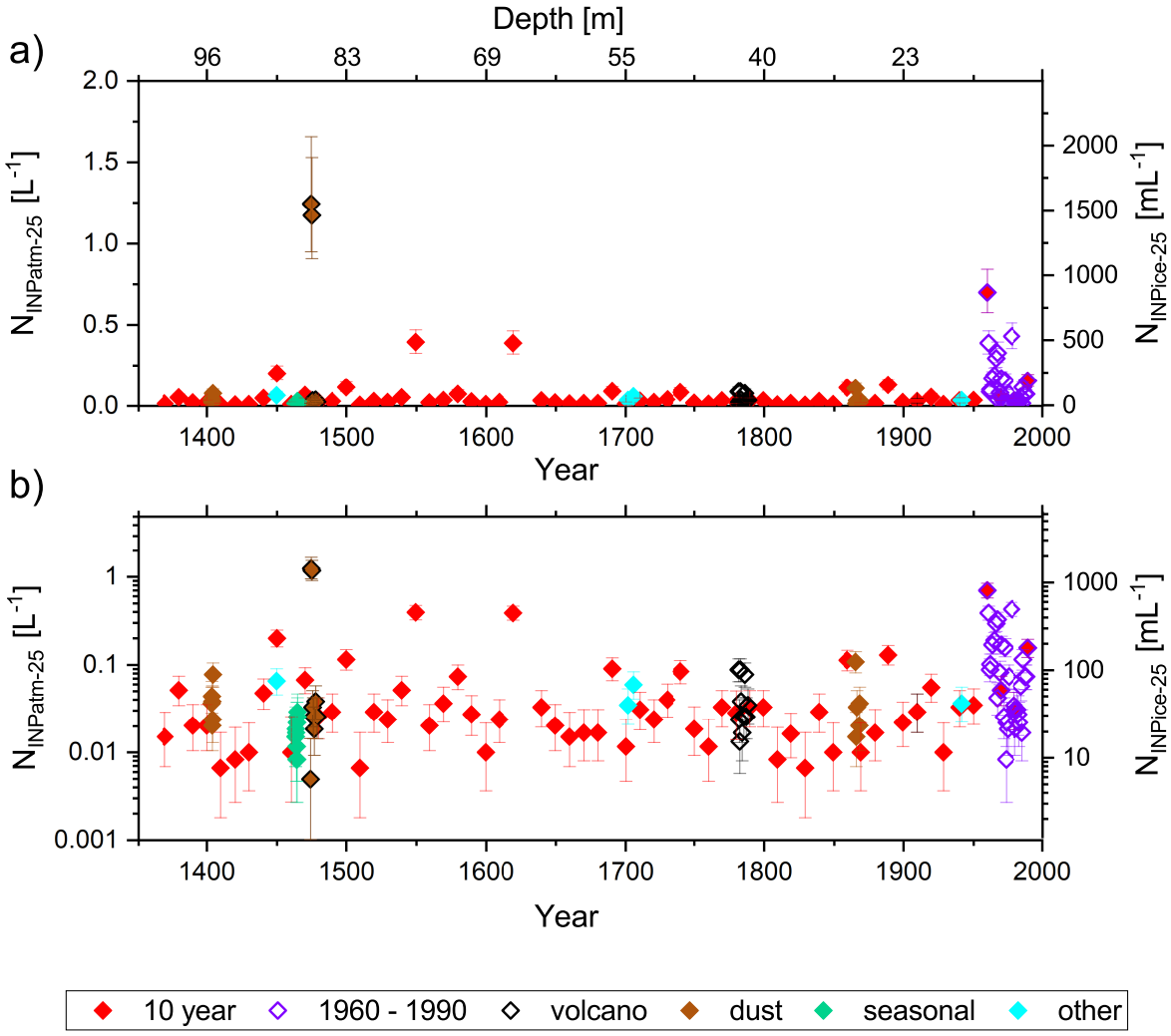

Figure 6. INP concentrations (right scale: per volume of ice, left scale: per volume of air) at −25 °C on both linear (a) and logarithmic (b) ~~scaling~~scale. Symbol colors correspond to the different sample groups as introduced in Fig. 1. The ice core's (nonlinear) depth from the top is added for reference on the top x-axis.

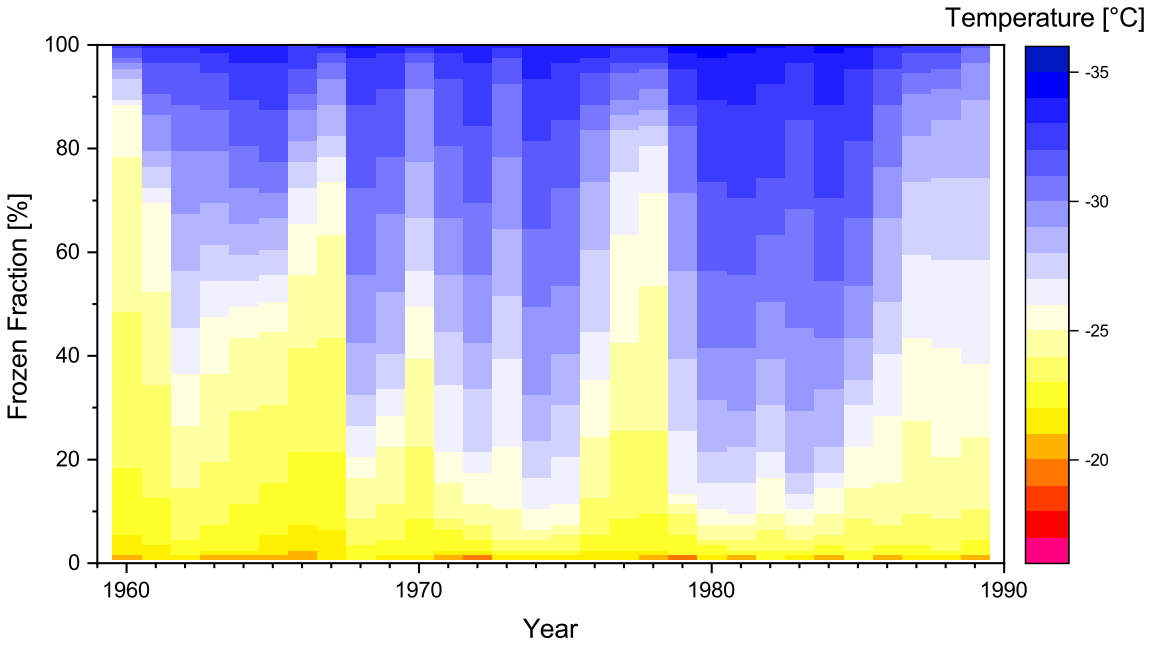

Figure 7. Frozen fractions of the modern day samples depending on freezing temperature (colors). ~~Note, that the~~ The temporal coverage of an individual sample typically averages over about six month. However, data points are interpolated in time to generate ~~a~~ yearly columns of regular width. The non-interpolated data ~~set~~is presented in Fig. S2.

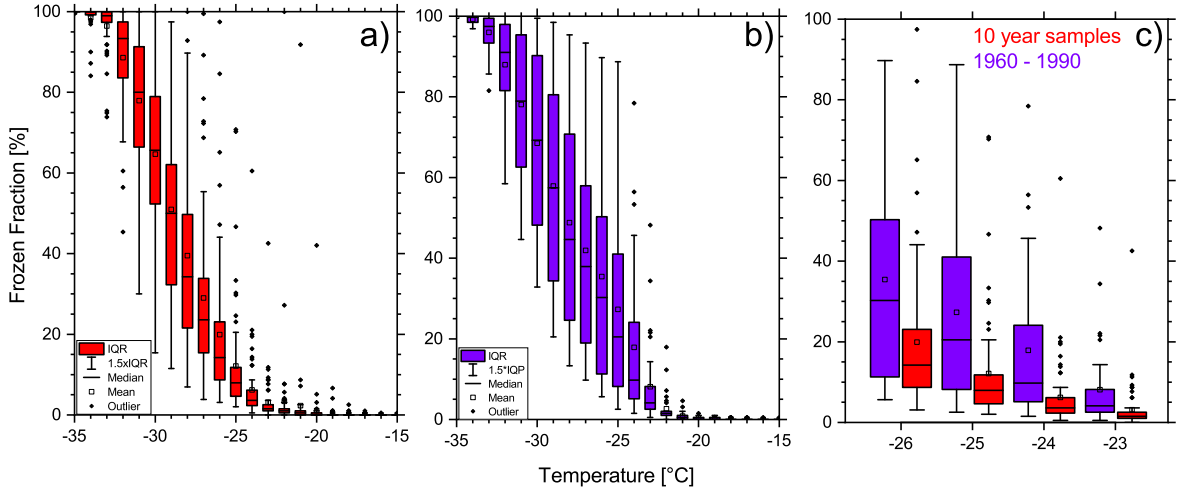

Figure 8. Box-Whisker plots of the frozen fraction of the 10 year samples (a) and the modern day samples (b) for the complete temperature range and a detailed comparison of both data sets at medium supercooled temperatures (c).

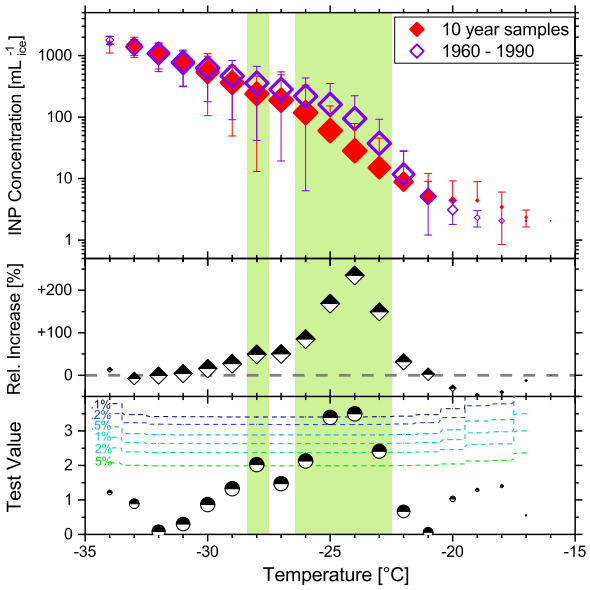

Figure 9. Upper panel: Average INP concentrations ± standard deviation (error bars) of the 10 year samples (red) and the modern day samples (purple). Negative error bars are not shown, when the standard deviation is greater than the average. Mid panel: Relative difference in the INP concentration between both groups. Positive values mean modern day samples are higher. Lower panel: Test values of a two-sided T-test to evaluate ~~if~~ whether the average INP concentrations of both groups are significantly different from each other. Dotted colored lines indicate the significance level of the test. Average INP concentrations that differ significantly from each other at $p < 0.05$ are highlighted in green. Symbol sizes in all panels correspond to the respective number of ice-active samples at each temperature (maximum number for 10 year samples: N = 58, maximum number for 1960 – 1990 samples: N = 31). Note, that the 1630 sample is excluded from this figure.

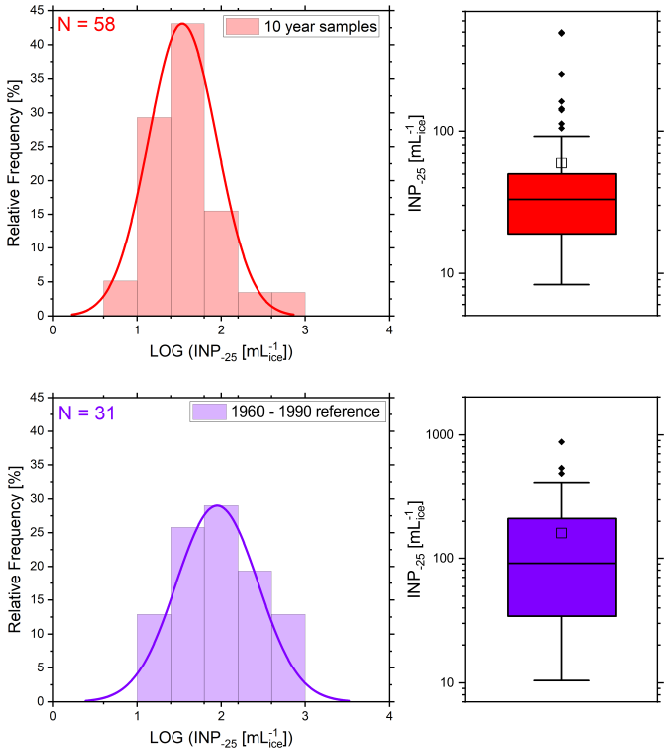

Figure 10. Empiric probability density function (bars) of the logarithmic INP concentration at $-25\,^{\circ}\mathrm{C}$ of the 10 year samples (top, red) and the modern day samples (bottom, purple). The data follows a log-normal distribution (fitted curve). The right panel shows the corresponding Box-Whisker plot.

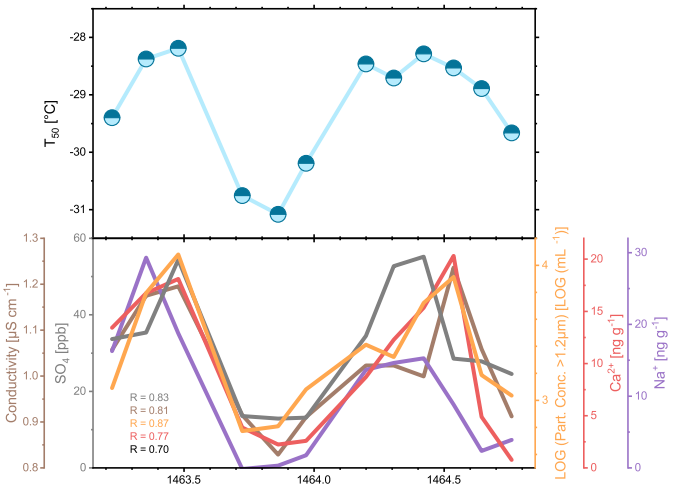

Figure 11. Upper Panel: Nucleation temperature at which 50% of the droplets were frozen during a ~~high resolution~~ high-resolution period around 1464 (sample resolution: 1 – 2 months). Lower Panel: Corresponding average concentration of IC (SO_4^{2-}) and CFA (conductivity, insoluble particles, Ca^{2+} and Na^+) parameters. Pearson coefficients for correlation of parameters to INP concentration are indicated (all $p < 0.05$). Please note that the x-axis may entail some temporal offset, as they refer to individual analyses performed separately on the core which may differ in their depth assignment by 1 – 2 cm.

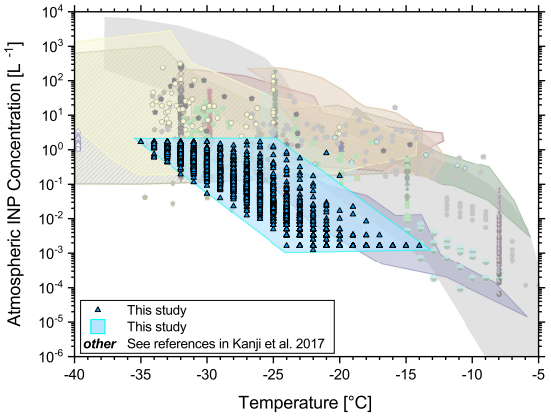

Figure 12. Estimated atmospheric INP concentrations of the ice core samples compared to data from other studies of a diverse set of environments as presented in Kanji et al. (2017).