Author response to Reviewer 1

First of all, we would like to thank the reviewer for reading and commenting on our manuscript. The comments and remarks helped us a lot to focus more on the methodological aspects and to improve the structure of the manuscript.

In the following, the reviewer comments are written in bold and our answers in italics. Text passages from the revised manuscript are in quotation marks, modified or newly added passages are marked in green.

General comments

In this study, the authors present an offline method for characterizing ice nucleating particles (INPs) by coupling an offline diffusion chamber, the FRankfurt Ice nucleation Deposition freezinG Experiment (FRIDGE), with a scanning electron microscope (SEM). The approach is potentially useful to provide comprehensive information of INPs, including their chemical composition, morphology, and size, and to improve the parameterization in the corresponding models. However, the advantages of combining the two instruments are not well demonstrated from the case study at JFJ. The FRIDGE-SEM coupling technique is not new and no convincingly new findings are shown in this study compared to the former studies at the JFJ. The methodology needs more details as intended to, in particular the coordinate system that allows for recovery of the particles, which is critical to determine whether particles are original or processed INPs. Statistical significance is also a big concern. It is unlikely to use the data present in this study to evaluate the INP-type-specific parameterizations in the model. In addition, the manuscript is not very well structured. The potential contribution of this study is within the scope of AMT. However, the current manuscript is behind publication quality due to the reasons as mentioned above. Therefore, I recommend that substantial revision needs to be done before considering publication.

We have revised the entire manuscript (see our responses to the major and minor comments below as well as our responses to the other two reviewers for details). Structural changes have been made, to focus more on the method. The entire method section has been revised to make it less manual-like, as it was suggested by the reviewers. The case study discussion has been shortened, in favor of a more concise and focused methodological manuscript better fitting the scope of AMT.

The coupling of FRIDGE and the SEM is now described in more detail and in a more structured way in the methods section, where advantages, drawbacks and uncertainties are discussed and a general overview of the potential of the method is provided.

The case study in this manuscript is intended to illustrate that the method presented provides reliable results for the main INP groups, despite relatively low identification rates, and not primarily to present new atmospherically relevant results. The discussion of the results has been adapted to emphasize comparability with other studies. Despite the small number of analyzed INPs, we have decided to show a comparison of air masses before and during a Saharan dust event, as the potential of the unambiguous particle assignment to the corresponding ice crystals becomes obvious here.

We do not claim that the presented results of our case study are sufficient to be used for model evaluation, we just want to express that this type of results could be used for a closure study as suggested to Burrows et al. (2022).

Major Comments

The novelty of this study is supposed to be the technical details and direct measurement of INPs. However, it needs more details to convince the readers that the individual particles can be fully recovered after measurement cycle of the FRIDGE. Additional controlled experiments may need to be done and shown to prove that hypothesis. Otherwise, the SEM measurement would be on the IRs rather than original INPs.

Based on the definition by Cziczo et al. (2017) the particles activated in FRIDGE are INPs because they were activated under defined conditions after the collection of the total aerosol. In the electron microscope, we are able to locate and analyze these INPs at the positions of crystal origin.
Of course, in this context one could also speak of ice residuals (IR), since the particles have already been processed in FRIDGE. IRs are defined as particles remaining after the collection of atmospheric ice crystals and subsequent evaporation of the ice phase. In this case, there is a risk that additional particles deposited on the surface of the original ice crystal are subsequently identified as ice forming particles. This problem does not exist in our method. This is why we refer to the analyzed particles as INPs.

"*Based on the definition by Cziczo et al. (2017) we refer to the identified particles as INP, as they were activated under defined conditions after the collection of the total aerosol and not sampled as ice crystals. Therefore, we are able to investigate truly activated particles in contrast to methods analyzing IRs, which face challenges in order to distinguish between IRs and scavenged particles. However, some of the INPs analyzed with SEM may have undergone changes (see Sect. 2.6) due to the measurement procedure in FRIDGE, but we assume that these changes are of minor importance for the main INP classes that we can analyze with this method.*"

It is good that comparisons with previous studies at JFJ are discussed. However, the authors may want to add more discussion on the differences and emphasize the new findings.

In our opinion, a case study in a methodological paper should exemplarily showcase the capabilities of a measurement system by presenting plausible results that, in the best case, agree to previously published literature. As shown in the revised manuscript the results indeed are in good agreement to those from Eriksen Hammer et al. (2018) and Lacher et al. (2021) that were obtained from the same campaign, as well as to those of Worringen et al. (2015), Kamphus et al. (2010) and Ebert et al. (2011) measured at JFJ but a few years prior. For a paper that focuses on atmospheric measurements and their implications, we agree with the reviewer that it is important to discuss differences and, above all, to focus on new findings, however, we think that such an in-depth discussion would be beyond the scope of an AMT paper. In fact, to strengthen the methodological focus of the paper, we have streamlined the case study section.

The results were based on 200 individual particles from 5-week measurement, and only half of the total analyzable area of each wafer was analyzed by SEM. The author should evaluate the statistical significance, discuss more about the representativity, uncertainty and limitations.

Of course, 200 INPs for a period of more than 5 weeks is comparatively low. Therefore, we do not claim that our results are representative of an average composition of INPs over the entire campaign period. This is now also noted in the manuscript.

"Although the number of identified INPs appears comparatively low for a campaign period of five weeks, these INPs were identified with a high degree of reliability (Sect. 2.5.2). The small number of particles identified bears the risk that individual, time-limited variations occurring randomly during the sampling periods may influence the resulting total composition to a certain degree. It should

therefore be noted that the results presented below may not comprehensively reflect the main composition of the INPs over the entire campaign period. Nevertheless, it can be shown that the method provides valid results for the main groups of INPs (see confidence intervals for Fig. 9 in the supplement (Tab. S2)).”

However, by comparing air masses before and during a Sahara dust event (see Fig. 9 in the revised manuscript), we were able to show that it is possible to identify important trends in INP-relevant groups. This illustrates the great strength of our method, which has low identification rates, but identifies the INPs with high accuracy and thus still delivers credible results. Confidence intervals for the chemical distribution are given in the revised supplement (Tab. S2).

The structure of this manuscript needs revision. The introduction, method and results sections have several overlaps, which need to be improved. E.g., in the introduction section, L 126 to 130 belongs to method part; Section 2.6 Chemical classification should be merged into Section 3.4 INP chemistry or go to supporting information; Section 3.1 Sampling site needs to go to method and/or introduction; Section 3.3 Method evaluation needs to go to method section.

We have revised the structure of the paper and created a distinct separation between the general methods section and the results of the case study. With regard to the points mentioned, we have proceeded as follows:

L126 to L130 from the introduction section was moved to the method part as an introduction.

Section 2.6: We have decided to leave this section (renamed as "individual particle analysis") in the methods section and have adapted it accordingly. It no longer describes the specific particle classes found at the JFJ but defines a general classification scheme and discusses strengths and limitations of the individual particle analysis.

Section 3.1: For a paper focusing on the results, we would agree with the reviewer. But in our opinion, in this case, the sampling site description belongs to the case study, because the method part describes and discusses the coupling procedure and the sampling site is part of the case study.

Section 3.3: As the identification rates are highly dependent on the total wafer loading, which is influenced by the aerosol concentration and activated fraction during the sampling time, the values for the JFJ campaign are not universally valid. We have therefore not included these values in the methods section. However, we understand the reviewer's point, which is why we have decided to include the identification rates with the corresponding restriction in the method section (Section 2.5.2 "INP identification").

“The number of INPs that can be unambiguously attributed to an ice crystal origin is significantly influenced by the total wafer loading, which is determined by the sampling parameters (e.g., flow rate, sampling time, deposition efficiency) in combination with the aerosol concentration present. However, even if the aerosol concentration is known, it is difficult to specify a suitable collection volume in advance, as the ratio of potential INPs to the total aerosol also plays a role. This ratio is variable and usually unknown prior to measurement. As a result, the amount of atmospheric aerosol and the proportion of INPs deposited on a wafer are highly variable. This variability is also seen in the identification rates, which is why it would be misleading to give an average identification rate for the method presented. However, a specific identification rate for the case study conducted at the high-altitude research station Jungfraujoch (Sect. 3) can be given here as a guideline. The average INP identification rate was calculated to be 30% (ranging from 13% to 50%). Furthermore, the study identified the presence of multiple particles at 45% of the locations (ranging from 7% to 81%), while the remaining 25% (ranging from 2% to 66%) were found to be blank positions.”

The comparison between the different ice crystal counting methods (formerly Fig. 5) was also moved to the method section (Section 2.4 "identification of ice crystal positions") and replaces the graphical representation of coordinate determination (formerly Fig. 2), which has been moved to the supplement.

Minor Comments:

L33: Please remove "e.g." from the citation and do it through the entire manuscript.

We have removed the "e.g.," in many cases. In some cases, however, we have left it to indicate that the reference cited is just an example.

L41-42: What is the temperature range you mentioned? Please add the values and explain why the main focus has been on such range.

The temperature range for heterogeneous nucleation in mixed phase clouds is 0°C > T > -38°C. At temperatures colder than -38°C spontaneously homogeneous freezing might dominate the formation of ice. In the case of homogeneous freezing no INPs are needed to exceed the energy barrier. That is why the main research focus for INPs has been on the temperature range between 0°C and -38°C.

However, these sentences have been deleted in favor of a more focused introduction with less of a review character.

L44: Quantify the "small fraction". How much%?

The sentence has been adapted and now reads:

"Only a small fraction of the total aerosol can act as INPs and their concentrations can show variations of several orders of magnitude in space and time (DeMott et al., 2010; Kanji et al., 2017)." Values for the proportion of INPs in the total aerosol are given in the two references.

However, later in the Introduction (L96-97) we give values:

"… extremely low number of INPs within a sampled air volume compared to the much higher number of non-INP particles (ratio ~ 1/ 10^4 – 1/ 10^6),…"

L46 & 51: Change "history within the atmosphere" to "atmospheric processing"

Changed as requested. The entire section has also been shortened. The new sentence now reads as follows:

"In addition to the prevailing environmental conditions i.e., temperature and humidity, the potential for an INP to become activated is dependent upon individual particle properties (surface imperfections (Kiselev et al., 2016), chemical composition and specific chemical properties, crystal structure, coating (Kanji et al., 2008), etc.) as well as its atmospheric processing including potential agglomeration or pre-activation (Marcolli, 2017)."

L60: Mineral dust is a good INP, rather than an important factor in ice nucleation.

Changed as requested.

"Mineral dust, which is emitted from arid and semi-arid regions and is globally distributed in the atmosphere (Perry et al., 1997; Ansmann et al., 2003; Schepanski et al., 2018), is a good INP at temperatures below -15°C (Hoose & Möhler, 2012)."

L76-93: Please consider remove or shorten this part. Lab, field and model studies are the main approaches for atmospheric science. This is very basic and general, not specific for ice nucleation studies.

We have removed the entire section. The references for laboratory and field experiments have been moved to the following section.

"Although there is a variety of methods to determine the INP concentration in the laboratory (Hoose & Möhler, 2012; Hiranuma et al., 2015; DeMott et al., 2018; Hiranuma et al., 2019) and in the field (Wex et al., 2019; Schrod et al., 2020b; Brasseur et al., 2022; Lacher et al., 2024), only a few of them are simultaneously able to report on the chemical characteristics of individual ice-nucleating particles."

L103-104: The sentence is unclear. Please revise.

Revised sentence: "In another approach, the particles are activated under defined conditions in an online reaction chamber (e.g., Rogers, 1988) after the collection of the total aerosol."

L105-106: It is unclear why the IR and INP are in the brackets. Please add more descriptions.

The entire section on the collection of INPs/IRs has been rewritten and shortened. As a result, the entire definition of INPs and IRs (including this sentence) has been removed.

L111: What are the problems? Please elaborate.

Online systems may have problems to resolve low concentrations of INPs as they have typically a lower sampling flow, resulting in low INP counts in the range of background counts. Offline methods, on the other hand, can enrich the number of INPs on the sample substrates due to higher sampling flows and longer collection times.

L116-122: You might want to emphasize more on the advantages of EM over online measurement technique. For example, the morphology and quantitative results that SPMS generally does not provide without reference instrument. Note that SPMS can provide information of mixing state, which is not only obtained by the EM.

We removed the mention of the mixing state in the section about EM.

L131: I am not convinced that the particles characterized by SEM are INPs rather than IRs.

The particles originally collected and activated in FRIDGE are INPs, since they were collected as total aerosol and not as ice crystals. The processing in FRDIGE (repeated activation/evaporation) can undoubtedly lead to changes in particle properties in some cases, which is why one could also speak of IRs in EM. However, according to our understanding, these changes are more likely to affect the soluble/volatile components, which are not known to contribute significantly to ice nucleation in the considered temperature range. Since our method does not allow us to detect the small volatile components well, we assume that the majority of particles which can be analyzed with our method do not undergo serious changes during the activation/evaporation processes. Therefore, we stick to the definition of Cziczo et al. 2017, according to which we collected and activated INPs. In addition, the coupling allows for investigating truly activated particles in contrast to methods analyzing IRs, which face challenges in order to distinguish between IRs and scavenged particles.

L133-148 Figure 1: It is unclear regarding the second and the third pictures, please consider adding B1, B2 and B3 for second and third pictures regarding the FRIDGE, C1, C2 and C3 for SEM. Please add the missing legends for the bars and pie chat. Please add missing units for the x-axes on the

EDX spectra and the time series of INP conc., respectively. Please increase the resolution of the pictures, especially the scales and labels which are too vague for current version.

The desired labels (B1, B2 and B3 for the FRIDGE as well as C1, C2 and C3 for SEM) and the missing labels for the pie chart and the bars have been inserted. The labels for the pie chart and the bars have been kept general (TA, TB, TC and Class A, Class B, …) to make it clear that this is only a sketch of the method and that no real results are shown. The missing units have also been added and the scales and the font size of the labels have been increased.

L174: Change "at" to "in".

Changed as requested.

L205: Will measurement cycle change e.g., morphology or properties of particles? If no, you need to give the proof.

Please, see comment on INP discussion above. Of course, the morphology, especially for soluble particles can change during the activation/evaporation process. Since most of the particles we identified as INPs consist of non-soluble components, we believe that this does not significantly affect the results.

L204: Change "electron microscopy" to "EM". The full name only needs to be mentioned when shown for the first time in the manuscript (from introduction section).

Changed as requested.

L223: What is ImageJ? Please explain.

ImageJ is a free image processing software. We added this information to the text.

"The ice crystal positions are identified by image analysis using the internal particle analyzer of the free image processing software ImageJ (Schneider et al., 2012), with a minimum size of 30 pixels proven to be useful."

L231: Consider changing "time-consuming" to "labour-intensive" or other more appropriate word. Please revise and give the approximation of the duration of such analysis.

The corresponding section has been rewritten for the purpose of a less manual-like writing style, as it was requested by the reviewers. The wording is no longer used in the new section.

L247: Give full name for "FEI"

FEI is the official company name. It stands for "Field Electron and Ion Company".

"A Quanta 200 FEG Environmental Scanning Electron Microscope (ESEM) by FEI (Field Electron and Ion Company; Eindhoven, Netherlands) coupled to an energy dispersive X-ray detector (EDX) (EDAX, AMETEK, Tilburg, Netherlands) was used for analysis."

L254: Remove the full name of SEM.

Changed as requested.

L267: How much is the uncertainty? Please give the value.

This uncertainty is based on the calculation of the ice crystal origin and the coordinate calibration. We added a comment on the uncertainty for the ice crystal calculation in Section 2.4.

"Nevertheless, a potentially imperfect radial symmetry of the ice crystal growth, coupled with the restricted resolution of the FRIDGE images (20 x 20 µm), may result in an uncertainty in the calculation of the ice crystal origin. As the size of an ice crystal increases, the probability and extent of such a non-symmetrical growth also increases. The quantification of this uncertainty proved to be difficult, as it depends on the symmetry deviation present. To reduce this uncertainty based on an imperfect radial symmetry, the ice crystal position calculation should be performed on the basis of FRIDGE images, that show the ice crystals in a state close to activation."

The coordinate calibration uncertainty is mentioned in Section 2.5.1.

"Due to the limited resolution of the FRIDGE images of about 20 x 20 µm, the calibration has of course an uncertainty in the same order of magnitude."

Regarding the accuracy of the coordinate, the following is stated in the INP identification section (Section 2.5.2):

"Each ice crystal position, based on a real grown ice crystal, is inspected by SEM to identify the presence of particles. Given the uncertainties associated with the ice crystal identification process (Sect. 2.4) and the coordinate calibration (Sect. 2.5.1), it is crucial to consider not only the exact calculated coordinate but also the surrounding area. This area must take into account the aforementioned uncertainties and, at the same time, limit the probability that several particles will be observed in the scanned area. In this context, a radius of 50 µm has proven to be useful. While the previously discussed uncertainties may suggest a lager radius to be beneficial, in fact, the high substrate loading often proves to be the limiting factor."

L294: How much smaller? Please give the value.

The section has been rewritten:

"The number of INPs that can be unambiguously attributed to an ice crystal origin is significantly influenced by the total wafer loading, which is determined by the sampling parameters (e.g., flow rate, sampling time, deposition efficiency) in combination with the aerosol concentration present. However, even if the aerosol concentration is known, it is difficult to specify a suitable collection volume in advance, as the ratio of potential INPs to the total aerosol also plays a role. This ratio is variable and usually unknown prior to measurement. As a result, the amount of atmospheric aerosol and the proportion of INPs deposited on a wafer are highly variable. This variability is also seen in the identification rates, which is why it would be misleading to give an average identification rate for the method presented. However, a specific identification rate for the case study conducted at the high-altitude research station Jungfraujoch (Sect. 3) can be given here as a guideline. The average INP identification rate was calculated to be 30% (ranging from 13% to 50%). Furthermore, the study identified the presence of multiple particles at 45% of the locations (ranging from 7% to 81%), while the remaining 25% (ranging from 2% to 66%) were found to be blank positions."

L302: "appearance", do you mean morphology?

Yes, we mean morphology. We changed the wording.

"Therefore, the morphology of the particles may have undergone alterations."

L305: Consider changing "excellent" to "efficient"

Changed as requested.

L374 Figure3: The scales and labels are too vague. Please increase the resolutions.

Changed as requested. The y-axis of the EDX-spectra are not important, as they show only the counts, which are dependent on the EDX sampling time and the current of the electron beam.

L437-438: Please separate the samples into cloudy and clear sky cases and discuss accordingly.

As requested by the reviewers, the case study section was shortened to emphasize the focus on the methods section. To emphasize the potential of the method, we decided to show a separation for airmasses influenced by an SDE and prior to that event. Although the suggestion to separate the samples into cloudy and clear sky cases is certainly interesting, we fell like that this would go beyond the scope of an AMT paper.

L440-444 Figure 6: Cloudy and clear sky cases should be separated.

As previously mentioned, we have decided to distinguish the SDE air masses from the air masses prior to that event, as this illustrates the potential of the method. Despite low particle numbers, the high accuracy in identifying the INPs allows significant differences between different air masses to be recognized.

L634-636: Consider archiving data in a reliable public data repository.

The complete data set is available for the community and can be accessed by request to the corresponding authors.