

Author response to Reviewer 3

First of all, we would like to thank the reviewer for reading and evaluating our manuscript. The comments helped us to improve the manuscript and strengthen the desired focus on the methodological part.

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.

In this manuscript, the authors present an offline method that combines an ice nucleation counter, the FRankfurt Ice nucleation Deposition freezinG Experiment (FRIDGE), with Scanning Electron Microscopy (SEM) to analyze the chemical composition, size, and morphology of Ice Nucleating Particles (INPs) collected from ambient air. The authors begin by providing an overview of the methodology, followed by a case study demonstrating its application to ambient aerosols collected during the 2017 CLACE/INUIT campaign at the Jungfraujoch station.

The methodological section appears unfinished, as it fails to demonstrate all the potential features the authors claim the method can analyze (e.g., morphology, pores). Additionally, the lack of standards in this section raises concerns about evaluating the performance of the technique and estimating statistical error, particularly for size measurements and the coupling of particle size with ice nucleation efficiency.

The methodological part of the manuscript has been improved. Uncertainties (e.g., for the identification of ice crystal origins (Sect. 2.4 in the revised manuscript) and the coordinate calibration for SEM (Sect. 2.5.1 in the revised manuscript)) are now defined and discussed more clearly. Please note that the pure FRIDGE method including statistics has already been evaluated by Schrod et al. (2016).

Sect. 2.4: “It can be assumed that this coordinate represents the position of the corresponding INP, since an approximately radially symmetric ice crystal growth can be observed in the range of the selected activation conditions in FRIDGE. 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.”

Sect 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.”

The method evaluation from the case study was also included in the methodological section. The comparison between the different ice crystal counting methods (formerly Fig. 5) was 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. The discussion on the identification rates was included in section 2.5.2 (now called “INP identification”).

Sect. 2.5.2: “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.”

Section 2.6 (now called “individual particle analysis”) has been generalized, to show the potential of the coupling method. The morphology is now mentioned in Sec. 2.6 as it can be used to classify INPs. We included

also a BSE picture showing a particle with different chemical compositions on its surface (Fig. 4 in the revised manuscript), to illustrate that it is also possible to see the element distribution on the particle surface.

“The analysis by SEM and EDX is an efficient method for characterizing INPs in detail, as it provides information on elemental composition and distribution as well as on morphology and surface properties. The morphological information can be used for source apportionment (e.g., biological particles, soot, spherical particles from high temperature processes). With this detailed information, it is possible, for example, to determine the mixing state of a particle (see Fig. 3 and Fig. 4).”

The size of the particles can be determined with high precision due to the high resolution of the electron microscope, in contrast to the FRIDGE camera, where the resolution is limited.

For more details we refer also to our following responses and our comments to Review 1 and 2.

The case study lacks sufficient statistical analysis and fails to provide a clear connection to other parameters measured during the campaign (e.g., aerosol size distribution and number concentration).

The focus of the manuscript is the methodological description and discussion of the FRIDGE-SEM coupling. Therefore, the case study Section was shortened. Nevertheless, for statistical purposes, we have calculated the confidence intervals (Supplement Fig. S2) for the chemical composition shown in Fig. 9 (revised manuscript). Additionally, we have connected our INPs size measurement to the aerosol size distribution from the CLACE INUIT campaign provided by Weber (2019). For more details see our comment on Fig. 7 below.

It appears the authors did not clearly decide whether to (A) describe and evaluate the method in detail, suitable for AMT journal or (B) focus on the CLACE/INUIT campaign with further analysis. As a result, the manuscript presents two incomplete studies that are not well connected.

We can see that a reader may get this impression. In fact, the decision between ACP and AMT was under discussion for a long time. In the end, we decided on AMT, but it seem that the manuscript was not sufficiently adapted to this decision.

For the revised version, we have placed a clear focus on the methodological discussion and shortened the case study.

Specific comments

- A clearer explanation is needed as to why deposition and condensation freezing modes are grouped together as the two primary ice nucleation modes. Specifically, the cycles with FRIDGE include measurements taken below water saturation at RH=100%, which would typically prevent condensation freezing. Is this grouping due to uncertainty in the RH measurements, which could allow for RH to exceed 100%?

Apart from an uncertainty in the RH measurement, the two nucleation modes are mainly combined, as we measure both below RH=100% water saturation and specifically beyond RH=100% (95% / 97% / 99% / 101%). While INPs are activated solely by deposition freezing at RH distinctly below 100%, condensation freezing also takes place around/above 100%.

As more INPs are usually activated at higher RH, the series of measurements around RH=100% are better suited to the coupling method.

- The authors argue that volatile compounds are not detected and that these compounds are generally not known to be efficient INPs. Is there any estimation of which type of volatile material is lost, a lower estimation of vapor pressure? How does this affect SEM measurements, notably for carbon? Could there be potential effect of freezing point depression, such as the competition for adsorption on active ice nucleating sites between water and other volatile compounds?

We work under near-vacuum conditions in both the FRIDGE and the ESEM. Before starting the measurement, a vacuum is created in the FRIDGE chamber ($p < 0.1$ mbar). After each measurement cycle, the chamber is evacuated again until the chamber pressure from before the measurement is restored. This is to ensure that all water vapor that has been added to the chamber during the measurement, and thus also the ice crystals, is removed again before starting the next measurement cycle. So typically, the chamber is evacuated 13 times for one sample. In the SEM, the samples are analyzed in a high vacuum at approx. 10^{-6} mbar. All compounds, which are stable under the vacuum conditions can be analyzed with SEM/EDX.

A second limitation is the stability under the electron beam. All particles which are not stable under the electron bombardment can possibly be seen, but no chemical classification is possible as they evaporate during the spot analysis. In SEM, HVOCs and (ammonium)nitrates are particularly problematic, whereas sulfates, nitrates and especially carbon-rich particles as an important INP compound can be analyzed by SEM/EDX. As a consequence, the limitation for the analysis of volatile particles is not given by SEM.

Nevertheless, we observe that the dominant secondary atmospheric particles of the atmosphere are not visible on the wafers in the EM. It is therefore reasonable to suspect that these particles are lost during the sampling collection or processing. In the manuscript we say the following:

“At this point, it should also be noted that our findings revealed an absence of small volatile compounds on the wafers in the EM, which are typically present in larger numbers in the total aerosol. Presumably, there is a loss of these components during sampling collection or processing. However, as these volatile particles are not known to be efficient INPs in the considered temperature range (Murray & Liu, 2022), it can be assumed that their absence does not significantly affect the results.”

- The case study part focuses primarily on chemical composition and size analysis, but the title of the paper also mentions morphology. The conclusion, line 594, states, " This coupling allows for detailed analysis of various INP properties, such as chemical composition, mixing state, size, morphology, and surface properties like cracks or pores." Yet, no information is provided regarding the mixing state, morphology or surface properties.

It is true that the case study was primarily focused on the chemistry and size of INPs. Nevertheless, the detailed single particle analysis by SEM and EDX provides, in addition to the chemical composition, information on the surface structure (secondary electrons) and the element distribution (backscattered electrons). Even if it is not possible to define the exact origin of the ice growth on the particle surface, with the current setup, the method can generally be used to investigate the mixing state, morphology and surface of the identified INPs.

The potential of the method is described in more detail in the new version of the manuscript in Section 2.6. There we mention, that the morphology can be used to identify certain particle classes (soot, biological particles) and sometimes to determine the origin of particles (e.g., irregular geogenic minerals vs. fly ash). We have also added an example of a mixed particle which, in contrast to the mixed particle in Fig. 3 of the old manuscript, allows clear differentiation of the regions with different chemistry.

- Figure 3: The x and y axis are not readable. Only few EDX spectra are provided in figure 3 for the case study analysis. How can we evaluate the reliability of the chemical composition on all particles?

The labeling of the x-axis has been adjusted. The y-axis provides information on the number of counts which depend on the parameters set during the EDX analysis. The exact numbers are of no further importance for the evaluation carried out here, the peak intensities are clearly visible.

The entire description of the particle classes was isolated from the case study and generalized. This section now highlights the potential and discusses the limitations of this method for analyzing INPs. We provided example EDX spectra in Fig. 7 (revised manuscript) to illustrate the classification of INP types. We think it would be overly excessive and uninformative to present those for all particles.

- Figure 4: How is the 5-day average calculated and plotted? Why are there no error bars? What is the background level? How many measurements were performed per wafer, 1 only? Schrod, J. et al. (2016) provided statistical analysis for FRIDGE.

The 5-day average is a running average which is calculated for each day from the two previous, the current and the two following daily values.

For a detailed discussion and analysis of the INP concentrations at the JFJ, error bars would be essential, we agree with the reviewer. However, such a discussion is not within the scope of this paper. At this point, we show the Figure to give the reader an overview and to illustrate why we focus on the activated INPs at -30°C for the analysis. In this case, we see no need to discuss uncertainties in the INP measurement in depth. This FRIDGE method was evaluated by Schrod et al. (2016).

As you have already mentioned, Schrod et al. (2016) provides a statistical analysis of the FRIDGE method. A value of 20% is given for the statistical fluctuation of the determined ice crystal number. A statistical fluctuation

of the same order of magnitude can be assumed for the concentrations shown here, which is based on 1 measurement. This is now also described in the manuscript.

“The concentration for each sample is calculated on the basis of one measurement. The relative error of the counting uncertainty for individual measurements is 20% (Schrod et al., 2016), so the error of the concentrations given here is also in this range.”

Typically, even cleaned wafers show low ice formation activity at -30°C . As already mentioned in chapter 2.1, this is typically around 10 counts per wafer. These counts are normally subtracted from the number of ice crystals before the concentration is calculated. The concentrations are therefore usually already background corrected. For the campaign at the JFJ, particular emphasis was paid to the cleanliness of the wafers, as we expected very low INP concentrations in advance. The background counts for -30°C were less than 3 counts per wafer. This results in a maximum background concentration of 0.03 L^{-1} for a collection volume of 100 L. As the collection volumes were generally larger than 100 L, the value decreases accordingly.

- Figure 5: What is the red curve, is this the ideal version with 1:1 ratio?

Yes, the red line shows the 1:1 ratio. A description was added to the figure caption.

- Figure 6: Why is $n=199$, shouldn't it be 200? Are the same particles active at all RH values (95%, 97%, 99%, 101%)? The percentages should be linked to the previous figure, as you mention the total chemical INP composition, but only 15% of all INPs are considered. Additionally, there are no error bars. Soot accounts for 1% of the total INP, does this fall within the uncertainty range?

One artifact is excluded from further analysis, that's why it is only 199. This is now clearly stated in the text.

“One particle with attached gold traces was classified as an artifact and therefore excluded from further discussions.”

In FRIDGE all samples were activated at a set of 3 temperatures (-20°C , -25°C and -30°C) and a minimum of 4 relative humidities (95% / 97% / 99% / 101%). Since measurements at higher humidities typically show a larger number of ice crystals, we have chosen the measurements cycles at $\text{RH}=99\%$ and $\text{RH}=101\%$ for the coupling procedure. $\text{RH} = 95 / 97\%$ was chosen for one sample due to cluster formation at higher RH. We added the information to the corresponding figure captions.

In consideration of the representativeness of our findings, we have included the following additional information.

“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 data 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)).”

For the chemical composition (Fig. 9 in the revised manuscript) we have calculated the 95% confidence intervals and provide these in the supplement (Tab. S2). Of course, for the minor particle classes the differences in the abundance are within the uncertainty range, but for the major components it is possible to derive type-specific conclusions. The discussion of the results was shortened and more generalized.

- Figure 7 and discussion: No details comparison is made between initial size distribution of particles and size of INP, which do not enable correct estimation how size affect ice nucleation. In lines 556-566, the range referred here may be biased by simply higher initial concentrations. You need to better connect this part to size distribution measurements in lines 571-584, with statistical analysis.

Our INP size distribution is now compared to the particle size distribution over the whole campaign period provided by Weber (2019). The comparison with the size distribution of the total aerosol during the same campaign period shows that the maximum of our size distribution is shifted to larger diameters compared to the total aerosol. As we laid more emphasis on the methodological part of the manuscript, we chose to describe the likely enrichment of larger particles as INPs based on the size distributions presented in Weber (2019) in a more qualitative manner.

“In comparison to the total aerosol size distribution from the whole campaign period (Weber, 2019), the maximum of the INP size distribution is significantly shifted towards larger diameters. We hypothesize that, in addition to the primary suitability of larger particles as ice nuclei, the absence of the small volatile aerosol components (nitrates, sulfates, and volatile organics) may play a role here (see Sect. 2.6).”

The comparison to Lacher et al. (2021) and Worringen et al. (2015) has been rewritten and divided according to a comparison of the INP size and a comparison of the size-resolved chemical composition.

“Lacher et al. (2021) and Worringen et al. (2015) provide size distributions for INPs/IRs measured with different techniques at the high-altitude research station JFJ up to a size of 3 μm and 5 μm , respectively. In both studies, the highest concentration was found for IRs smaller than 0.5 μm , but the broad maximum (diameters between 1.3 μm and 5 μm) from Lacher et al. (2021) agrees reasonably well to our findings. The same is the case for particles collected with the Ice Selective Inlet by Worringen et al. (2015), which also showed a secondary maximum at 1 - 1.5 μm . The shift towards larger particle diameters in our results in comparison to the maxima from Lacher et al. (2021) and Worringen et al. (2015) may be caused by the differences in sampling and ice activation. INPs in FRIDGE are activated through deposition nucleation / condensation freezing under defined conditions, while the IRs collected from ambient air are activated under natural and even more complex conditions, including the potentially more important immersion freezing mode (Ansmann et al., 2009; Murray et al., 2012).

The comparison of such INP size distributions with chemical information from different methods is difficult, since in addition to the influencing factors discussed in Sect. 3.3, a possible size selection or limitation of the sampling process, and different techniques of particle sizing may also play a role. Nevertheless, the results for our main groups are in reasonable agreement with the results from Worringen et al. (2015). In our results, both the metal oxides and the few soot particles were observed at very small diameters, which is comparable to carbonaceous particles/soot and metal oxides predominantly detected in the submicron range by Worringen et al. (2015). Terrigenous particles, including silicates and Ca-rich particles, were primarily found in the larger size ranges, while our mineral components were distributed over all size ranges, with silicates domination for particles from $d_{pa} > 0.5 \mu\text{m}$. In contrast to Worringen et al. (2015), our C-rich particles were present over the entire size range. The reason for this is possibly that our classification scheme assigned the larger potentially biological particles as C-rich.”

Technical corrections

- Line 350 “natural mineral dust” correct to dust

The typo has been corrected.

-Line 401: “This was not the case for -20°C, because Saharan primarily activate as temperatures below -20°C.” reference?

*Niemand, M., Möhler, O., Vogel, B., Vogel, H., Hoose, C., Connolly, P., Klein, H., Bingemer, H., DeMott, P., Skrotzki, J., Leisner, T.: A Particle-Surface-Area-Based Parametrization of Immersion Freezing on Desert Dust Particles, *J. Atmos. Sci.*, 69 (10), 3077-3092, doi: 10.1175/JAS-D-11_0249.1, 2012*

*Murray, B. J., O’Sullivan, D., Atkinson, J. D., Webb, M. E.: Ice nucleation by particles immersed in supercooled cloud droplets, *Chem. Soc. Rev.*, 41, 6519-6554, doi: 10.1039/c2cs35200a, 2012*

The references were added to the manuscript.