

Dear editor,

please find below our answers to the referees questions and remarks. According changes in the manuscript are color-coded reviewer-specific. Furthermore, the reviewers requested general phrasing changes, which are marked in red text color.

Please note that the Schmidt et al. (2014) publication, to which we refer, was accepted by ACPD, but is not yet available online, so we could not yet provide the correct DOI.

Finally, please note that we had to change the authors list due to the substantial manuscript modifications.

With best regards,

A. Worringen, K. Kandler, S. Weinbruch on behalf of the co-authors

## Interactive comment on “Single-particle characterization of ice-nucleating particles and ice particle residuals sampled by three different techniques” by A. Worringen et al.

Anonymous Referee #1

Worringen et al. paper present the characterization of single-particle ice-nucleating, based on three different techniques. The paper is very interesting and a valuable contribution to the ice nucleation community; however, major corrections are needed before this manuscript can be accepted. Many sections of the paper are not clear and are written with not good flow, forcing reading the sections several times in order to understand it. It seems that different people wrote different sections and the writing is not uniform. That is why I will recommend the authors to rewrite so sections in order to increase their clarity and flow.

Details on the PCVI and CVI that were used in this work are missing, for example what type or model were used, what conditions were used in order to get cutoff sizes?

Details on the used instrumentation is given in the companion paper in AMTD (Schenk et al., 2014), which was just published during the time of the review. This paper is correctly referenced now. Details on the Ice-CVI are given in Mertes et al. 2007, which was referenced in the manuscript.

Detail on comparison between the three methods is missing, the authors mentioned that they were not measure at the same time, but do the authors know if all methods can see the same particles, and detect the same IN.

We are totally aware that in many cases parallel sampling was not performed. This is shown in Fig. 1 and discussed in the details. This is certainly a limitation of the current data set. Still, we believe that this data set is valuable for the scientific community. In addition, we address this point in the recommendation for future work (new chapter in the manuscript).

Where there any comparisons between these methods before the fieldwork to make sure they all see the same thing?

There were comparative previous measurements in a joint field campaign, whose results were used to optimize the instrument performance. However – added in the new recommendation section – we have to conclude that additional comparative measurements are necessary in future (an according laboratory campaign is scheduled for March 2015).

Each method had different artifact that should be mentioned with more details

We do not understand this comment as a major part of the manuscript addresses the artifacts.

It seem that the sampling with the different methos did not had any overlap, where each method used at different time, the author combine all the data to one data,

The author combine the data from all method at some part for the entire time period, does all days had the exact same conditions, is it possible to assume that some days had different IN types and the differences between the instrument come because of that?

See above (comment on non-parallel sampling).

### Specific comments

#### Abstract:

The abstract is not clear I will recommend rewriting it again.

We agree and have completely rewritten the abstract.

Page 23029 lines 1-8

The sentence is too long I will recommend to separate it to at least two sentences.

Changed as requested, now three sentences.

Page 23029 line 2

I think using the two terms ice-nucleating particles (INP) and ice particle residuals (IPR) is a bit confusing for the reader, the term ice-nuclei residuals (INR) will be a better term since the analysis is for IN particles. If the author wants to use both I will recommend on using ice crystal residuals (ICR) instead of IPR.

We did not change the acronyms, as they were chosen by the INUIT consortium (after long discussions), and are used in all INUIT papers.

Page 23029 lines 11

Use the term January-February and not January/February

Changed.

Page 23029 lines 12-19

Sentences are not clear

We have added the word "instrumental" to the expression "contamination artifacts". In addition, the measurement artifacts are now explained explicitly.

Page 23029 lines 14

I think it will be better to use the term FINCH+ PCVI than the term FINCH+IN-PCVI, it is obvious that the PCVI is used for IN residuals and that that FINCH was used for IN analysis.

We did not change the acronyms, as they were chosen by the INUIT consortium (after long discussions), and are used in all INUIT papers.

Page 23029 line 24

The choice of word yielded is not recommended I will replace it with something else

Replaced by "obtained".

## 1 Introduction

The introduction is missing many things as the principle behind a PCVI or CVI method. Examples of laboratory and field works that used this technique not just for IN but also for CCN Elements that should be expected in IN particles

The PCVI and CVI principle were discussed in previous literature, e. g., Boulter et al. (2006), and are thus not explained in the manuscript. Technical details of the used specific instruments are given in the cited references (Mertes et al., 2007; Schenk et al., 2014).

Tell the reader about previous IN measurement in the Jungfraujoch station.

We have added an according section to the introduction.

Page 23030 line 17-18

I will recommend not to use the sentence as it is because it seems negative. Instead, I recommend the authors to use a sentence like this: although, in the last decade, large attention has been given to field studies at different parts of the world (e.g., Prenni et al., 2009a,c; Santachiara et al., 2010; Ardon-Dryer et al., 2011; Conen et al., 2012; Ardon-Dryer and Levin, 2014), these measurements cover a small fraction of the world and many field works are still needed.

Changed as requested.

Page 23030 line 20

I think this will be a better way (e.g. Hoose and Möhler, 2012, and references therein)

Changed as requested.

Page 23030 Line 24-26

The sentence is not clear and it should be rewritten

We have rephrased the sentence

Page 23030 line 26- page 23030 line 1

Rewrite the sentences

Changed as requested

Page 23031 line 4

Replace the word 'reached' with another word

Replaced by "realized".

Page 23031 lines 11-14

The authors should not include the FRIDGE in this part, since it is impossible to separate the activated particles from the non-activated ones in FRIDGE and FRIDGE samples the particles on a substrate.

Indeed they are not separated by FRIDGE, but they can be distinguished. Sentence was rephrased.

Page 23031 lines 20-21

Use the term PCVI instead of pumped counterflow virtual impactor

Changed as requested.

Page 23031 lines 24-28

Rewrite the sentence it is cumbersome

After reading this sentence several times, we came to the conclusions not to change it. We believe that the message is quite clear.

## 2 Experimental

I suggest to separate this section into three parts: sampling site, sampling the ice crystals (all CVI) and last section analyzing of the IN property (as microscope and laser) or combine it with the CVI part.

We agree and have restructured the experimental section

Page 23032 lines 1-10

Rewrite it, the flow of this paragraph is bad, the description is bad, give more explanation on the station, why sampling there.

We agree and have rewritten this section.

A figure with experimental set up will be very helpful for the reader; it might be even better than table 1.

We disagree and think that the information in table 1 is sufficient.

### 2.1 INP/IPR differentiation

The whole section is not clear, it will be better to use each section in the explanation of the chambers or setup instead here

We agree and have changed the according section

Page 23032 line 12

Bundke et al., 2008 did not use a PCVI in this paper, rewrite it

Bundke et al. 2008 introduced the basic principles of FINCH. We have added the reference Schenk et al. 2014 who describe the current instrument setup.

Page 23032 lines 1-18

"Two-stage impactor system (see above)", what does the author mean, not clear. The explanation seems to

appear afterword is at line 20.

Section was rewritten (see above)

### **2.1.1 Coupling of FINCH and IN-PCVI**

Page 23033 line 6

Use the word by, counted by an optical

Use the word was and not the word is, "The OPC used in this instrument was able"

Changed as requested.

Page 23033 lines 9-11

Not clear

We still believe that this sentence is clear.

Page 23033 line 13

There is not reference for this paper Schenk et al., 2014, there is one for Schenk, 2014

Corrected

Page 23033 lines 12-15

Rewrite this sentence, say how they were separated with what, this is a suggestion for this sentence: The activated IN grow into an ice crystals. The ice crystals were separated from the non-activated particles and from the small-supercooled droplets by using the PCVI

Page 23033 lines 14-21

These sections are not clear at all

We have rewritten these sections to make them clearer.

What does it mean: "This is realized by a counterflow that meets the FINCH output flow which is at the same time the IN-PCVI input flow".

Does the authors mean that the flow from FINCH was the same as the input value that needed for the PCVI in order to get a cut off size of 4.5-8 micron, is this the 50% cut off?

Rewritten to make it clearer.

What values were used for input and output for the PCVI that gave values of 4.5-8 micron? please write it.

Please refer to the according publication (Schenk et al., 2014).

### **2.1.2 Ice-CVI**

The whole section is not clear, as setup figure would be helpful

This section is only a short summary, as the setup was described in detail in the cited paper by Mertes et al. 2007.

Page 23033 line 24

Delete the words "so-called"

Changed as requested.

### **2.1.3 Ice Selective Inlet (ISI)**

Well written, it is clear.

Thank you!

### **2.1.4 Laser Ablation Spectrometry (LA-MS)**

Page 23035 lines 9-10

What is the meaning of 104h and 32h?

It is hours. This is now explained in the text.

Perhaps this sentence will be better: Total of 1809 particles mass spectra were sampled with the LA-MS. A

1663 mass spectrum were when the Ice-CVI was in use and 146 when the ISI was in use.

Changed as requested.

## 2.2 Sample analysis by electron microscopy

Were only 46 particles analyzed or each sample contained many particles, please explain. In addition the author does not mention after which equipment this sampling were taken from.

We are talking about samples. We now include the number of samples obtained from each technique (as requested). Thus, the meaning of "samples" should now be clear.

## 2.3 Particle classification

Is this a combination of all the analysis methods if so say it?

The chapter particle classification is now part of the electron microscopy chapter. Thus, it is now clear that we talk about particles classification in SEM analysis.

Why there is a classification of droplets if the author mentioned that all droplets should evaporated or cut by the CVI? is there a sampling error, if so mention it before, which sampling method gave droplets?

In principle, the particles should have dried until reaching the impactors. However, evidently this was not always the case, and some arrived as droplets. Thus, we included a separate class for them.

Why there is definition of other with many elements? Are the materials are what the CVI built from or material of the grid itself, please explain.

These are not artifact particles. The 'other' group simply contains different particle types which have only singular or very rare occurrence. We have added a comment on their low abundance.

Was there any compression between the different analysis methods? Or the author assume they are all measure the same parameters?

The major objective of the present manuscript is to investigate the differences of three techniques applied to separate and analyze INP/IPR! We discuss the differences of the techniques in detail and it is not assumed that they measure the identical parameters.

Page 23036 line 1

Use the word were and not the word are

Changed as requested.

## 3 Results

I will recommend to combined the result with the discussion it will be better to understand and will allow the author to make stronger points about their findings

After careful consideration of this comment (we took it very serious) we came to the conclusion not to combine these sections. The main reason is that in the discussion section we go beyond the method comparison, which is central subject of the results section. Combining results and discussion chapter would not give appropriate weight, for the example to the comparison with other field experiments.

### 3.1 Artifact particles

Information on the amount of artifact particles from the total particles that were sampled could tell the reader how this sampling methods had on the artifacts amounts

We do not understand this comment, as this information is given in Figs. 3 and 7 (formerly 3 and 5).

It will be clearer to mention what each CVI or chamber was built from and to state that some of the artifact could be due to that, the way it is written now is not clear.

We have added a comment on the materials used for manufacturing or as calibration aerosol. We have also rewritten the Pb-artifact discussion regarding the Ice-CVI.

### 3.1.2 Potential INP/IPR sampling artifacts

Can the author explain how or by with methods these particles were sampled, is it by all methods or just by some?

We do not understand this comment, as this information is given in Fig. 7 (formerly 5).

### 3.2 Composition of INP/IPR at the Jungfraujoch in winter

The author should mention in the text how many particles were sampled by each methods, and not just show it in figure 5

We give a total number in the text, but we think that this information is more appropriate in the figures.

Why are the artifact part of the figure if the authors say that artifact are not an IN source and will not be shown (page 23037 line 21)

Droplets, sulfate and sea-salt are classified as POTENTIAL sampling artifacts. We came to the conclusion that the current knowledge is not sufficient for unambiguous identification of sampling artifacts. The discussion in the literature is still controversial. We show these groups in the figures and tables in order to allow the reader to come to his/her own conclusion on the basis of the full data set.

The comparison between the instruments (fig 7) is good because finally there are two samples that were taken at the same time, however perhaps some of the difference appear in Fig 7 are due to the different sampling methods, I think that the author should mention it in the text.

We agree and have added an according sentence.

### 3.3 Size distribution of INP/IPR components

How was the size determined?

We give the sizes as equivalent projected area diameter determined in electron microscopy, given in section 2.2.1

Are the artifact taken into account in this calculations?

Artifacts are excluded from this discussion. An according sentence was added.

More information and comparison with the literature will improve this section

The size distribution can't be compared between the instruments due to different inlet transmission efficiencies and – in part – yet uncharacterized instrument transmission efficiencies. We are not aware of size distribution measurements for individual INP/IPR compounds.

### 3.4 Composition of total aerosol

Does the author think that such small sampling time represent the total aerosol type in that area for the entire period?

I think it would have been better to start and end every experiment by looking on the total aerosol composition and not just sample it for such small period.

Why only showing on Fig 9 the sample from the 16 and not all the times that were sampled?

We agree that this short sampling time is not representative for the campaign. Therefore, we removed section 3.4 and modified section 4.2 considerably.

## 4 Discussion

### 4.1 Which particle classes can be regarded as INP/IPR?

Page 23044 line 13

There is no need to writer Al- but only write Al unless the author wanted to say Al-rich

This is exactly what we want to say (Al-rich). Thus, no change is required here.

In addition, it is not clear if these are particles who only had these elements or perhaps they were parts of particles with other elements for example mineral dust particles contained many elements as Si, Al, Mg, K, Ca and Fe.

Silicates would have been classified separately as such (section before). Therefore, these particles are metal oxides.

Page 23045 lines 12-13

I think this sentence is unnecessary in this part.

We think that this sentence is appropriate at this part of the manuscript.

#### 4.2 Relative ice nucleation ability of the different particle classes

I am not sure if it is correct to do this comparison since the total aerosol composition represent small period of time from this experiments.

This discussion was removed from the manuscript.

Why should the author compare with dust particles as Feldspar when there is no dust event that were sampled and the chances for such particles to reach the station at winter is very low.

Mineral dust particles are still the major fraction of INP/IPR on Jungfraujoch in winter. Thus, a discussion of the silicate composition is meaningful.

I am not sure if what written in page 23047 is relevant under this section, perhaps a better place will be under section 4.1

The comment does not apply anymore, as this section was restructures considerably.

#### 4.3 Comparison between FINCH+IN-PCVI, Ice-CVI and ISI

I think that this section is very important and it should be in an earlier part of the paper.

We believe that the reader will recognize the importance of this chapter independent of its location in the manuscript. In addition, we have added a more extended discussion.

#### 4.4 Comparison with other field experiments

The author have already compared some of these result in previous sections, I will recommend to combine all of it to one section

Combined as suggested into chapter 4.1

Page 23049 lines 12-16

I do not agree with combining all the data from the different methods due to their limitation of sampling at different times, but in any case, such information should have been included in the result section

We are aware of the limitation of the dataset. However, we have shown in Fig. 4 that (with exception of organics/carbonaceous) the relative abundances of the INP/IPR classes between the techniques do not differ extremely. Thus, we find it justified to combine all data to increase the statistical significance.

We kept these sentences as short introduction to the discussion, which would be otherwise difficult to understand

Page 23049 lines 17-16

Perhaps a figure or a table with these comparisons will be clearer

We agree and have compiled a short table (Table 4)

Page 23050 lines 12-19

The author does not say much about the different days that were sampled therefore I am not sure if this paragraph is appropriate.



We have removed this paragraph.

Page 23050 lines 20-28

The author already discuss about this point at an earlier stage I will recommend combining the two.

Section was combined with a previous one.

#### 4.5 Comparison between scanning electron microscopy analysis and laser ablation mass spectrometry

I think this section should be in an early part of the paper, perhaps a better place will be to combine the result and the discussion to one part.

Results and discussion are intentionally not combined (see above comment to chapter 3).

We agree that this section does not fit perfectly into the general manuscript outline, as it discussion a special technical point. However, we feel that it fits better into the discussion section as into the results section.

In addition, I do not think it is a good idea to compare something that was not measure in parallel because there could be many elements that could affect the comparison.

From the flow restriction it was not possible to have both techniques working in parallel. As the measurements were intermittent, there is no reason to assume a systematic difference based on this non-parallelity.

#### 5 Summary and conclusions

I would recommend rewriting this part based on the artifact which should be taken out from all calculation. In addition, the author should say that although three methods were used they were not used in parallel.

We believe that the information on the artifacts is an essential part of the manuscript. Thus, we would like to keep it into the summary.

We explicitly mention the non-parallel sampling now.

#### Table 1

The freezing mechanism should not be included for IN-CVI or ISI since they both measure ice crystal after they nucleate

Nevertheless, they were subject to a freezing mechanism (occurring naturally in the atmosphere).

#### Figure 1

This figure is not clear, what are the gray or the colored marked represent.

Are the values of aerosol concentration, temperature, wind are they daily average, it will be good to mention it here and in the text as well.

We have added an explanation in the caption. Continuous curves are shown for concentration, temperature, wind parameters.

#### Figure 3

This figure is not so clear and it seem that the effect of the artifact is too big, a different way of presenting this information might be better.

Box plots are a standard way of displaying point and interval estimates of measurement data. The artifacts are shown as they are.

#### Figure 6-7

I would suggest to delete the artifact from these figures

We have discussed above why we want to keep the potential sampling artifacts in the figure (note that Fig. 7 was removed and the numbering has changed).

## Figure 9

This figure is very important and show the reader about the type of particle found in that area, however the author should mention that these particles were sampled on vary narrow time period, only on the February the 16 and for short period of time.

Fig. 9 was removed as request from the other reviewers. Reason was the extremely short sampling interval and the subsequent potential statistical uncertainty.

## Figure 10

The author should mention at lease in the text which one is the current project and with one is the other for example “inuit- current project”

Changed as requested.

## References used in reply

Boulter, J. E., Cziczo, D. J., Middlebrook, A. M., Thomson, D. S., and Murphy, D. M.: Design and Performance of a Pumped Counterflow Virtual Impactor, *Aerosol Sci. Technol.*, 40, 969-976, 10.1080/02786820600840984, 2006.

Mertes, S., Verheggen, B., Walter, S., Connolly, P., Ebert, M., Schneider, J., Bower, K. N., Cozic, J., Weinbruch, S., Baltensperger, U., and Weingartner, E.: Counterflow Virtual Impactor Based Collection of Small Ice Particles in Mixed-Phase Clouds for the Physico-Chemical Characterization of Tropospheric Ice Nuclei: Sampler Description and First Case Study, *Aerosol Sci. Technol.*, 41, 848-864, 10.1080/02786820701501881, 2007.

Schenk, L. P., Mertes, S., Kästner, U., Frank, F., Nillius, B., Bundke, U., Rose, D., Schmidt, S., Schneider, J., Worringer, A., Kandler, K., Bukowiecki, N., Ebert, M., Curtius, J., and Stratmann, F.: Characterization and first results of an ice nucleating particle measurement system based on counterflow virtual impactor technique, *Atmos. Meas. Tech. Discuss.*, 7, 10585-10617, 10.5194/amtd-7-10585-2014, 2014.

## Interactive comment on “Single-particle characterization of ice-nucleating particles and ice particle residuals sampled by three different techniques” by A. Worringen et al.

Anonymous Referee #2

The paper by Worringen et al. presents data on the characterization of ice nucleating and ice residual particles collected at an alpine site. The data itself is a worthy addition to the literature, however there are scientific and editorial issues which require attention before publication can be recommended. In general the manuscript was disorganized and at times difficult to read. However, as there are in my opinion only two major scientific issues I feel that this manuscript could be made publishable without too much difficulty.

Major issues:

INP compositions have been reported via activation by the FINCH instrument, however no mention was made of the operating temperature and relative humidity of FINCH. Were they constant? Chosen to match ambient conditions? If operating conditions were not constant or based on ambient, I would recommend extreme caution about presenting the FINCH results as a single data set. Likewise if the FINCH temperature (RH) is significantly lower (higher) than ambient then comparing FINCH results with the IPR compositions might not be appropriate.

FINCH operation temperature was set relatively constant to  $-22^{\circ}\text{C}$ , which is usually close to the cloud conditions at JFJ. However, weather fluctuations prevented that during all measurements FINCH conditions were similar to outside ones. To illustrate that, we provide FINCH operating temperatures now in Fig. 1 together with outside temperatures. Supersaturation was varied in FINCH and is provided together with temperature as separate table in the supplement. We agree with the reviewer and also would prefer to compare FINCH and other instruments on a case by case study for the thermodynamic conditions. However, the extremely low concentration of INP at JFJ would result in most of the samples having less than 50 particles and, thus, would prohibit a case-wise discussion due to statistical uncertainty.

The Ice-CVI reports much higher numbers of lead-containing particles. However after large amounts of discussion regarding lead containing particles, it is quietly mentioned on page 23045 that one of the components (the impactor) of the Ice-CVI is constructed from a lead containing aluminum alloy. If it hasn't been done already, I would strongly recommend running tests with a test material to confirm that the impactor is not the source of the unusually high levels of lead particles in this instrument. I find it hard to believe that even though ISI, FINCH and the Ice-CVI were run at random times during the whole campaign (and FINCH was run for much longer time periods) the much higher lead signal in the Ice-CVI is entirely natural.

We have moved the discussion on lead contamination from the results section to the instrumental artifact section, as it was not our intention to obscure the potential error source. We also provide arguments, why we think that lead in this case is not to be considered as an artifact. We agree with the reviewer that future tests are needed to fully exclude the Ice-CVI as potential source of lead-containing particles. These tests are planned for a laboratory campaign in 2015 and new field measurements in 2016 and, thus, can't yet be part of the present manuscript.

Other issues/comments:

Throughout, repeated references to parallel measurements have been made. However, according to Figure 1 no parallel measurements were made. Please remove/reword these comments.

We now refer to the non-parallel sampling where appropriate

There is no actual explanation of how the particle classes are assigned, especially for internally mixed particles. For example, would a gypsum particle ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) be classified as Ca-rich + inclusion or Sulfate + inclusion? Either provide a thorough description or a brief description and a more in depth reference.

We have changed the notion to 'major elements' to express that a major part of the particle needs to consist of the element used for classification. Gypsum did not occur during the experiment, but would have been classified as Ca-rich particle.

Inclusions are classified when they are visually observed.

Particles containing lead are classed as lead bearing regardless of amount – is there any way of telling the actual and/or relative concentration of lead?

In most cases lead was a minor compound in these particles (leading to a weak signal). Thus, we can't provide reliable lead concentrations.

The analysis of the data could go further – temperature and wind direction data is provided in figure 1; the trend of composition with ambient temperature or wind direction (as there is only 2) could produce an interesting result.

Unfortunately the low particle numbers do not allow for this more detailed analysis. In particular for the southerly winds, only a few particles could be collected.

I would caution against the terms inclusion and coating. For me, coating has an implication that the additional substance was part of the primary ice nuclei, rather than an aerosol captured during post-freezing aggregation or accretion (e.g. Kumai, 1951). Likewise, inclusion implies that the second component is part of one large particle, rather than a secondary aggregated particle acquired separate to the freezing process.

We use the two terms in a geometric sense.

We have added the explanation "Inclusion refers to a small object with different chemical composition inside a particle. Residuals are compounds left after evaporation of a volatile matrix. Coating is a small film on the surface of a particle. Agglomerates are composed of distinguishable objects of similar size".

In addition to compositions, FINCH should have been able to measure INP concentrations. Is this data available and not planned for separate publication? If so please include it here.

According data is presented by Schenk et al. (2014)

The analysis of the data could go further – temperature and wind direction data is provided in figure 1; the trend of composition with temperature or wind direction (as there is only 2) could produce an interesting result. For example, Figure 1 suggests that ISI data was mostly with a cold south wind whereas the ICE-CVI periods were nearly all with a north wind.

Indeed a part of the differences between ISI and Ice-CVI might be explained by different airmasses, as it is already mentioned in the manuscript (now Section 3.2). However, particle numbers are too low for a more detailed significant discussion.

Pg. 23033, lines 2-11. Does FINCH take all ambient aerosol or is there a size distribution? What happens to any ice crystals or droplets in the flow – are they evaporated before insertion into FINCH?

FINCH collects aerosol via the total aerosol inlet. Hydrometeors are evaporated and their residues are kept in the flow. This is now explicitly mentioned in the manuscript.

Pg. 23034, line 6. Some small droplets could pass the pre-impactor without an impact. Please provide the d50% cut-off diameter for this section.

The d50% cut-off diameter is given a few lines below. For detailed information, the reader should refer to the cited Mertes et al. (2007).

Pg. 23034, lines 17-22. Larger droplets could cool significantly during evaporation, and also not completely evaporate. Is there any estimate for the amount of freezing that may occur due to evaporative cooling? What is the liquid droplet break-through diameter?

While evaporative cooling does take place, this has a very small effect on the droplet temperature: we have calculated the difference between ambient temperature and droplet surface temperature to be on the order of -0.5 K or less (depending on the ambient temperature and the droplet diameter). Consequently, we do not believe that the evaporative cooling of the droplets has any significant influence on freezing of evaporating droplets within the evaporation chamber.

Whether there is sufficient time for a liquid droplet to evaporate inside the chamber is dependent on the evaporation rate of the droplets and the residence time of the droplet. Both the evaporation rate and the residence time are in turn dependent on the temperature. The times required to evaporate droplets of a given start diameter, based on mass transfer calculations, as well as droplet residence times inside the chamber, are shown in Fig. 3 of Kupiszewski et al. (2014). As shown in this figure, the droplet residence time in the chamber is more than sufficient for evaporation of droplets of 20  $\mu\text{m}$  diameter, even if the mass accommodation coefficient were to be as low as 0.01 (as discussed by Kupiszewski et al. (2014), there is no consensus on the value of the mass accommodation coefficient). Therefore, the liquid droplet break-through diameter is considerably above 20  $\mu\text{m}$ , or even 50  $\mu\text{m}$ , depending on the assumed mass accommodation coefficient and on the temperature. Please note also that the evaporative cooling feedback discussed above is taken into account in the calculations of the droplet evaporation times.

Pg. 23035, line 17. Please explain or provide a reference for how the diameter was calculated.

Information is given now in the manuscript ('equivalent projected area diameter').

Pg. 23035, line 24. Particle classes combined into particle classes. Please change one of these to a word other than classes.

Typo, should be 'groups'. Changed.

Pg. 23037-8, Section 3.1. The effort to investigate and quantify artefact particles should be commended. As well as the Steel and Aluminum artefact particles, do the systems have any plastic and or rubber tubing that could be the source of carbonaceous particles? Additionally the comment regarding the lead content of the Ice-CVI needs to be moved here from pg. 23045.

Ice-CVI does not have any internal plastic or rubber parts. FINCH has a part of the saturation chamber machined from plastic, as well as a water reservoir. As the aerosol flow is slow inside the chamber, we think that an abrasion from the chamber walls is improbable. ISI also does not use any carbonaceous tubing except for a short piece of conductive silicone tubing, which contains also carbon. However, no emission of purely carbonaceous particles is expected from the latter (due to its composition and due to the flow conditions).

The lead discussion was moved here as requested.

Pg. 23040, line 12. Please clarify - FINCH and Ice-CVI have high amounts and much higher absolute numbers of silicates at submicron sizes.

Changed as requested

Absolute numbers for these graphs should not be compared due to different sampling times, inlet efficiencies and SEM analysis areas.

We agree. We mention this now explicitly and have removed the referred sentence.

Pg. 23041, lines 1-6. Maybe I am reading figure 8 wrong due to the y-axis, but the percentages given for

ISI in the text look wrong.

Thanks for pointing that out! Numbers in the text as well as the graph were based on inconsistent tables. This is corrected now.

Pg. 23041, lines 7-19. I have a number of issues with this section. I find the comparison of 28 samples with 395 difficult, especially since the Ice-CVI sees less than 1/28 of many of the particle classes. The FINCH sample is taken during the middle of the day when the sun is high and while aerosol concentrations are rising, whereas the Ice-CVI sample is at the end of the day (just before sunset) and the aerosol concentrations are dropping, suggesting that the two sampling periods are not that similar. Also, according to Table 1 FINCH samples  $>2\text{ }\mu\text{m}$  whereas Ice-CVI samples  $>5\text{ }\mu\text{m}$ . This difference in size distribution could explain the larger numbers of the particles that would be expected to be smaller, such as carbonaceous and secondary.

We agree and have removed the discussion on the minor compounds. Also, we have added a comment on meteorology.

Pg. 23041, section 3.3. I didn't get it from the earlier sections. Why are there so few Ice-CVI particles at  $>1\text{ }\mu\text{m}$ ? Is this real or instrumental? If instrumental could this explain the differences elsewhere?

The difference in size distribution between Ice-CVI and FINCH is also observed by others (Schenk et al., 2014; Schmidt et al., 2014). However, there is no obvious explanation why the Ice-CVI finds so many more small particles.

As we consider supermicron and submicron particle composition separately, we expect that the results of the chemical classification are not influenced considerably.

Pg. 23042, lines 2-3. Again, maybe I am reading figure 8 wrong due to the y-axis, but it looks like the soluble has a definite tendency to be submicron.

The relative abundance of the soluble compounds has no pronounced size dependence. Of course, this does not apply for the absolute numbers, where small particles prevail. We have added the expression 'in the relative abundance' to clarify.

Pg. 23043, section 3.5. When comparing table 3 with Figure 6 I would suggest that for most particle classes reporting mixed/unmixed ratios in ISI is a bad idea due to the very low particle numbers.

We do not agree, as a total of approx. 200 particles yields reasonable estimates for major and minor components ( $>5\%$ ).

Pg. 23047, lines 6-9. Without defining the term 'rich', these sentences make no sense. What decides how strong the peaks in the EDX are? For K-feldspar, there are 3 Si atoms and 1 Al atom for every K.

EDX peaks are roughly proportional to mass concentration.

Would this fit the definition of 'not rich in potassium'?

Practically all silicates had an atomic K/Si ratio  $< 0.1$ . We have clarified this and avoid the term 'rich' in this context.

Pg. 23047, lines 14-16. Zimmermann et al. showed that calcite is similar in deposition nucleation ability to quartz. However many other minerals, with better or worse abilities than quartz, can be classed as silicates.

We have removed this comment.

Pg. 23047, lines 26-27. The definition of Ca-rich in table 1 includes carbon oxygen and sulphur. Is it possible therefore to be certain that the particle did not include some carbonaceous/secondary coating? Also note that the calcium carbonates primarily associated with this class are unstable in an aqueous environment, especially in the presence of acids.

If the coating is not visible in the electron image, we can't exclude its presence in this particular case. Calcium carbonates might be dissolved in an acidic environment, but after evaporation of the solution the Calcium will be still present and detectable. Note that we have not detected considerable amounts of Ca-S-containing particles.

Pg. 23048-9, section 4.3. The first paragraph of this section describes the campaign and analysis steps in general and should appear much nearer the beginning of the manuscript.

We have checked this paragraph, but it does not really contain campaign and analysis description. Thus, we don't understand the comment.

The second paragraph is direct repetition of parts of section 3.5 and should be removed.

Removed as requested.

Pg. 23049, lines 13-16. According to section 4.1, sulphate particles are not INP/IPR. Why do they appear here?

We treat the sulphate particles consistently now as 'potential sampling artifact' in the manuscript (which was handled inconsistently before).

We have opted to include them in all graphs, as we came to the conclusion that the current knowledge is not sufficient for unambiguous identification of sampling artifacts. The discussion in the literature is still controversial. We show these groups in the figures and tables in order to allow the reader to come to his/her own conclusion on the basis of the full data set.

Pg. 23050, lines 12-19. The past literature has found a dependence upon temperature and air mass history. This could be done – at least in comparison to wind direction and temperature.

The number of particles is too low for a significant statement, that's clearly a limitation of the current work. If we try to split the data according to wind or temperature regimes. In particular, most of our data are for northerly situations.

Pg. 23050, lines 20-28. If the lead comes from avgas combustion as suggested, then due to the addition of lead scavengers to the fuel it could be expected to be found in the form of lead (II) bromide or chloride. Was bromine or chlorine seen in the EDX spectra? Why is ISI not included in the discussion?

In this work, lead was associated with different compounds, also with Cl-containing material. In previous work, more detailed investigation shows that lead was present as lead sulfide (Ebert et al., 2011).

No lead-containing particles were found in ISI samples. This might be linked to the short sampling period of ISI.

Pg. 23051, lines 3-11. Please provide some information on the compared sampling periods. When was the LA-MS run? What were the meteorological conditions then? Was the SEM-EDX data limited to similar conditions or was the whole data set used?

LA-MS sampling times are now shown together with SEM sampling times in Fig. 1. The two instruments couldn't be operated in parallel due to flow restrictions, instead they were used intermittently. Due to the low particle numbers, the whole dataset was used. This is already explicitly stated.

Pg. 23051, lines 12-19. According to pg. 23035, LA-MS measures between 150-1500 nm, whereas the SEM particles (for ISI at least) go up to 3  $\mu\text{m}$ . Could the authors speculate if this might have an effect? Could the SEM data be limited to particles in the same size range?

We have performed this test. For the Ice-CVI, the result is indistinguishable; for ISI, the abundance of carbonaceous, metal oxide and sulfate particles increases slightly at the expense of mainly silicates and a few droplets. We have added a comment on this to the manuscript.

Pg. 23052, lines 3-5. How are elements classified as 'major' and 'minor'? Is Pb neglected if it is minor? 'Pb-bearing' is classified so, as soon as Pb can be detected. We have added a comment in the method section.

'Major' and 'minor' are roughly distinguished at 10 % relative contribution. A regarding comment was added to this section.

Pg. 23060, Table 1. Was FINCH operated out of cloud?

Inside and outside.

Is this data included in the other analysis/figures,

Yes, it is included. As cloud elements are evaporated by the total inlet, all the original particles before cloud activation are supposed to be samples by FINCH, so the combination make sense. This is now explicitly stated in the method section.

was there an observable difference between in and out of cloud INP?

Hampered by the low particle numbers, we could not observe a difference.

Please clarify the final column for FINCH – does  $d > 2 \mu\text{m}$  refer to the aerosol inlet or the FINCH -> IN-PCVI transfer?

This was a mistake, the column must be empty, as FINCH does not explicitly sample ice particles, but aerosol. Details on the transmission of the FINCH + IN-PCVI system are available now in Schenk et al. (2014).

Pg. 23071, Figure 9. This figure implies that the total aerosol samples were taking during an in-cloud scenario. This seems unusual to me. Considering how the data is swamped with droplets, I would wonder if it is of any benefit.

The figure was removed due to request of the other reviewers (too short sampling time).

Technical issues:

General: many paragraphs are formed of what seem to be lists of sentences with no flow or connection, making them difficult and unrewarding to read. This is especially true of the abstract and sections 2 through 4. Please try to remedy. In some sections the start and end of paragraphs seems to be a bit arbitrary, for example section 2.1 and 4.4. Throughout the manuscript is written in a mixture of past and present tense.

We rewrote considerable portions of the manuscript.

Introduction: Please include definitions of any abbreviations that were defined in the abstract.

Added as requested.

Pg. 23031, lines 9-12. Is the IN-PCVI used in combination with FRIDGE? If not please re-organize this sentence to clarify.

Yes, it is used in connection. Section was rearranged.

Please also reference some of the other methods used for the collection and identification of atmospheric INP (for example PALMS, Cziczo et al., 2006).

Cziczo et al. (2006) didn't contain any specific information on an ice-separation technique. However, that is found in Cziczo et al. (2003), which we have added as example for the CFDC techniques.

Pg. 23031, line 19. I'm assuming this personal communication reference refers to the in-prep AMTD paper, please update the in-text citation.

Updated.

Pg. 23032, line 12. Is the FINCH+IN-PCVI reference Bundke et al. 2008, Schenk 2014 or both?

One describes the FINCH, one the combination, so it is both.

Pg. 23032, line 21. Please use  $\text{L min}^{-1}$  to be consistent with flow rates reported later on.

Changed as requested.

Pg. 23032, Section 2.1. The second paragraph in this section seems to have been inserted at a later date. Please proof this section properly. Specifically the use of (see above) and the use of INP and or IPR.

Section was rearranged, and in the course we have updated the references.

Pg. 23033, line 17. Please clarify the IN-PCVI cut-off diameters – are the sampled particles larger than 8



µm, larger than 4.5 µm or between?

The cut-off diameter had variations. Section was rephrased.

Pg. 23034, section 2.1.3. There are no references in this section.

The ISI technical paper was published meanwhile, and the reference is added.

Pg. 23039, section 3.1.2. Please provide references where things are expected – lines 4,15,17.

We have rephrased the paragraph and added a reference.

Pg. 23039, lines 20-21. Change to 'as a box-plot', or pluralize the sentence.

Changed as requested.

Pg. 23040, line 10. Change to 'INP/IPR independent of sampling technique.'

Changed as requested.

Pg. 23042, line 24. I think this is supposed to read 30 January?

Section was removed on request by other reviewers.

Pg. 23044-6, section 4.1. I would argue that most of this section is discussing whether a particle class is real or artefact. It is also much more introductory in nature. As such, I would suggest moving this section further forwards as part of section 3.1. Having read many pages of discussion regarding figures 6-10, this is not a good point to be informed one of the categories isn't an INP/IPR. Several of the paragraphs in this section are very similar and seem to have been partially cut and pasted. Please reword them.

As this section is rather discussion than result presentation, we think that it should stay in the discussion section.

We have corrected the wording regarding the soluble salts, as we do not consider them as artifacts, but as 'potential sampling artifacts'. Thus, this section does not cover any more categories, which are surely not INP/IPR.

In addition, we have modified the phrasing to be less uniform.

Pg. 23044, lines 5-7. The way this sentence is written implies that it is wrong to classify calcite as a component of mineral dust. Please reword.

Changed in order to avoid this misunderstanding.

Pg. 23046, line 5. Please make it easier for the reader by providing a number to go with the 'cold temperatures'.

Changed as requested.

Pg. 23046, lines 9-11. I don't understand. If sulfates are not considered as INP/IPR, then why are they still included? Justify.

This was an error. Sulfates are considered as potential sampling artefacts, and these are included for completeness. Corrected.

Pg. 23046, lines 24-28. Please decide. Are sulfates INP/IPR or not?

The former section 4.2. was removed on request of other reviewers.

Pg. 23047, line 1. Replace considerable with considerably.

The former section 4.2. was removed on request of other reviewers.

Pg. 23049-50, section 4.4. This section is particularly disorganized and hard to read. Please rework it.

Section (now 4.1.2) was shortened and a Table is provided.

Pg. 23050, line 10. Found an enrichment relative to what?

Corrected to 'an enrichment in the INP/IPR fraction relative to the total aerosol'

Pg. 23050, line 16. What is 'low-Z'?

Paragraph was removed. (low-Z would be low atomic number)

Pg. 23061, Table 2. Column 4 header – should be Morphology.

Corrected.

Pg. 23062, Table 3. Please provide a more informative and clearer caption. Specifically, what do the percentages relate to?

Corrected to 'Number fraction of internally mixed particles in each particle class for each technique'

Pg. 23063, Figure 1. Please specify in the caption how the 'Homogeneous time periods' are marked. I must have missed it within the main text, what is the significance of time periods B-F?

Notion on homogeneity was removed, as well as the periods B-F, which have no significance any longer.

Pg. 23066. Figure 4. I'm not certain that this figure adds much to the manuscript – consider its removal.

Fig 4 (now 6) shows, how droplets can be distinguished from other particles with same composition, which is only possible, if particle shape/morphology is regarded (i. e. specific to image-providing techniques). For that reason, we would keep the figure in the main manuscript.

Pg. 23072. Figure 10. Secondary has become C-O-(S)-bearing in the legend – please make consistent with the rest of the figures.

For sake of comparability, we used the same classification scheme as in the previous publication, and we also used the names from that publication to express the difference to the current scheme. We have added a remark to the caption.

Pg. 23073. Figure 11. Please make the color scheme consistent with the rest of the figures

Colors of metal oxides and silicates were corrected.

## References used in this reply

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## Interactive comment on “Single-particle characterization of ice-nucleating particles and ice particle residuals sampled by three different techniques” by A. Worringen et al.

Anonymous Referee #3

Received and published: 18 October 2014

Review of “Single-particle characterization of ice-nucleating particles and ice particle residuals sampled by three different techniques” by Worringen et al.

This manuscript presents the characterization of individual ice nucleating and ice residual particles using SEM/EDX analysis. The ice nucleating particle and ice particle residuals were collected by three different instruments. This study provides very useful information/insights on the comparison of sampling instruments/techniques for ice nuclei. The subject of the manuscript is suitable for publication in ACP. I recommend the authors to consider addressing the following comments/issues for the revision.

Major comments:

1. the manuscript didn't provide sufficient description on the FINCH+IN-PCVI experiments. First, was there size selected inlet applied (i.e., were the ice crystals removed before FINCH)? or it take all the particles including ice crystals and evaporate the ice before their enter the FINCH for ice nucleation activation? What were the experimental temperature and RH conditions for FINCH ice nucleation measurements? These are crucial information for the comparison with other two techniques. If the ice crystals were removed before FINCH, then it is comparing the non-activated particles with ice crystal residuals (activated particles) even if they were sampled the same air mass spontaneously.

FINCH+IN-PCVI is operated at the total inlet, which samples aerosol and all cloud elements without a size selection. No ice crystals are removed, all hydrometeors are evaporated. We have added an according statement.

Experimental conditions of FINCH are shown in Fig. 1 and Table S1 in the supplement now.

2. It is not very clear what samples are compared. In Figure 1, were only the samples from the marked periods (A-F) compared? The only overlap of the sampling for all three instruments was the F period around Feb. 20, which also across about 24 hours. How many particles/samples were analyzed during this F period? It would be very useful to provide air mass backward trajectories (HYSPLIT data) in the supplement materials to validate that the same particle source during the sampling times which were compared. The sampling time for the background aerosol particles was only less than 30 min, additional evidences (e.g., HYSPLIT data) are needed to validate this comparison with background aerosol composition. Same for the comparison with LA-MS data set. It is also not clear when LA-MS data were collected, the sampling time of LA-MS data should also be marked in the Figure 1.

Periods B to F have no longer a meaning so they are removed from the graph. In the summarizing graphs, all samples are compared, and period A is used as an example, as for this one, comparatively many particles were available.

Trajectories for Period A are given in the Supplement now.

Discussion of background samples was removed from the paper as requested by other reviewers.

Fig. 1 shows now also the sampling times of LA-MS. SEM and LA-MS are unavoidably non-parallel due to the sample flow limit.

3. Section 4.2, a major part of the discussion on the comparison of ice nucleation ability for the different particle classes is not appropriate, since the manuscript didn't provide sufficient supporting information of this type of comparison. First, Strictly speaking, when comparing the nucleation ability, data on freezing temperature/RH, activation fraction, or nucleation rate are needed for each particle types. We agree and are aware of that problem. Due to the low particle numbers, however, we are not able to differentiate all the different thermodynamic/kinetic conditions during the campaign.

Second, the enrichment is not quantitatively determined and background aerosol information is not sufficient (this study only has background aerosol data on a very short period of time). It is recommended to rewrite this section or leave it out.

We removed the section 3.4 (total aerosol) and modified section 4.2 accordingly.

4. Section 4.3, the discussion on the comparison of these three techniques can be extended in more details. We think that the present data set is not suited for a comparison of details of the different sampling techniques. In particular, we do not have enough parallel measurements for such a comparison. However, the INUIT consortium will carry out a closure experiment in March 2015 at a large aerosol chamber (AIDA, Karlsruhe) in which we hope to get a data set consisting of strictly parallel measurements.

It would be also important for the community if the manuscript can discuss briefly the limitations and advantages of each technique and provide some recommendations to improve the sampling or measurements in the future.

We have added a set of recommendations regarding the techniques and their development. Lacking a reference method, it is at this point not possible to rate each technique against another.

Specific comments:

1. P23030, l21-24, these two statements are oversimplified and it is not true. This should be reworded. For example, sea salt and sulfate can be efficient ice nuclei, e.g. Gregory P. Schill and Tolbert [2014] G. P. Schill and Tolbert [2013], Abbatt et al. [2006].

We have rephrased this section.

2. P23031, l3-4, there are a few studies that investigated the effect of mixing state of particles on ice nucleation and characterizations of ice nucleating particles from different field campaigns using SEM/EDX and other X-ray analysis technique (Hiranuma et al. [2013], [Knopf et al., 2010; Knopf et al., 2014]; Wang et al. [2012]).

We have rephrased the sentences and added references.

3. P23031, l25, the sampling for three techniques was not in parallel.

Corrected.

4. P23032, l23-25, Please provide a more detailed description on collecting particles onto different substrates. Are both two substrates used in all three different sampling instruments? How chemical composition was quantified for the particles these two substrates (the X-ray background of these two substrate is different)?

Both substrates were used with all techniques. This is stated explicitly now.

Chemical quantification in SEM/EDX always has to regard the contribution from the substrate. For that reason, usually non-interfering substrates are chosen (B and thin-film C, in our case). This is stated now. More details are later discussed in section 2.2.1.

5. P23033, l16 and l19-21, Do you mean "INUIT-JFJ 2013" or "INUIT-JFJ 2014"? Please provide more information regarding the ice nucleation experiments. It is not sufficient by just saying "supersaturation and freezing temperature were varied during the campaign."

Section was rephrased.

We give now details on the working conditions in the text, in Fig. 1 and as supplement.

6. P23035, Section 2.3, the manuscript didn't provide sufficient descriptions/criteria on the particle classification for both SEM/EDX and LA-MS techniques. What is the "Droplet", any chemical information on these particles? It could be very useful to show representative SEM images and X-ray spectra for each particle class (can be in the supplemental materials).

We have extended Table 2.

For the LA-MS classification, the paper of Schmidt et al. (2014) provides the details. Our table of classification was modified.

Information on droplet composition is given already in the original manuscript (page 23034, lines 4-9) – they mainly consist of sulfates.

We show in the manuscript specific artifacts of this investigation. Information on the Pb-rich particles can be found in more detail in Ebert et al. (2011). Other aerosol types are already described throughout the literature (Ebert et al., 2004; Kandler et al., 2007; Vester et al., 2007; Adachi and Buseck, 2008).

7. P23037, L10-16, since there are abrupt increases in particle concentrations which may come from local source, why it is only a "minor local influence"?

The samples were actually collected before and after that distinct spike in particle concentration. As this is not obvious from the graph, we have added a statement to the text.

8. Combining discussion in P23041, L18-19; p23045, L2-13; and P23050, L23-25, It is stated that lead-bearing particles in the whole INUIT campaign is 1% for FINCH+IN-PCVI and from Figure 6, no lead-bearing particle was detected from ISI sampling. If assuming that FINCH+IN-PCVI captured all the lead-bearing particles that nucleated ice (or nucleated ice on all the lead-bearing particles), does that mean 90% of lead-bearing particle (9% out of 10%) determined by Ice-CVI was artifacts?

This conclusion could only be drawn, if no variation would occur during the campaign, and if no statistical uncertainty would exist (which is high here due to the low numbers).

We have added a new discussion on lead as artifact to section (now) 3.1.1. We conclude that the homogeneous lead-rich particles (<10 % of all lead-bearing) are probably artifacts, but the others are probably not.

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## Interactive comment on “Single-particle characterization of ice-nucleating particles and ice particle residuals sampled by three different techniques” by A. Worringen et al.

Anonymous Referee #4

Received and published: 21 October 2014

This paper focuses on chemical characterization of ice-nucleating particles and the results from different sampling techniques are compared. The scientific results are interesting and the comparison of different techniques is necessary. The results from this paper are an important contribution to the fields of ice nucleation and aerosol chemistry; however, I can only recommend this paper for publication after major revisions. The paper was confusing as written and is missing several pieces of information that are essential to interpreting the results.

General Comments:

1) The introduction and experimental sections are poorly organized and have some pieces of information twice, while other key pieces of information are missing. Please revise and make more clear and concise, while also giving more details about the various techniques.

We have rewritten considerable parts of the experimental section. Furthermore, the technical papers are published meanwhile (Kupiszewski et al., 2014; Schenk et al., 2014).

2) Information is missing about the various techniques. For instance, transmission efficiency of the pCVI is not included. A paper is cited as in prep that might have this information in it; however, I cannot interpret these results without seeing that paper. Additionally, the reference for the ice selective inlet is a personal communication. If there is no reference that gives detailed information about the technique/inlet, then substantial data needs to be given in this paper regarding its performance including transmission efficiencies.

The papers of Schenk et al. (2014) and Kupiszewski et al. (2014), containing the technical details, were meanwhile published in AMTD.

3) More information is needed regarding the LA-MS technique. Representative mass spectra should be given of different particle types. How were the mass spectra classified? By hand? With a clustering algorithm? Does Table 2 refer to only SEM classifications or LA-MS too? Please state this in the caption.

Details on the LA-MS technique are published now in a companion paper (Schmidt et al., 2014), which was unfortunately delayed. We refer to this paper.

4) Operating temperatures and supersaturations in the FINCH are necessary to interpret the chemical results. These must be given every time the FINCH data is presented. How did the FINCH temperatures compare to the ambient temperature in the clouds? This is also a crucial piece of information when comparing the different techniques.

Fig 1 shows now the temperature of FINCH, which was set constantly at around -22°C. In addition, Table S1 in the Supplement gives now more details on the FINCH operating conditions for each sample. In most of the cases, the temperature difference between FINCH temperature and outside temperature was less than 5 °C. However, FINCH could not follow the weather fluctuations in detail.

5) Size distributions of particles from the 3 different techniques are briefly discussed, but there is no mention of how these correspond to the transmission efficiencies for the different techniques. The ISI sees a larger mode, while the others do not. Is this because the ISI is the only inlet that transmits large sizes effectively? Please discuss this more.



The size distributions shown were not meant for intercomparison, as the particle transmission function for the instruments is not yet well characterized. An according sentence was modified and a second one removed. The size distribution are intended to show which particle types occur in which size ranges, and how good the counting statistics is for these particles.

6) There are a lot of bar graphs and it would be clearer if the instrument or technique used was displayed at the top of each graph. This would allow for easier identification of what the graph is showing, especially for Figures 9 and 10.

Fig 10 now says 'from Ice-CVI'. Fig. 9 is removed on reviewer's request.

7) Table 3 is confusing because the percentages add up to over 100%. It would be clearer, if you included mixed particle types separately. This would also add more information about mixing state.

Caption was misleading. We give the fraction of internally mixed particles for each class (i. e. the number of internally mixed ones divided by the total number for this particle type).

## References used in reply

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## Abstract

In the present work, three different techniques to separate ice-nucleating particles (INP) as well as ice particle residuals (IPR) from non-ice-active particles are compared. The Ice Selective Inlet (ISI) and the Ice Counterflow Virtual Impactor (Ice-CVI) sample ice particles from mixed-phase clouds and allow after evaporation in the instrument for the analysis of the residuals. The Fast Ice Nucleus Chamber (FINCH) coupled with the Ice Nuclei Pumped Counterflow Virtual Impactor (IN-PCVI) provides ice-activating conditions to aerosol particles and extracts the activated particles for analysis. The instruments were run during a joint field campaign which took place in January and February 2013 at the High Alpine Research Station Jungfraujoch (Switzerland). INP and IPR were analyzed off-line by scanning electron microscopy and energy-dispersive X-ray microanalysis to determine their size, chemical composition and mixing state. On-line analysis of the size and chemical composition of INP activated in FINCH was performed by laser ablation mass spectrometry. With all three INP/IPR-separation techniques high abundances (median 20–70 %) of instrumental contamination artifacts were observed (ISI: Si-O spheres, probably calibration aerosol; Ice-CVI: Al-O particles; FINCH + IN-PCVI: steel particles). After removal of the instrumental contamination particles, silicates, Ca-rich particles, carbonaceous material and metal oxides were the major INP/IPR particle types obtained by all three techniques. In addition, considerable amounts (median abundance mostly a few %) of soluble material (e.g., sea salt, sulfates) occurred. As these soluble particles are often not expected to act as INP/IPR, we consider them as potential measurement artifacts. Minor types of INP/IPR include soot and Pb-bearing particles. The Pb-bearing particles are mainly present as an internal mixture with other particle types. Most samples showed a maximum of the INP/IPR size distribution at 200 nm to 400 nm geometric diameter. In a few cases, a second super-micron maximum was identified. Soot/carbonaceous material and metal oxides were present mainly in the sub-micrometer range. Silicates and Ca-rich particles were mainly found with diameters above 1  $\mu\text{m}$  (using ISI and FINCH), in contrast to the Ice-CVI which also sampled many submicron particles of both groups. Due to changing meteorological conditions, the INP/IPR composition was highly variable if different samples are compared. Thus, the observed discrepancies between the different separation techniques may partly result from the non-parallel sampling. The differences of the particle group relative number abundance as well as the mixing state of INP/IPR clearly demonstrate the need of further studies to better understand the influence of the separation techniques on the INP/IPR chemical composition. Also, it must be concluded that the abundance of contamination artifacts in the separated INP and IPR is generally large and should be corrected for, emphasizing the need for the accompanying chemical measurements. Thus, further work is needed to allow for routine operation of the three separation techniques investigated.

# Single-particle characterization of ice-nucleating particles and ice particle residuals sampled by three different techniques

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# 1 Introduction

The impact of clouds – and in particular cloud-aerosol interactions – on the earth’s radiation balance is still one of the most uncertain aspects in our understanding of the climate system (Flato et al., 2013). The understanding of tropospheric cloud ice formation processes is crucial for predicting precipitation and cloud radiative properties. Aerosol-cloud interactions play a key role in determining cloud properties like phase, size distribution and colloidal stability of the cloud elements, as well as the lifetime, dimensions and precipitating efficiency of a cloud. Though there has been an advance during the last decades, in particular for aerosol-cloud-interactions, the level of scientific understanding is still classified as “very low” to “low” (Flato et al., 2013). A considerable uncertainty of the response of aerosol and cloud processes to changes in aerosol properties still arises from the lack of fundamental understanding of the interaction of aerosol particles with the cloud ice phase (Lohmann and Feichter, 2005). Although large attention was given to field studies in the last decade (e.g., Richardson et al., 2007; Prenni et al., 2009a; Prenni et al., 2009c; Santachiara et al., 2010; Ardon-Dryer et al., 2011; Conen et al., 2012; Ardon-Dryer and Levin, 2014), these measurements cover only limited geographic regions as well as a limited time. Thus, additional field work is certainly needed.

Many ice nucleation experiments were performed under laboratory conditions (e.g., Hoose and Möhler, 2012, and references therein), and provided valuable knowledge on ice-nucleating particle (INP) properties of pure components and artificially generated mixtures. Mineral dust and biological particles are regarded in general as efficient INP, while experiments disagreed on the INP abilities of soot and organics (Hoose and Möhler, 2012). Sea-salt and sulfate are often not considered as INP (Pruppacher and Klett, 1997). However, this conclusion is challenged by several authors (Abbatt et al., 2006; Schill and Tolbert, 2014). Furthermore, it was shown recently in laboratory work for NaCl particles that a partial efflorescence under suitable conditions might lead to ice activation (Wise et al., 2012). The situation is even more complex in the ambient atmosphere, where particles are present as complex mixture of different compounds. In addition, the particles may be modified by heterogeneous processes, which may change their ice nucleation ability. In laboratory experiments, these effects are currently addressed for single substances (Hoose and Möhler, 2012; Wex et al., 2014), but the level of atmospheric mixing complexity is not yet realized. Though mixing state was regarded by previous investigations (Knopf et al., 2010; Ebert et al., 2011; Hiranuma et al., 2013; Knopf et al., 2014), the data basis is still sparse and further field work is needed.

During the last decade, several techniques emerged which are capable to distinguish ice-nucleating particles (INP) or ice particle residuals (IPR) for subsequent chemical analysis. Particles are usually exposed to thermodynamic conditions favoring ice nucleation, either in the airborne state or on a substrate. Examples for these techniques are the Fast Ice Nucleus Chamber (FINCH) (Bundke et al., 2008) in combination with the IN-pumped counterflow virtual impactor (IN-PCVI) (Schenk et al., 2014), the Continuous Flow Diffusion Chamber (CFDC) in combination with the laboratory counter-flow virtual impactor (LCVI) (Cziczo et al., 2003) and the Frankfurt Ice Nuclei Deposition Freezing Experiment (FRIDGE) (Bundke et al., 2008; Klein et al., 2010). While in FINCH+IN-PCVI and CFDC-LCVI the particles are kept airborne, ice nucleation occurs on an ice-inert substrate in FRIDGE. In contrast, analysis of IPR relies on the natural selection of INP by a cloud. While for cirrus clouds all cloud elements can be investigated (Cziczo and Froyd, 2014), for mixed phase clouds the ice particles need to be separated from droplets. Ice particle separation can be accomplished with different techniques. In the Ice Selective Inlet (Kupiszewski et al., 2014) droplets present in the sampling flow are evaporated in an ice-saturated environment and the remaining ice crystals are subsequently separated from non-activated particles using a PCVI. Alternatively, cloud elements can be impacted on a cooled surface collecting the droplets while bouncing the ice particles for further analysis (Ice Counterflow Virtual Impactor, Ice-CVI) (Mertes et al., 2007).

In the present work, three state-of-the-art techniques for INP/IPR sampling – ISI, Ice-CVI and FINCH+IN-PCVI – were operated in a joint field experiment to sample atmospheric mixed-phase clouds and characterize the sampled INP/IPR with respect to their morphology, chemical composition, particle size and mixing state. The High Alpine Research Station Jungfraujoch

(Switzerland) was chosen as field site for logistic reasons (easy access to a location with frequent presence of mixed phase clouds). In addition, as INP and IPR were investigated recently at this location in a number of studies, a considerable data base is available for comparison. In the previous work, enrichment of mineral dust (Kamphus et al., 2010; Chou et al., 2011; Ebert et al., 2011), metal oxides (Ebert et al., 2011), Pb-containing particles (Cziczo et al., 2009b; Ebert et al., 2011) as well as carbonaceous material/black carbon (Cozic et al., 2008; Ebert et al., 2011) among INP/IPR was reported.

## 2 Experimental

In January/February 2013, a field campaign of INUIT (Ice Nuclei Research Unit) was performed at the High Alpine Research Station Jungfraujoch in Switzerland (JFJ, 3580 m a.s.l., 46.55° N, 7.98° E). Ice particle residuals (IPR) were separated from the interstitial aerosol and droplets by ISI and Ice-CVI. Ice-nucleating particles (INP) were sampled from the total aerosol by FINCH+IN-PCVI (Table 1). INP/IPR were either collected by impactors and analyzed by scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (EDX) or analyzed on-line by laser ablation mass spectrometry (LA-MS).

### 2.1 INP/IPR sampling

INP and IPR were sampled by three different techniques. INP were detected by the FINCH + IN-PCVI (details of the experimental setup are given in Bundke et al., 2008; Schenk et al., 2014). IPR were collected via selective sampling of small ( $< 20 \mu\text{m}$  aerodynamic diameter) ice crystals with Ice-CVI and ISI. Subsequent heating of the sampled ice crystals releases IPR. The extracted IPR were collected for scanning electron microscopy with a two-stage impactor system. The setup consisted of circular nozzles with 0.7 and 0.25 mm diameter operated at a flow rate of  $0.45 \text{ L min}^{-1}$  (volume), leading to approximate 50 % cut-off efficiency aerodynamic diameters of 1 and  $0.1 \mu\text{m}$ , respectively (for details on impactor dimensions see Kandler et al., 2007). Transmission electron microscopy grids (type S162N9, Plano GmbH, Wetzlar, Germany) and polished elemental boron embedded in a conductive resin were used as impaction substrates for all methods. Both substrates provide a background signal with low interference with respect to the particle composition.

#### 2.1.1 Coupling of FINCH and IN-PCVI

FINCH + IN-PCVI was operated in clouds as well as during cloud-free periods. Aerosol particles and cloud elements were sampled from the atmosphere by a total aerosol inlet (Weingartner et al., 1999) with an aerosol flow of approximately  $2.25 \text{ L min}^{-1}$ . The aerosol was dried by heating to evaporate the water of the hydrometeors. The dried aerosol containing all interstitial particles and cloud element residuals was then transported into FINCH, in which a super-saturation with respect to ice is achieved by mixing air flows of different temperature and humidity. INP are activated, grow while flowing through the chamber, and are counted by an optical particle counter (OPC). The OPC used in this instrument is able to distinguish between super-cooled water droplets and ice crystals by analyzing the polarization ratio of the scattered circular polarized light (P44/P11 ratio of the scattering matrix; Hu et al., 2003). In addition, the auto-fluorescence resulting from the excitation of the grown particles with UV light is detected (Bundke et al., 2010), which is an indication for biological particle material.

The ice crystals are then separated by the PCVI from the non-activated particles and from the small super-cooled droplets (Schenk et al., 2014). As the PCVI input flow must be identical to the FINCH output flow, the counterflow must be continuously adjusted to achieve this requirement. This adjustment leads to variable cut-off diameters between 4.5 and  $8 \mu\text{m}$ . Finally, the sampled FINCH ice particles evaporate while they are transported in a dry particle free air.

The freezing temperature during the campaign was slightly varied around -22.1 °C, which matched for most of the samples the outside air temperature with less than 5°C difference. The ice supersaturation was varied between 1.14 and 1.80 with a mean of 1.54 for all samples. Details on the sampling conditions are given in Table S1 in the supplement.

### 2.1.2 Ice-CVI

From the mixed-phase clouds prevailing at JFJ, the ice particle residuals were collected by the Ice-CVI (Mertes et al., 2007). It consists of a series of different modules that allow the sampling of small ice particles by a simultaneous pre-segregation of all other cloud constituents. The vertical, omnidirectional inlet already reduces the sampling of ice crystals larger than 50 µm, including precipitating or windblown ice particles. A virtual impactor downstream the inlet horn limits the upper size of sampled hydrometeors to 20 µm. This limit is reasonable, because the collection efficiency is nearly 1 for these ice particle sizes. The ice particle break-up is minimized in the subsequent Ice-CVI components, and ice particles in this size range grow by water vapor diffusion, i.e. they should contain only the former INP as a residual particle. Downstream of the virtual impactor a pre-impactor removes super-cooled drops by contact freezing on cold impaction plates. Ice particles bounce and pass the impaction plates. A conventional CVI (Mertes et al., 2005a; Mertes et al., 2005b) is located downstream of the pre-impactor to reject interstitial particles smaller than 5 µm. Thus, only ice particles in the 5–20 µm diameter range completely traverse the Ice-CVI. As with a conventional CVI these small ice crystals are injected into a particle-free and dry carrier gas which leads to evaporation and allows the analysis of the ice particle residues.

### 2.1.3 Ice Selective Inlet (ISI)

The novel Ice Selective Inlet (ISI; for details refer to Kupiszewski et al., 2014) was designed to extract small ice crystals from mixed-phase clouds, simultaneously counting, sizing and imaging the hydrometeors contained in the cloud with the use of WELAS (white light aerosol spectrometers) 2500 sensors and a Particle Phase Discriminator (PPD-2K). The core of the ISI is a droplet evaporation unit with ice-covered inner walls, removing droplets using the Bergeron-Findeisen process, while transmitting the ice crystals. In the final stage of the ISI, a pumped counterflow virtual impactor removes interstitials and cloud condensation nuclei released in the droplet evaporation unit from the sample flow, thus ensuring only ice crystals are transmitted. The extracted ice crystals are subsequently sublimated, releasing the ice particle residuals (IPR), which are transferred into the laboratory for further on- and offline characterization of their physical and chemical properties.

## 2.2 Sample characterization

### 2.2.1 Scanning electron microscopy

Thirty six samples (18 from FINCH, 13 from Ice-CVI, 5 from ISI) were acquired during the field campaign. All samples were analyzed by scanning electron microscopy (FEI Quanta 200 FEG, FEI, Eindhoven, the Netherlands) and energy-dispersive X-ray microanalysis (EDX, EDAX, Tilburg, the Netherlands). The particles of the different samples were manually characterized with respect to their chemical composition, size, morphology, internal mixing state and stability under electron bombardment. Particle size was determined as average geometrical diameter (equivalent projected area diameter) from the electron images.

Based on chemical composition, morphology, mixing state and beam stability, 18 particle groups were defined and combined into 11 particles classes. Table 2 lists the particle groups, particle classes and classification criteria for the manual analysis.

Pb-bearing particles were classified according to the presence of Pb only (i.e. as soon as Pb could be detected). They might be homogeneous Pb-rich particles or particles containing Pb-rich inclusions. In the latter case, the main matrix particles can be carbonaceous, soot, sulfate, sea-salt, silicate,

metal oxide, a droplet or belong to the “other” class. Droplets are identified by their typical morphology of larger residual particles centered in a halo of small residuals, originating from the splashing of the droplet at impaction. The center of the residual can consist of unstable **material** (e.g., sulfate) or stable sea-salt, silicate, metal oxide, Ca-rich particles, or mixtures thereof. The halo particles are usually unstable under electron bombardment. Particles which could not be classified into one of the classes mentioned above are summarized in the particle class “other”. This particle class contains for example Zn-rich, Mg-rich particles as well as Sn-, Ba-, Bi- and Br-bearing particles **with a total abundance of usually less than 1 %**.

Due to the difference in sample substrate composition between TEM grids and elemental boron, in particular for the detection of carbonaceous particles and thin carbonaceous coatings, systematic deviations **may** occur with a **potential** bias towards better detection of these particles on boron.

## 2.2.2 Laser Ablation **Mass Spectrometry (LA-MS)**

**Laser ablation mass spectrometry was carried out with** ALABAMA (Aircraft-based Laser Ablation Aerosol Mass Spectrometer), which was originally developed for aircraft operation (Brands et al., 2011), but **was also used** in several ground-based measurement **campaigns**. It provides the chemical composition of single aerosol particles in an aerodynamic particle size range between 150 and 1500 nm, including refractory compounds such as metals, dust, and soot. It was used during the INUIT-JFJ campaign for the analysis of background aerosol particles and IPR (Schmidt et al., 2014). **A total of 1809 IPR mass spectra were collected: 1663 with the Ice-CVI (104 operation hours) and 146 with ISI (32 operation hours).**

## 2.3 **Sampling location and meteorology**

The JFJ station is located in a saddle between the mountains Jungfrau and Mönch, which is oriented WSW – NNE. This topography results in a channeling of the atmospheric flow leading to a near-binary distribution of wind directions as either NW or SSE. The atmospheric conditions during the campaign are illustrated in Fig. 1. Hourly 5 day backward trajectories for the JFJ station were calculated with the HYSPLIT model based on GDAS data (Draxler and Rolph, 2013).

**At the top of Fig. 1, a period (labelled A) with comparatively homogeneous atmospheric conditions is marked. It was chosen for instrumental comparison based on individual samples. Homogeneity was determined from meteorology, particle concentrations and changes in air mass origin (see also Fig. S1 in the electronic supplement). Period A (2 February/13:00–18:00 UTC) can be described as follows. During the last day before arrival, air masses travel approximately along the Rhine valley at altitudes between 1.5 km and 2.5 km. Two days before arrival, the air mass backward trajectories cross the North Sea and the United Kingdom in the same altitude range. For the rest of the trajectory length, the air masses were over the Northern Atlantic Ocean in the region of Iceland. Wind, temperature and in-cloud conditions were very stable during this period. While the JFJ is usually in the free troposphere during the winter months (Collaud Coen et al., 2011), abrupt increases in particle concentrations may indicate a rise in the atmospheric boundary layer height to the station altitude, which leads to a local influence. This effect is visible as a sudden increase in particle concentration in the middle of this period. The samples were collected before (FINCH + IN-PCVI) and after (Ice-CVI) the highest particle concentrations, so we consider period A as of Atlantic/free-troposphere origin with minor local influence.**

## 3 **Results**

### 3.1 **Contamination artifact particles from the INP/IPR sampling instruments**

The sampling instruments yielded different types of artifact particles indicated by their clear non-atmospheric origin. **They consisted either of compounds used for manufacturing the instruments (e.**



g., aluminum, stainless steel) or had the same composition and morphology as calibration aerosol (e.g., Si-O spheres). Therefore, they were removed from further analysis. Fig. 2 shows secondary electron images of the most common contamination artifact particles and their energy-dispersive X-ray spectra. The relative abundance of the dominating artifact particles for each instrument is shown in Fig. 3 as box plots.

With all three sampling techniques, small amounts of Fe-Cr particles are observed as an artifact. They may derive from internal abrasion of the instrument or tubing. In addition, for the samples collected on boron substrates, Cu-rich particles are present, which are most likely fragments from the embedding material of the boron substrates (an epoxy resin containing copper chips for increased conductivity).

In the ISI samples, mainly Si-O spheres with a size of approx. 1  $\mu\text{m}$  are observed as artifacts. These particles were most likely introduced into the instrument during calibration of the optical particle spectrometers contained within the inlet. The abundance of Si-O spheres in the samples ranged from 26 to 94 %. Including the Fe-Cr-rich and Cu-rich artifacts, the abundance of all artifact particles ranged from 46 to 94 % during the measurement period.

In the FINCH+IN-PCVI samples, Fe-Cr-rich and Cu-rich particles as well as a few Au/Ag particles (not shown as image) are identified as instrumental artifact. Their total abundance ranges from 0 to 60 % with a median of 20 %.

In the Ice-CVI samples, Al-O particles – probably aluminium oxides/hydroxides – occur as artifacts. The relative abundance of these Al-O particles varied in the range of 0 to 94 % by number. If we consider a particle break-up during impaction as indicated by their small size in relation to the nominal impactor cut-off size, the relative number abundance might be lower for airborne particles. As all Al-O particles are classified as artifacts in the present paper, potentially occurring atmospheric aluminium oxides/hydroxide particles in the Ice-CVI would be overlooked. However, it can be safely assumed that this potential error is minor, as no Al-O particles with the characteristic morphology (Fig. 2) were identified with the other two sampling instruments. The abundance of other artifact particles in the Ice-CVI sample is small (range of 0 to 8 %).

Lead-bearing particles are frequently found in the Ice-CVI samples, but also to a much lesser extent in FINCH+IN-PCVI samples. These particles are regarded as effective INP in previous work (Cziczo et al., 2009b; Ebert et al., 2011). However, as parts of the Ice-CVI are manufactured from a Pb-containing aluminum alloy, we performed additional tests to evaluate whether the Pb-bearing particles are an instrumental contamination artifact. SEM inspection of the surface of the impaction plates revealed the presence of large, homogeneous Pb-rich particles which consist of Pb, C and O (usually without an Al signal, when removed from the plates). The atomic Pb/O ratio varied between 3 and 1, indicating a composition of partially oxidized metallic lead. No halogenides or sulfides could be detected on the plates. In contrast, the particles found as INP/IPR are mostly internally mixed with other aerosol compounds, except for a few (less than 10 %) homogeneous Pb-rich particles with a composition similar to the Pb particles encountered on the impaction plates. Therefore, the latter (homogeneous Pb particles) are considered as artifacts. In previous campaigns at the JFJ station, Pb-rich IPR inclusions in other particle types were identified as PbS (Ebert et al., 2011), indicating a non-artifact origin. This interpretation is also supported by the observed particle sizes. The Pb-rich particles on the impaction plates are larger than 1  $\mu\text{m}$  (geometric diameter), in contrast to the Pb-bearing IPR which are mostly smaller than 1  $\mu\text{m}$ . The Pb-rich inclusions within the Pb-bearing IPR have sizes of few tens to few hundreds of nanometers. In addition, considering the low impaction speeds inside the Ice-CVI (Mertes et al., 2007), in particular an abrasion of submicron particles can be considered as improbable. The Pb-rich particles are predominantly observed in the Ice-CVI samples, but also to a lower extent in FINCH+IN-PCVI samples, where no Pb-containing alloys were used. This observation also indicates that the majority of Pb-rich particles are not instrumental contamination artifacts. However, for the minor amount of large homogeneous Pb-rich particles an instrumental source is likely.

In summary, it must be concluded that the abundance of contamination artifacts in the separated INP and IPR is generally large and cannot be neglected. Thus, the INP/IPR concentrations must be corrected to obtain accurate results. It is highly recommended that measurements of INP/IPR

concentrations are always accompanied by chemical and morphological single particle characterization in order to avoid large systematic errors caused by contamination artifacts.

### 3.2 Composition of INP/IPR at the Jungfraujoch in winter

During the field campaign 5 ISI, 18 FINCH + IN-PCVI, and 13 Ice-CVI samples were analyzed with a total (non-artifact) INP/IPR particle number of 2627. Due to the low particle number on individual samples, the INP/IPR from all samples were integrated for each technique (Fig. 4) to yield better statistics. Particles were classified according to their size in a sub- and supermicron range.

Silicates are the main group of INP/IPR independent of sampling technique and size range (with the exception of submicron particles encountered in ISI). Ca-rich particles are predominantly found in the supermicron range with all three sampling techniques, in contrast to soot and sulfate particles, which occur mainly in the submicron range. Metal oxides are present in both size ranges with a tendency to the submicron range while sea-salt particles tend to be in the supermicron range. However, if the low number of analyzed particles and the resulting statistical uncertainty are considered, the observed differences between the techniques are regarded only as a trend. In addition, the three instruments could not be operated strictly in parallel and thus, sampled different time periods. In particular, ISI samples were taken only at the end of the field campaign.

The main difference in composition trends between the three sampling methods are the high content of carbonaceous particles measured downstream of the ISI, and the high content of Pb-bearing particles obtained by Ice-CVI. The high concentration of carbonaceous particles in the ISI-samples may result from different air masses being sampled at the end of the field campaign, when the ISI was operated. During this time, higher black carbon concentrations were measured than during the earlier periods (not shown). The Pb-bearing particles are discussed later in Sect. 3.4 in more detail.

If the eleven particle classes are grouped into four simplified components – particles of potential terrigenous origin (i.e., silicates and Ca-rich particles), C-dominated particles (carbonaceous, soot), metal-oxides-dominated and soluble particles (sulfate, droplets, sea-salt) – the terrigenous particles are the main component with relative abundances of 32 % (ISI), 51 % (FINCH+IN-PCVI) and 55 % (Ice-CVI). The C-rich particles show a higher variation due to sampling of different air masses and range from 9 % (Ice-CVI), 13 % (FINCH+IN-PCVI) to 34 % (ISI). The soluble particles vary between 22 % (ISI and Ice-CVI) and 32 % (FINCH+IN-PCVI).

The composition of the INP/IPR-samples varies between different cloud events as well as between the INP/IPR sampling techniques. The heterogeneity of the INP/IPR composition is illustrated with the example of February 2<sup>nd</sup> (Fig. 5), where relatively stable atmospheric conditions prevailed. During this period, two samples were taken between 17:40–18:10 (Ice-CVI) and 14:50–17:11 (FINCH+IN-PCVI). The relative number abundance of the major components is quite similar, i.e., dominating silicates with a fraction of 71 % (Ice-CVI) and 65 % (FINCH+IN-PCVI) as well as the presence of organics and metal oxides. The relative abundance of the minor INP/IPR classes seems to differ considerably. However, due to the small number of particles sampled by FINCH + IN-PCVI, no further conclusions can be drawn. In addition, a part of these differences may be caused by the different INP/IPR sampling techniques and short-term changes in meteorological conditions.

#### 3.2.1 Potential INP/IPR sampling artifacts

In addition to the clearly identifiable instrumental contamination artifacts, potential INP/IPR sampling artifacts may occur. We define potential sampling artifacts as particles, which pass the selection mechanisms similar to INP/IPR, while being questionable to act as INP/IPR (e.g., Pruppacher and Klett, 1997). The potential sampling artifacts include sea-salt particles, sulfate particles and particles which impact on the sampling substrates as droplets. As we cannot exclude that these particles are INP/IPR, we do not exclude them from further analysis in contrast to the instrumental contamination artifacts.

Droplets are characterized by their morphology of a residue with a halo (Fig. 6). While in principle the heating and drying line should lead to total evaporation of particle-bound water, obviously some

particles were still in liquid state during impaction sampling. As we cannot distinguish incompletely dried ice residuals from super-cooled droplets, which were falsely identified as INP/IPR, we consider droplets as **potential INP/IPR sampling** artifacts. Sulfate particles were preferentially found in the submicron size range, while sea-salt particles have a tendency to be of larger **size**. Droplets, however, occur rather uniformly in **both size ranges**.

The relative number **abundances** of the three potential sampling artifacts (droplets, (non-droplet) sulfate and sea-salt) **are shown as box plots (in Fig. 7)**, separately for each INP/IPR sampling instrument. All **potential** INP/IPR sampling artifacts are observed for all three techniques, and their relative abundances are on comparable levels of 0–10 % for each particle type. However, in particular the Ice-CVI extracted a higher number of sea-salt particles as INP/IPR. For single measurements, the abundance of these potential sampling artifacts can reach up to 40 %.

### 3.3 Size distribution of INP/IPR components

To allow for the display of a size distribution (Fig. 8), we combined the classes into generalized components of INP/IPR to achieve higher particle counts for each particle size interval. **Instrumental contamination artifacts and Pb-bearing particles are excluded in this presentation.** Note that size distributions obtained with the different techniques cannot be compared directly due to different inlet and transmission efficiencies. However, all three methods yield a maximum between 0.3 to 0.5  $\mu\text{m}$  geometric diameter. In addition, ISI shows a secondary maximum around 1 to 1.5  $\mu\text{m}$ . **With ISI and FINCH-IN-PCVI**, silicates and Ca-rich particles are predominantly found at the larger particles sizes. The relative abundance of carbonaceous/soot **as well as metal oxides is higher within the submicron range**. The soluble and secondary particles do not show a particular size preference **in their relative abundance**. **For the Ice-CVI, there seems to be a trend towards a higher abundance of soluble/secondary material with increasing particle size. However, this cannot be regarded as significant due to the extremely low particle numbers for supermicron particles (less than 10 for each sample and size interval). In the submicron range, no size dependency is visible.**

### 3.4 Mixing state and Pb-bearing INP/IPR

A significant fraction of the INP/IPR consists of particles with coatings or inclusions (see groups in Fig. 4). The relative abundance of internally mixed particles for each particle type is summarized in Table 3. It is apparent that mainly silicate particles and to a lesser extent metal oxides are internally mixed. Mixing partners are mostly sulfate and carbonaceous matter, but also sea-salt, if present in the total aerosol. The other particle types are less frequently internally mixed. Regarding differences between the sampling techniques, in particular INP measured by FINCH+IN-PCVI are considerably more frequently internally mixed than IPR **of ISI** and Ice-CVI. The (non-droplet) sulfates obtained as INP/IPR contain in most cases no heterogeneous inclusions. Also, most of the soot and Ca-rich particles have no coating, which is consistent for all sampling techniques. In contrast, the mixing state of carbonaceous particles was found to be highly different, rarely mixed for ISI (7 %) and frequently mixed for FINCH+IN-PCVI (64 %).

In previous IPR measurements at the JFJ station (Cziczo et al., 2009b; Ebert et al., 2011), Pb-bearing particles were found at high abundance. For comparison with the previous work (Fig. 9), we have selected the Pb-bearing particles from the total INP/IPR and determined their mixing partner. For comparability, the particles were classified in the same way as for the CLACE 5 campaign (Ebert et al., 2011). Pb-bearing particles are only found with Ice-CVI and FINCH+IN-PCVI. The Pb inclusions occur within the same main particle classes identified as INP/IPR in general, i.e., mainly silicates, Ca-rich particles, sulfates, sea-salt, and carbonaceous particles. In addition, externally mixed (homogeneous) Pb-bearing particles are present at minor abundance. While fewer externally mixed Pb-bearing particles were observed in the present field campaign (compared to Ebert et al., 2011), the abundance of the other Pb-bearing groups seems to be similar.

## 4 Discussion

### 4.1 Composition of INP/IPR

#### 4.1.1 Which particle classes can be regarded as INP/IPR?

Silicates **were** identified as common INP/IPR in laboratory experiments as well as in field experiments (Hoose and Möhler, 2012; Murray et al., 2012). Also in our field campaign, silicates are the most abundant INP/IPR **component**. Ca-rich particles – e.g., carbonates like calcite – are not frequently regarded as **INP (e.g., Murray et al., 2012)**. However, **according to** laboratory experiments calcite can act as INP (Zimmermann et al., 2008). **Therefore, the** Ca-rich particles are regarded as INP/IPR. Metal oxides are **also** commonly **observed as** ice residuals in field experiments (Chen et al., 1998; DeMott et al., 2003). Similar to our study, Fe-rich particles are **usually** the main group within the metal oxides. In addition, Al-, Ti-, Zn-, Cr-, and Ca-rich particles were found in **the present investigation** and by Chen et al. (1998).

Based on field experiments and laboratory studies, Pb-bearing particles are in general regarded as good ice nuclei (for a detailed discussion refer to Cziczo et al., 2009b). In the present study, **lead is found in two forms: as Pb-rich inclusions in other particles (major abundance) and as homogeneous Pb-rich particles (minor abundance). The minor fraction of homogeneous Pb-rich particles is regarded as instrumental artifact (see discussion above), but due to its low abundance of less than 10 % (equaling about 10 particles), it is neglected from the further discussion.**

The ice nucleation ability of soot and carbonaceous particles is discussed controversially in **the** previous literature. While an enrichment of black carbon in ice residuals **was** observed in field experiments (Cozic et al., 2008), there are also other findings where organic-rich particles preferentially remain unfrozen (Cziczo et al., 2004). It has to be mentioned, however, that carbon-rich particles are **often** named ambiguously depending on the technique used for analysis (see also Murray et al., 2012; Petzold et al., 2013). Thus, **discrepancies may arise from the fact that different types of carbonaceous material (e.g., nano-crystalline graphite, organic material) are compared.** Laboratory experiments show that the ice forming activity of soot is influenced by size, surface area and the concentration of the surface chemical groups that can form hydrogen bonds with water molecules (Gorbunov et al., 2001; Koehler et al., 2009). According to the latter, the ice forming activity of soot is close to that of metal oxides. In summary, we conclude that soot and carbonaceous particles observed in our samples were active as INP.

**Also for secondary aerosol particles,** the ice nucleation ability is discussed controversially. As in the case of soot and carbonaceous matter, secondary aerosol particles are found in field measurements of INP (Abbatt et al., 2006; Prenni et al., 2009b) and in laboratory experiments under cirrus cloud conditions (Hoose and Möhler, 2012). In contrast, Cziczo et al. (2004) report that organic-rich particles (internally mixed particles of sulfates and organic species) preferentially remain unfrozen. Based on our data, where secondary material is present in many INP/IPR samples, we consider these particles **to be** INP/IPR.

Sea-salt as INP/IPR was described by Cziczo and Froyd (2014) and Targino et al. (2006). While crystalline salts were found to be able to act as INP under upper-tropospheric conditions (Zuberi et al., 2001), there has been a lack in clarifying the process by which a hygroscopic and soluble material should act as IN. However, recently Wise et al. (2012) explained this behavior by fractional crystallization of the solute component under decreasing temperatures. Based on these findings, we consider sea-salt as **potential sampling artifacts**.

**Similar to sea-salt, no agreement exists on the** ice nucleation ability of sulfate particles. Sulfates may act as INP in cirrus clouds in the upper troposphere and lower stratosphere, both in immersion and deposition **mode** (Abbatt et al., 2006, and references therein; Hoose and Möhler, 2012). Sulfates acting as INP are found **at increasing abundance with decreasing temperature under cirrus conditions (-56 °C to -39 °C; Twohy and Poellot, 2005)**, but usually not in the warmer mixed phase clouds as encountered during our field experiment. **Considering** the high relative abundance of sulfates in the

total aerosol (not shown), we cannot exclude the possibility that sulfates are an artifact of the INP/IPR discrimination techniques not having perfect (i.e., 100 %) discrimination efficiency. Thus, we consider sulfate particles as potential sampling artifacts. Similar considerations apply to the observed droplets.

As explained in the methods section, contamination artifact particles were removed from the further analysis, while potential sampling artifacts are included in the data.

#### 4.1.2 Relative abundance of particle classes among INP/IPR

If all INP/IPR particles of the three sampling methods are summed up, the following averaged INP/IPR composition of the whole field campaign is obtained: 52 % terrigenous particles (38 % silicates, 9 % metal oxides, 5 % Ca-rich particles), 14 % C-rich (12 % carbonaceous particles, 2 % soot), 1 % secondary particles, 11 % sulfate, 11 % droplets, 4 % sea-salt, 5 % Pb-bearing particles, and 2 % other particles.

A compilation of INP/IPR composition encountered in mixed-phase clouds is shown in Table 4. In general, the results of the present study are in good agreement with the findings of previous work. Silicates are the most abundant component of INP/IPR with a relative number abundance varying between 40 and 71 %. The second most abundant component is carbonaceous material (16 – 43 %), followed by salts (sea salt, sulfates, droplets) with a relative number abundance between 5 and 27 %. The high abundance of coated particles observed in the present study is in good agreement with Targino et al. (2006) who observed sulfur coatings for all groups indicating ageing and in-cloud processing.

An overview of IPR compositions found during 13 field campaigns of cirrus clouds is given by Cziczo and Froyd (2014). Also here, the main particle types are mineral dust, metals, BC/soot, sea-salt, sulfate, and biomass burning.

A relative high abundance of Pb-bearing particles, in particular internally mixed ones, seems to be characteristic for IPR at the JFJ station. They were found in previous work (Cziczo et al., 2009b; Ebert et al., 2011) and during the present field campaign. However, the fraction of Pb-bearing particles in the whole INUIT campaign is 1 % for FINCH+IN-PCVI, and 10 % for Ice-CVI. In contrast, a higher fraction of up to 20 % was found during CLACE 5. As helicopter flights – where Pb-rich particles might be emitted due to leaded fuel usage – around the JFJ station were more frequent during CLACE 5 than during the present field campaign, the decrease in the abundance of Pb-bearing particles indicates a considerable contribution of local emissions to the INP formation at the JFJ station.

#### 4.2 Significance of mixing state and particle class for ice nucleation

A significant fraction of the INP/IPR occurs as internal mixtures (Table 3). This fraction is similar to previous literature data. Chen et al. (1998) reported a fraction up to 25 % of INP which were mixtures of sulfates and elements indicative of insoluble particles. The same relative abundance of mixtures of metal oxides/dust with either carbonaceous components or salts/sulfates was reported by Prenni et al. (2009a). For the JFJ station, a slightly lower fraction of internally mixed particles was found during the CLACE 5/6 campaigns: 9–15 % by Ebert et al. (2011) and up to 15 % by Kamphus et al. (2010).

Especially notable is the observed difference between silicates and Ca-rich particles. While silicates are usually internally mixed, the Ca-rich particles do not have a detectable coating. This may indicate that for silicates a coating is less effective in reducing their IN ability than for Ca-rich particles, pointing to a more pronounced processing (e.g., destruction of the surface structure) of the latter. However, the influence of coatings on the ice nucleation ability of silicates is discussed controversially. In field experiments, coatings on silicates and metal oxides are commonly observed (Chen et al., 1998; Targino et al., 2006; Prenni et al., 2009a). In laboratory experiments, conflicting results are obtained. While Cziczo et al. (2009a) as well as Hoose and Möhler (2012) reported a deactivation of the ice nuclei due to coatings, Sullivan et al. (2010) found that coatings do not always effect the ice nucleation ability. In contrast, Archuleta et al. (2005) and Zuberi et al. (2002) discuss



mineral dust as efficient nucleus for ice in  $\text{NH}_4\text{SO}_4\text{-H}_2\text{O}$  aerosols and demonstrated that mineral particles coated with sulfate increase the freezing temperature up to 10 K compared to pure sulfate solutions. In addition, Richardson et al. (2007) reported that soluble coatings favor condensation-freezing nucleation and inhibit nucleation by vapor deposition. But they also mention, that coatings itself may act either to increase or decrease ice nucleation efficiency independent of the nucleation mechanism.

Beside the mixing state considerations, some general comments on the ice nucleation ability can be made by comparing the abundance of different particle classes among INP/IPR in the present field campaign with previous literature data. Feldspar minerals and in particular K-feldspars (e. g. microcline) were discussed as efficient INP (Atkinson et al., 2013; Yakobi-Hancock et al., 2013). Despite the fact that we did not determine the mineralogical phase of the silicate particles, we can show by SEM-EDX that they have low potassium contents (K/Si atomic ratio < 0.1). Thus, it is concluded that K-feldspar particles do not occur as INP/IPR at JFJ in winter. Ca-rich particles appear in the supermicron fraction with a number abundance ratio of 0.1 to 0.33 relative to silicates (depending on method and sample), which is in the range reported for natural mineral dust (Kandler et al., 2007; Coz et al., 2009; Kandler et al., 2009; Kandler et al., 2011). Thus, Ca-rich particles can be considered as similarly effective IN as silicates.

#### 4.3 Comparison between FINCH+IN-PCVI, Ice-CVI and ISI

A reasonable agreement between the different sampling techniques is obtained for the major particle classes observed among the INP/IPR. However, the variation in INP/IPR composition due to meteorological conditions in connection with the non-parallel sampling introduces a systematic error. The non-parallel sampling could not be avoided during the present field campaign, as the sampling techniques were not yet in a state allowing for synchronized operation and the available flow from the INP/IPR samplers was insufficient for a sampling for SEM and operation of LA-MS in parallel. Consequently, INP/IPR composition snapshots from different time periods needed to be integrated for comparison of the INP/IPR composition.

The reasons for the different instrumental contamination artifacts were identified. Thus, these artifacts can be avoided in future. The relative abundance of potential sampling artifacts is in general low (median < 5 %), except for sea-salt particles sampled by the Ice-CVI with a median of 10 % (Fig. 7).

Despite the frequent non-parallel sampling, the major INP/IPR classes found by all three techniques include silicates, Ca-rich particles, carbonaceous material, and metal oxides. In addition, soot was observed as minor component in the fine fraction (< 1  $\mu\text{m}$  diameter) by all methods. These observations are also in general agreement with previous work (see above).

In contrast, in the fine fraction a considerably higher relative abundance of carbonaceous material was found by ISI and a higher relative abundance of silicates and silicate mixtures by Ice-CVI. These differences are most likely caused by the non-parallel sampling. It must be emphasized again that samples from the ISI were only obtained during the last week of the field campaign (Fig. 1).

#### 4.4 Comparison between scanning electron microscopy and laser ablation mass spectrometry

The results of offline analysis (energy-dispersive X-ray microanalysis in the scanning electron microscope, SEM-EDX) of the collected INP/IPR particles can be compared to the findings of online laser ablation mass spectrometry (LA-MS). Unfortunately, both techniques could not be run in parallel because of the limited available sample flow that could be provided by the sampling systems. Due to the low INP/IPR concentrations, it was necessary to integrate all available data, which may lead to systematic errors due to significant variations in the IPR chemical composition as function of changing air masses and meteorological conditions. Furthermore, for a comparison between SEM-EDX and LA-MS a more general particle classification scheme, combining the detailed SEM-EDX classes, was necessary.

The average particle class number abundance, derived by SEM-EDX – separately for all IPR from the ISI and Ice-CVI – is compared in Fig. 10 to the results of the LA-MS (Schmidt et al., 2014). The most obvious difference between the two analysis techniques is the presence of 10–18 % of secondary particles (mostly mixtures of sulfates/nitrates and/or organics), pure sulfates and droplets (residuals of volatile species like nitrates and organics) in SEM-EDX. These classes are completely absent in LA-MS. This difference can be explained by the fact that due to technical issues anions were not measured by LA-MS during the present campaign. Without the detection of anions, sulfate and nitrate cannot be identified by LA-MS, such that these particles are classified according to their dominant cations and are assigned to one of the listed particle groups.

For the other classes, a fair agreement of the results is obtained. First, the sum of mineral dust, sea-salt, carbonaceous material and soot (red and green colors in Fig. 10) contributes 70–90 % to the IPR. Second, metal oxides (based on SEM-EDX: mainly iron oxides) occur at an abundance of 5–10 %. Third, Ice-CVI samples contain Pb-rich particles (5–10 %), while these particles are absent in the ISI. These results do not change considerably, if for SEM-EDX the particles outside the LA-MS size range (> 1.5 µm diameter) are neglected.

However, pronounced discrepancies exist between SEM-EDX and LA-MS data, in particular for Ice-CVI. For this sampling technique, a lower abundance of carbonaceous material is found by SEM-EDX, and a higher abundance of silicates. This quantitative comparison of compositional data from both analysis techniques is hampered by the different approach in particle characterization. The particle classification with SEM-EDX relies on the characteristic X-ray signals, which can be used to quantify the chemical composition of a particle. Our classification scheme uses mainly the major elements (i.e., relative contribution excluding oxygen larger than 10 atom %) detected inside a particle to assign it to an according group. Minor elements (less than approximately 10 atom %) are mostly neglected in particle classification. Trace elements (less than 0.5 atom %) cannot be measured at all. In contrast, single particle LA-MS relies on ionized compounds, so ionization efficiency plays a major role. Thus, strong signals often originate from the atoms or molecules, which can be ionized best in LA-MS, but are not necessarily a major component of the particle. While LA-MS works usually well for externally mixed particles, problems can arise for the classification of internally mixed particles. In our particular case, it cannot be excluded that, for example, a silicate particle with a thin organic coating is classified as silicate in SEM-EDX (based on Si as major element), but as carbonaceous particle in LA-MS (based on a strong signal of ionized carbonaceous matter). This example clearly demonstrates the need for further systematical comparison between these two analytical techniques.

## 5 Summary and conclusions

For the first time, the chemical composition of individual INP/IPR collected by three techniques – ISI, FINCH+IN-PCVI and Ice-CVI – was analyzed in a field experiment. In winter, the INP/IPR composition at the Jungfraujoch station is composed of five main classes: the dominating terrigenous silicates/Ca-rich particles, carbonaceous particles, metal oxides/hydroxides (Fe-, Ti, or Al-oxides/hydroxides), soot, and soluble particles like sea-salt, sulfates and droplets. However, the latter class of soluble particles was considered as potential sampling artifacts. Lead inclusions occur in several INP/IPR, while large homogeneous Pb-rich particles are considered partially as artifacts. The composition is generally similar to earlier field experiments. Despite the non-parallel sampling the methods agree roughly regarding major and minor components. Thus, we consider this experiment as a successful step in improving the accuracy of measuring the INP/IPR chemical composition.

For all three INP/IPR separation techniques, different contamination artifacts and potential sampling artifacts were identified. These artifacts are easily detectable by the chemical and morphological analysis. In contrast, counting or size distribution techniques would consider these contamination and sampling artifacts as real INP/IPR and, consequently, overestimate the INP/IPR concentration. Thus, the present work provides information suitable for correction of counting techniques, for the contamination artifacts as well as for sampling artifacts. While for the former

correction is necessary, interpretation of the latter might change with advancing knowledge regarding the INP/IPR abilities of soluble compounds.

Deeper data investigation reveals that beyond the agreement in maximum of the INP/IPR size distribution there are considerable differences between the instruments pointing to different efficiencies in INP activation and IPR separation. This is particularly obvious when we consider the large difference in internally-mixed particle abundance. While a part of these discrepancies might be explained by atmospheric variability in connection with non-parallel sampling (an issue, which is expected to be overcome in future experiments by increased stability in instrument operation), they also indicate lack in understanding regarding the chemical selectivity of the different INP/IPR-discriminating techniques.

Finally, a few statements regarding limitations of the investigated techniques as well as recommendations for future work on INP/IPR can be made:

a) Measurements of INP/IPR concentrations should be always accompanied by characterization of the INP/IPR chemistry to avoid strong contributions of instrumental artifacts. Although different techniques are in principle possible, scanning electron microscopy with high resolution instruments has proven to be especially suited for this purpose.

b) More work is needed to clarify the ice nucleation ability of sea salt and sulfates in mixed phase clouds.

c) More emphasis should be placed on the particle mixing state in the atmosphere. Due to its complexity, laboratory tests on the performance of the different INP/IPR sampling techniques may lead to overconfidence in the results of field measurements.

d) Substantial work is still necessary to develop the here presented approaches of INP/IPR sampling to robust routine techniques.

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**Table 1: Techniques and operation principles used for ice-nucleating particle (INP) and ice particle residual (IPR) differentiation.**

INP/IPR-separating technique	Principle of operation	Mode of operation	Ice nucleation location	Separated particle type	Freezing mechanisms	Size fraction of sampled ice hydrometeors
Fast Ice Nucleus Chamber (FINCH) + Ice Nuclei pumped Counterflow Virtual Impactor (IN-PCVI)	activation of INP under suitable thermodynamic conditions, separation of INP by inertia	in-cloud and out of cloud, continuous in periods	instrument	INP	deposition, condensation, immersion	not applicable
Ice-Counterflow Virtual Impactor (Ice-CVI)	removal of supercooled droplets, transmission of ice particles	in-cloud, continuous	atmosphere	IPR	deposition, condensation, immersion, contact	$5\ \mu\text{m} < d < 20\ \mu\text{m}$
Ice Selective Inlet (ISI)	use of Bergeron-Findeisen process to evaporate supercooled droplets, separation of ice crystals by inertia	in-cloud, continuous	atmosphere	IPR	deposition, condensation, immersion, contact	$4.9\ \mu\text{m} < d < 20\ \mu\text{m}$

**Table 2: Classification criteria for particle classes and particle groups. Common features for certain particle types not used for classification are given in parentheses.**

<i>Class</i>	<i>Group</i>	<i>Major elements</i>	<i>Morphology</i>	<i>Mixing state<sup>a</sup></i>	<i>Beam stability</i>
Carbonaceous <sup>b</sup>	Carbonaceous	C	non-soot	no inclusion	
	Carbonaceous + inclusion	C	non-soot	inclusion	
Secondary	Secondary	C, O, S			
Sulfate	Sulfate	S, O, (Na, K)		no residual	unstable
	Sulfate + inclusion	S, O, (Na, K)		residual	unstable
Soot	Soot	C	soot-like	no coating	
	Soot mixture	C	soot-like	coating	
Sea-salt	Sea-salt	Na, Cl, (K, Mg)		no inclusion	
	Sea-salt + inclusion	Na, Cl, (K, Mg)		inclusion	
Ca-rich	Ca-rich	Ca, O, (Mg, S, C)		no inclusion	
	Ca-rich + inclusion	Ca, O, (Mg, S, C)		inclusion	
Metal oxide	Metal oxide	Fe, Al, Ti, (Mn)		no coating	
	Metal oxide + coating	Fe, Al, Ti, (Mn)		coating	
Silicate	Silicate	Si, Al, (K, Ca, Mg, Fe, Ti)		no coating	
	Silicate mixture	Si, Al, (K, Ca, Mg, Fe, Ti)		coating or agglomerates	
Pb-bearing	Pb-bearing	Pb present (also as minor component)			
Droplet	Droplet		particle centered in ring of smaller particles		
Other	other				

<sup>a</sup> Based on detailed SEM observations. Inclusion refers to a small object with different chemical composition inside a particle. Residuals are compounds left after evaporation of a volatile matrix. Coating is a small film on the surface of a particle. Agglomerates are composed of distinguishable objects of similar size.

<sup>b</sup> Carbonaceous particles are interpreted as organic compounds which condensed from the gas phase due to their unspecific morphology and the absence of tracer elements for primary biological particles (i.e. N, P, K).

**Table 3: Number fraction of internally mixed particles in each particle class.**

Particle class	FINCH + IN-PCVI	Ice-CVI	ISI
Silicate	61 %	37 %	59 %
Ca-rich	8 %	9 %	9 %
Metal oxide	67 %	40 %	4 %
Carbonaceous	64 %	29 %	7 %
Soot	14 %	6 %	13 %
Sea-salt	54 %	9 %	10 %
Sulfate	2 %	4 %	0 %

**Table 4: Average INP/IPR composition encountered in mixed-phase clouds for several field experiments.**

Location	Particle type	Reference	Terrigenous <sup>a</sup>	Carbonaceous <sup>b</sup>	Salts	Others
Alaska/Arctic	INP	Prenni et al. (2009a)	64 %	35 %	IM <sup>c</sup>	
Northern Scandinavia	IPR	Targino et al. (2006)	58 %	23 %	7 %	12 %
Jungfraujoch	IPR	Kamphus et al. (2010)	57 %	25 % <sup>c</sup>	IM <sup>c</sup>	15 %
Jungfraujoch	IPR	Ebert et al. (2011) <sup>d</sup>	40 %	43 %	12 %	5 %
Jungfraujoch	INP+IPR	this study <sup>d</sup>	71 %	21 %	5 %	3 %
Jungfraujoch	INP+IPR	this study <sup>e</sup>	55 %	16 %	27 %	2 %

<sup>a</sup> containing internal mixtures of terrigenous materials with sulfate and organics

<sup>b</sup> containing also sulfate

<sup>c</sup> IM = present in internal mixtures only

<sup>d</sup> excluding droplets and sulfate; Pb-bearing particles classified according to major particle composition

<sup>e</sup> including droplets and sulfate; Pb-bearing particles classified according to major particle composition

## Figure Captions

Fig. 1: Atmospheric **and FINCH operating** conditions and INP/IPR sampling periods in February 2013. Times are given in UTC. Particle number concentrations were taken from the World Data Centre for Aerosols homepage (WDCA, 2014). Temperature and wind direction were provided by the Jungfraujoch station operated by International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat. Cloud presence was detected by measuring the liquid water content using a Particulate Volume Monitor (PVM-100, Gerber Scientific, Reston, VA, USA) and a Cloud Droplet Probe (Droplet Measurement Technologies, Boulder, CO, USA). **Sampling phases for SEM are marked by wide, intensely-colored bars; sampling phases for MS are shown as narrower, pale-colored bars. 'A' marks a period used for case comparison.**

Fig. 2: **Secondary electron images and energy-dispersive X-ray spectra of instrumental contamination artifact particles. Characteristic X-ray peaks of elements are labeled.** Elements contained in the sample substrate are given in parentheses.

Fig. 3: **Box plots** of the different **instrumental** contamination artifact particles for each sampling **technique**. Shown are minimum, lower quartile, median, upper quartile, and maximum.

Fig. 4: Relative number abundance (**integrated over** all samples) of different particle groups **as function of sampling technique and particle size**. The total number of analyzed particles is shown above the bars.

Fig. 5: Relative number abundance of different particle groups among INP/IPR for 2 February determined by FINCH+IN-PCVI and Ice-CVI. **The total number of analyzed particles is shown above the bars.**

Fig. 6: Secondary electron images of droplets with their typical morphology of a halo around a residue.



Fig. 7: Box plots of impacted **droplets, (non-droplet) sulfate and sea-salt** abundance for ISI, FINCH+IN-PCVI and Ice-CVI. Shown are the minimum, lower quartile, median, upper quartile, and maximum.

Fig. 8: **Average of all single sample size distributions of major INP/IPR components** for ISI, FINCH+IN-PCVI and Ice-CVI. Particle groups were combined according to potential sources to obtain a sufficient number of particles in each size interval. **Left column: number size distribution in dN/dd. Note that the different size distributions cannot be compared directly due to different instrumental inlet and transmission efficiencies. Right column: relative number abundance. Size intervals with less than 15 particles are not shown.**

Fig. 9: Comparison of the composition/mixing state of Pb-bearing particles from INUIT **(present contribution)** and CLACE 5 **(Ebert et al., 2011)** **from the Ice-CVI. Note that classification criteria and nomenclature of Ebert et al. (2011) were used for this graph.**

Fig. 10: Comparison of particle class **relative number** abundance determined by SEM-EDX and LA-MS for IPR sampled by ISI and Ice-CVI. To allow for a comparison of the **two** different analytical approaches of SEM-EDX and LA-MS, classes were combined accordingly.