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°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 ($CaSO_4 \cdot 2H_2O$) 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 µm 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 µm, or even 50 µm, 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 µm whereas Ice-CVI samples >5 µm. 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 µm? 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 µm. 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 µm 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 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 the 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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