We gratefully acknowledge the comments from the anonymous referee 1 and include them in the manuscript. We believe that the changes help to improve the quality of the paper, especially in terms of clarifying our particle groups making the results better readable for a broader community.

> Reviewer comments and questions are printed in this font type.
>
> Our replies are written in Times New Roman.
>
> *Changes in the manuscript text is written in italic, sometimes underlining particular word changes.*

Interactive comment on "Composition of ice particle residuals in mixed phase clouds at Jungfraujoch (Switzerland): Enrichment and depletion of particle groups relative to total aerosol" by Stine Eriksen Hammer et al. Anonymous Referee #1 Received and published: 17 June 2018

Hammer et al. consider the properties of particles within ice crystals, aka ice particle residuals (IPRs), at the Jungfraujoch, a high altitude mountain site in Europe. For this work they use a published ice selective inlet aka 'Ice-CVI', and compare this to the total aerosol via a simultaneous heated inlet sample to provide all, aka 'total', particles. In total, they consider ~4k ICRs over 7 days and in the ~-10 to -20 deg C range (i.e., mixed phase clouds). These particles were deposited on substrates for off-line analysis with electron microscopy (EM). There are several papers over the last decade, many by the groups represented here describing such measurements at the Jungfraujoch so this is not altogether novel. It does represent important data in an area of atmospheric science that is currently in need of more information. My major concern, however, is that the way ice residuals are described seems very simplistic and not of use to the broader atmospheric science community. For example, what is a C-rich particle? How would someone using AMS or a modeler compare this to their understanding of the atmosphere? Since studies of this type have been published, again, many by this group, I believe they here have a responsibility to make the results more comparable, and therefore more useful, to the broader community. I therefore suggest the authors consider the following suggestions and, pending another review, that this paper could be published in ACP.

1. The literature seems to predominantly use the term 'ice residual' (IR) as opposed to IPR. Is there a reason the authors have suggested a new term? Is it different than IR? If so a comprehensive description – and difference from IR - needs to be made. As it reads it seems they are the same so, if there is no difference, could you please remain consistent with the literature term IR so as not to confuse the reader.
   - We now use the term ice residual (IR) in the paper.

2. Page 3 Line 8: The authors seem to suggest water vapour homogeneously nucleates ice at -38 deg C and 140% RH; but that is not correct. One must first have droplets. Please remove 'vapour or' from this sentence.
   - Removed as suggested

3. Page 5 Line 5 & 6: From the intro, the authors ‘assume’ the IPRs are INPs, not ‘consider’. This is a very important distinction. The authors discuss artifacts; thus they themselves show they cannot make the direct association implied by ‘consider’.
   - We changed the sentence according to reviewer II: *“The campaign lasted for five weeks with the aim to investigate IRs from mixed phase clouds which may reflect* <u>*the initial INPs active*</u> *in the cloud.”*

4. Table 1: Most aerosol composition measurements show the presence of sulfate and SOA particles as a dominant, if not the dominant, aerosol, at least by number. Is the ‘complex secondary particles’ this class? This seems to be implied later in the Discussion but is never clearly stated. If so, even if it is an assumption, this needs to be stated for clarity and comparability to the literature. (note: this seems to be suggested on Page 10 but warrants more than 1 line of text).
   - We agree. A new column is added to table 1 to make it easier to understand our classification and particle groups.

Table 1: Classification criteria and possible sources/ explanation for particle groups for both, total aerosol and ice particle residuals.

Group	**Major elements**	**Morphology/ beam stability**	***Source/ particle explanation***
Soot	C	Chain-like or more compact agglomerates of primary particles	*Combustion, black carbon*
C-rich	C	No soot morphology	*Organic aerosol, biomass burning**, biological***
Complex secondary particles	No X-ray spectra or S-peak	Most particles evaporating, some relatively stable	*Sulphur rich secondary organic aerosol, might also contain a substantial fraction of nitrates and other organics*
Aged – sea salt	Na, S (sometimes small amount of Cl and Mg)	Relatively stable	*Marine aerosol, sea spray, might contain organics*
Mixed –sea salt	Na, S (sometimes small amount of Cl and Mg) + mineral composition		*Marine aerosol mixed with mineral particles. Might contain organics.*
Ca-rich	Ca, C, O		*Mineral particles, calcium carbonates e.g. calcite*
Ca-sulphate	Ca, S,O		*Mineral particles, e.g. gypsum and anhydrite*
Silica	Si, O		*Mineral particles, e.g. quartz*
Alumosilicate	Al, Si, O		*Mineral particles, e.g. kaolinite*
Fe- alumosilicate	Al, Si, Fe, O		*Mineral particles, e.g. almandine*
Other-alumosilicates	Variable amounts of Na, K, Ca, Si, Al, O, Ti and Fe		*Mineral particles, e.g. feldspars, illite and smectite (montmorillonite)*
Metal/ metal oxides	Fe, O or Ti, O or Fe, Cr, Mn	Fly ash was detected as spherical particles	*Mineral particles like hematite, magnetite and rutile, or steel particles (alloys)*
Pb-rich	Pb, or Pb, Cl	Single particle or inclusions within particle	*Helicopters and small aircrafts, previously reported at Jungfraujoch*
Other	Particles which do not meet the classification criteria above		
Alumina*	Al, O		*Artefact, Ice-CVI*
Ni-rich*	Ni		*Artefact, Ice-CVI*
Cu-rich*	Cu		*Artefact, particle substrate*
Pure salt*	Na, Cl		*Artefact, hypothesised from secondary ice processes e.g. crystal break-up, marine origin***

**Most likely contamination. **Uncertain origin because the chemical characterisation and/or morphology was not the typical for this particle group.*

5. Similarly, biomass burning particles are often noted as being of abundance just below sulfates and SOA. Is this the C-rich class here? If so please state this. I stress here: while the authors are reporting what they observe with their EM technique, they also need to make it clear their classes relate to common particles types if they wish to publish in a journal such as ACP. Please make these comparisons.
   - See new table 1 (same as comment 4)

6. Similarly, what are Ca-rich particles? The discussion seems to suggest they are mineral dust? How are these associated with any common aerosol type?
   - See new table 1 (same as comment 4)

7. The authors discuss observations of biological IRs in the introduction. These don't appear on Table 1 or Figures 4 or 5. Are they not observed or is there an instrumental reason they can't be detected? Are they a subset of the C-rich category? This needs to be stated clearly in the paper, especially in Figure 5, as it goes directly to comparison to the literature on ice residual composition and in the location where Table 1 is described.
   - Primary biological particles are normally classified based on chemistry (C, O and tracer elements i.e., N, P, K) and morphology. We do not see the normal identification specifics in the C-rich group, but still, we cannot exclude that particles in this group might be of biological origin. We therefore added biological particles as a possible explanation of the C-rich group in the new table 1.

8. Page 7, Line 6. Please remove 'Unfortunately, only'. Data are what was collected.
   - Removed as suggested.

9. Sample S-2b looks rather like a local combustion event. This seems to be implied later in the discussion. If it is please state at the location of the Figure for clarity to the reader.
   - We state now that this is a combustion event in the figure caption.
     We changed figure caption to: *"Relative number abundance of the different particle groups within total aerosol samples.* <u>*Sample S-2b shows a combustion event with air mass history form the Po Valley, and sample S-5b is influenced by an analytical artefact from particle loss of volatile particles."*</u>

10. Given this, could you please present figure S2 at this location – move it into the main paper from the supplement - for the samples to give the origin some context? It is mentioned in the text in the discussion but really needs to be given at this location.
    - We moved Figure S2 to the main paper as suggested.

11. Sample S-5b looks rather like a mixed mineral and perhaps combustion event. Is this so? It again does not look like a clean troposphere. Is this so? If it is please state at the location of the Figure for clarity to the reader. Please also see last comment re: back-trajectories.
    - This sample cannot be explained by back-trajectories, but an analytical artefact from particle loss. We changed the figure caption to (same as comment 9): *Relative number abundance of the different particle groups within total aerosol samples. <u>Sample S-2b shows a combustion event with air mass history form the Po Valley, and sample S-5b is influenced by an analytical artefact from particle loss of volatile particles.</u>*

12. I am confused with Section 4.1, 'Methodological Problems'. I believe this all needs to do in the Experimental section (2), not held until after the data is presented. First, Figure S5 seems to indicate that most of the collected particles are artefact. Is this the case? If so please state the percentage in the Artefact section. Second the reader goes through the results but only after they are presented learns there are issues with the inlet and perhaps the EM data which appear to outnumber the real data by several factors. This is not a logical order. This all needs to be clearly stated and placed in Section 2, not held to Section 4.
    - We moved this section to methodology and added the following sentences to the start of the paragraph to make the contribution of artefacts clearer: "*<u>The IR samples are heavily loaded with artefacts (40-78% of the particles – alumina, Ni-rich and pure salt) easily characterised and removed in further analysis. The Cu-rich particles are a part of the substrates and can in principle be found in both IR samples and total aerosol samples.</u>*"

We gratefully acknowledge the comments from the anonymous referee 2 and included them in the revised manuscript. We believe that the changes help to improve the quality of the paper considerably.

Reviewer comments and questions are printed in this font type.

Our replies are written in Times New Roman.

Changes in the manuscript text is written in italic, <u>underlining particular word changes.</u>

Interactive comment on "Composition of ice particle residuals in mixed phase clouds at Jungfraujoch (Switzerland): Enrichment and depletion of particle groups relative to total aerosol" by Stine Eriksen Hammer et al. Anonymous Referee #2 Received and published: 9 July 2018

<u>General Comments</u>:

This paper discusses the most recent evaluation of the composition of ice crystal residues as measured by an ice-selective counterflow virtual impactor inlet (CVI) at the Jungfraujoch experiment station. The broader community is surely interested in this work, in general and to understand if all measurement artifacts have been solved to the point that a consistent and informative data set can be collected regarding the source of ice nucleating particles and other information on microphysical processes in winter clouds at this site. The short answer based on this paper is that, while some issues have been resolved, this remains a work in progress. While a potentially useful paper, this one could have used stronger editing prior to submission. The overall organization is generally good, but the discussion bounces around such that the various facts are not subjected to a structured discussion. As for specific critical revisions needed, a vital one is to bring forward the fact that a major measurement artefact remains unresolved, that of Al in many particles. I saw no clear discussion of the potential source for this contamination. Otherwise, I appreciated the attempt to categorize electron microscopy microprobe data, although I stumbled on the categorization of "sea salt", by which was meant an assortment of possibilities. This pointed to a general need to be more descriptive about the categorizations and how artefacts were defined in comparison to specific sources. With revision, this paper will become acceptable for publication, although it remains another step in the direction of attempts to extract information on ice nucleation processes through inspection of ice particles residuals. Specific questions/comments for potentially addressing are listed below.

Specific Comments:

Abstract: A few details here should be clarified.

I have no idea what a multi MINI impactor is, but it certainly does not need listing in the abstract. Just the basic technique should be stated.

- A multi MINI impactor is a particle sampler with the possibility to sample on two different substrates at the same time with different particle cut off size, and to change sample without opening the impactor (for up to 12 samples) (Ebert et al., 2016). We agree that only the basic technique should be stated and will change the sentence to: *“Particles were sampled behind an ice selective counterflow impactor (Ice-CVI) for IRs and a heated total inlet for the total aerosol particles.”*

It is not clear how a dilution setup allows for matching a total aerosol sample to the Ice-CVI sample. Can this be explained in plain language? Perhaps, “A dilution system was used to collect total particles at a similar rate to Ice-CVI particle collections”, although I do not know how that is managed, and it seems that it failed about 50.

- The dilution factor is set before sampling and does not vary with the real time INP concentrations, and will hence not lead to matching the exact number of particles. The dilution is in use to be able to have a particle load on the substrate which allows for individual particle analysis. We changed the sentence to: *“A dilution setup was used to collect total particles with the same sampling duration as for IRs to prevent overloading of the substrates.”*
- We changed the 2.1. “Sampling” section to contain a subsection of total aerosol sampling (ref. comment Page 3, paragraph 2).

State temperatures as “local” or “site”. These are not necessarily the cloud activation temperatures.

- Changed as suggested: “*Temperature at the site*”.
- We agree that the reported temperature is not necessarily the cloud activation temperature as we write in the discussion. Referring to a later comment, Page 18, lines 14-15: This statement regarding the association of sampling temperatures with actual ice nucleation temperatures should preface measurements in the discussion of methods. The statement is now moved to the method section. “*Temperatures was measured at the station, and can differ to the onset ice nucleation temperature of the particles depending on where in the mixed phase cloud nucleation occurred”.*

“Approximately 3000 total aerosol particles from five days in clouds were also analysed.” Is this referring to IPRs or to interstitial particles, or to all non-ice particles?

- 3000 total aerosol particles is referring to all particles, IRs and interstitial particles. We have now written: *“Approximately 3000 total aerosol particles (IRs and interstitial particles) from five days in clouds were also analysed.”*

Introduction:

Page 3, line 8 – Spontaneous freezing of supersaturated vapour? In the Earth's atmosphere? I have not seen such a statement in the literature in some time. Remove unless you can support the feasibility of any process other than homogeneous freezing, not "homogeneous ice nucleation".

- Changed according to reviewer 1: removed "*vapour or*".

Page 3, lines 12 to 15 – Add "hypothesized" to modes. The last sentence is repetitive with regard to mixed-phase temperatures where heterogeneous nucleation is the source of ice initiation.

- Changed accordingly: *"Heterogeneous ice nucleation can occur in different hypothesized modes; (1) deposition nucleation, (2) immersion freezing, (3) contact freezing and (4) condensation freezing. A detailed description of the different modes are found elsewhere (Vali et al., 2015; Kanji et al., 2017).*
- Changed the last sentence to: *"Mixed phase cloud temperature range between -40°C and 0°C (Storelvmo, 2017), with immersion and contact freezing as the dominating ice formation modes (Lohmann and Diehl, 2006)."*

Page 3, paragraph 2 – The need for this thesis-type material is questionable. I suggest to revise and reduce or even omit most of this and get straight to the point, which seems to be that information on the relevance and importance of different ice nucleating particle types has come from laboratory measurement, and these emphasize the importance of mineral dust particles except at very modest cloud supercooling. What this paragraph does not seem to mention are specific studies where activated ice nucleating particles have been studied for composition, not simply tested as single collected types in the laboratory.

- We changed paragraph 3 and 4 in the introduction to:

Ice nucleation ability was studied off-line and on-line in many laboratory and field experiments as well as by modelling (Hoose et al., 2010;Hoose and Möhler, 2012;Kanji et al., 2017), and references therein). Summarised from laboratory studies (Hoose and Möhler, 2012), biological particles seem to dominate the ice activity at higher temperature above -10 °C, whereas mineral dust is found mostly ice active below -10 °C, and organic particles and soot nucleate ice below -30 °C close to homogenous freezing. A model study of mixed phase clouds on a global scale by Hoose et al. (2010) shows that the main component of INPs are mineral dust particles. The findings of field experiments at different locations globally are presented by Kanji et al. (2017) as function of nucleation temperature. In this paper only broadly defined classes are given to characterise the ice nucleation efficiency from INP concentration in different environments. To summarise, biological particles from rural areas dominate at higher temperatures (-5 °C to -20 °C), marine particles from coastal areas show a lower ice activity in the higher temperature range than biological particles (-5 °C to -30 °C). Particles from Arctic and Antarctic locations seem to have relatively high INP abundance between -17 °C and -25 °C, and particles from areas with biomass burning show high INP concentration between -10 °C and -30 °C. Mineral dust rich regions show *particles with the highest ice activity in the range of -10 °C to -40 °C, and these particles seem to be the most ice active component. Exact number concentration are found in Kanji et al. (2017) and references therein. Particle groups determined based on chemical composition in cirrus clouds are reported as sulphates, organics, sea salt, mineral dust or fly ash, metal particles, soot and biological material in the IR fraction (Heintzenberg et al., 1996;Cziczo et al., 2004;Cziczo et al., 2013). Twohy and Poellot (2005) found highest abundance of salts and industrial particles in cirrus, followed by crustal, organic and soot particles. In mixed phase clouds, at the high altitude research station Jungfraujoch in Switzerland, different IR groups were reported to act as ice nuclei. With the use of electron microscopy and looking at the enrichment relative to interstitial aerosol, Ebert et al. (2011) interpreted complex secondary aerosol, Pb-bearing particles, and complex mixtures as ice nuclei. In contrast, Worringen et al. (2015) considered only particle groups as ice nuclei which were found with three different techniques (FINCH + PCVI, Ice-CVI and ISI). These groups included silicates, Ca-rich particles, carbonaceous particles, metal/ metal oxide and soot. Using single particle mass spectrometry, Schmidt et al. (2017) considered all particles observed in the IR fraction as INP (biological, soil dust, minerals, sea salt/ cooking, aged material, engine exhaust, soot, lead-containing, industrial metals, Na- and K-dominated and others). Kamphus et al. (2010) report mineral dust and fly ash (with and without some volatiles), metallic particles and black carbon as the most ice active particles, measured with two different mass spectrometers behind the Ice-CVI. Cozic et al. (2008) investigated black carbon enrichment with two PSAP simultaneously behind the Ice-CVI and a total inlet, and by aerosol mass spectrometry (AMS) and single particle mass spectrometer (measuring particles between 200 nm and 2 µm) behind the Ice- CVI during cloud events. They concluded, based on the enrichment, that black carbon is ice active.*

In-situ cloud measurements of ice particle residuals (IRs) can be done with an aircraft for pure ice clouds, like for cirrus clouds, with the use of a counter flow virtual impactor (CVI) (Ogren et al., 1985;Heintzenberg et al., 1996;Ström and Ohlsson, 1998;Twohy et al., 2003;Froyd et al., 2010;Cziczo and Froyd, 2014;Cziczo et al., 2017), and references therein). In-situ IR sampling in mixed phase cloud requires an extra step to separate ice crystals from droplets and is, therefore, up to now restricted to ground based measurements. A dedicated inlet system (Ice-CVI) was developed by Mertes et al. (2007) to sample freshly produced ice particles in mixed phase clouds and, after sublimating the ice, deliver the residuals (IRs) to connected sampling or analysing instruments. As described in Mertes et al. (2007), a residual particle can be interpreted as their original INP only when sampling small ice crystals. There are three reasons for this size restriction leading to sampling of rather young ice particles. The first reason is that only the small ice particles grows by water vapour diffusion, in contrast, larger ice particles could further grow by riming. Moreover, larger and older ice particles experience impaction scavenging by interstitial particles. Both processes add more aerosol particles to the ice crystal and thus the original INP cannot be identified any more after ice sublimation in the Ice-CVI. Last is a technical reason that larger ice particles would shatter and break-up at the inner surfaces of the Ice-CVI sampling system.

Page 4, line 4: Ogren et al. (1985) is not in the reference list. There is a substantial amount of literature since in which airborne CVIs have focused on ice clouds, and Cziczo, Froyd and colleagues have emphasized some other constraints on ice cloud sampling of IPRs (e.g., a focus on small ice, as done also in this study – line 6 statement, although no indication is given as to why fresh ice is needed). While an aside of sorts, the utility of sampling in mixed-phase clouds for ice nucleation studies using a non-ice-CVI is not reflected here, since the focus is on IPRs. The fact that one gets both IPRs and liquid cloud residuals when sampling in mixed-phase clouds is not necessarily a detriment, and this makes it suitable for ice nucleation measurements and subsequent collection of the activated INPs for compositional analyses (already mentioned in the preceding point). This is alluded to later in mentioning use of a FINCH for a similar purpose.

- See the new version of the paragraph in the comment above.
- We added Ogren et al (1985) to the reference list. Literature regarding characterisation and sample specifics with CVIs are additionally added to the references: *In-situ cloud measurements of ice particle residuals (IRs) can be done with an aircraft for pure ice clouds, like for cirrus clouds, with the use of a counter flow virtual impactor (CVI) (Ogren et al., 1985;Heintzenberg et al., 1996;Ström and Ohlsson, 1998;Twohy et al., 2003;Froyd et al., 2010;Cziczo and Froyd, 2014;Cziczo et al., 2017), and references therein)*
- We added an explanation to why fresh ice is important: *"A dedicated inlet system (Ice-CVI) was developed by Mertes et al. (2007) to sample freshly produced ice particles in mixed phase clouds and, after sublimating the ice, deliver the residuals (IRs) to connected sampling or analysing instruments. As described in Mertes et al. (2007), a residual particle can be interpreted as their original INP only when sampling small ice crystals. There are three reasons for this size restriction leading to sampling of rather young ice particles. First scientific reason is that only the small ice particles grows by water vapour diffusion. Larger ice particles could further grow by riming. Moreover, larger and older ice particles experience impaction scavenging by interstitial particles. Both processes add more aerosol particles to the ice crystal and thus the original INP cannot be identified any more after ice sublimation in the Ice-CVI. Last is a technical reason. Larger ice particles would shatter and break-up at the inner surfaces of the Ice-CVI sampling system."*

- We agree with the reviewer that collection of IRs and liquid cloud residuals are important in other cases. Due to the fact that the number density of supercooled droplets is much higher than of ice particles in a mixed-phase cloud, it is not possible to measure IR properties as long as the sampling is not ice selective.

Page 4, lines 8-10: But then this introduction is followed with these lines, which I could not understand - "Knowledge on particle groups acting as ice nuclei in mixed phase clouds is contradictory. IPRs are the residuals ice crystals formed on real INPs after they have been activated in the environment and the measured ice nucleation efficiency of these IPRs is then considered to be the same as for INPs." I expected the first sentence to be immediately supported. Is this a new paragraph? It is not a good one for sure. Rewrite it to be concise, and get to that point. Is the contradiction mentioned referring only to studies done at Jungfraujoch, or what other studies? Will this study seek to resolve contradictions? What is a "real" INP? I suggest to remove this terminology. I think I understand the last part to mean that the composition of IPRs is considered to be those of INPs that were active at the local temperature of observation.

- We agree with the reviewer. The confusion in this paragraph starts with the wrong use of the word *"contradiction"*. In this study, we think we are able to reach a good match between IR and INP because of our possibility to identify artefacts from the comparison of IR and total particles. As we already write this in the method, this part of the paragraph is now removed.

Experimental:

Page 5, lines 5-6: Please explain or omit the statement ". . .original true INPs." You will simply assume that IPRs represent INPs active at the cloud temperature of observation, correct? Are you trying to infer that other methods will not detect INPs? I think you are trying to say that the residuals reflect INPs that were activated in the cloud. But are you saying that every ice crystal contains an INP? I do not think that can be supported, if for example secondary ice formation processes were active.

- We corrected the sentence to: *"The campaign lasted for five weeks with the aim to investigate IRs from mixed phase clouds which may reflect the initial INPs active in the cloud."*
- Our intention is to sample primary small ice particles, which are freshly produced, but it is also possible to sample small fragments of the same size from secondary ice formation. These fragments could contain no aerosol particle, the INP (by chance), or scavenged particles. We cannot with our technique detect ice particles without a residual, and will therefore only know the chemical composition of the two latter. Sampling of secondary ice can explain part of the artefact particles.

Page 5, line 7: typo, "were" not "where"

- Corrected accordingly

Page 5, lines 9-10: Can you explain the need for dilution of the total aerosol sample a little better? i.e., there would be too many particles if collected for the entire time period?

- We changed the "2.1. Sampling" section to contain a subsection of total aerosol sampling (new section 2.2.) and added a sentence for explanation: *Without this dilution, due to the much higher concentration of total particles, these samples would be overloaded and not suited for single particle analysis."*

  "2.1. Sampling

  In January/February 2017 an extensive field campaign was conducted by INUIT (Ice Nucleation Research Unit funded by the German Research Foundation DFG) at the *high altitude research station Jungfraujoch in Switzerland (3580m asl). The campaign lasted for five weeks with the aim to investigate IRs from mixed phase clouds which are considered as the original true INPs. During mixed phase cloud events, IRs where separated from other cloud constituents like interstitial aerosol particles, supercooled droplets and large ice aggregates by use of the Ice-CVI (Mertes et al., 2007). Total aerosol particles (interstitial particles and IRs) were sampled in parallel. Particles where sampled by the use of multi MINI cascade impactors with the same design as described in Ebert et al. (2016) and Schütze et al. (2017), but with the use of only one stage with a lower 50% cut-off diameter of approximately 0.1 µm (aerodynamic). The multi MINI cascade impactor is equipped with purge flow and 5 min flushing of the system was always performed prior to sampling to avoid carryover of particles from previous samples. The particles were collected on boron substrates to allow detection of light elements including carbon (Choël et al., 2005;Ebert et al., 2016).”*

“2.2. Total aerosol sampling

Total aerosol particles were sampled in parallel to IRs behind a heated inlet (Weingartner et al., 1999) to study IR enrichment and depletion, identify contaminants and characterise the air-masses present. Total aerosol samples were collected with a dilution setup (Fig. 1) to match the longer sampling time (up to 5 hours) of the Ice-CVI. The dilution unit is build up by two valves to control the air stream in and out of the system, making it possible to send air through two filters to dilute the incoming aerosol flow. Without this dilution, due to the much higher concentration of total particles, these samples would be overloaded and not suited for single particle analysis.“

Page 6, lines 18-19: Why are pure salt, alumina, Cu-rich and Ni-rich particles considered as contamination? It would be nice to consolidate this information in one place. In the end, no source is identified or even suggested for the alumina particles assumed as contamination, and I find the fresh salt explanation to be questionable. I gather later that the Al is assumed to come from ice crystals striking the walls of the CVI, despite coating them with Ni, but it is almost incomprehensible how this contamination exceeds that found in any previous study (page 15).

- We added the possible source of the contamination particles in the new table 1 as requested by reviewer 1.
- The Ni-coating of the Ice-CVI was ineffective as we still detect alumina-particles and only a small fraction of Ni-containing particles.
- Higher relative amount of contamination particles than previously found can be explained by different INP concentration, meteorological conditions, as well as particle load on the substrate and the sampling time. As we believe, alumina particles are from the system, these factors will influence the relative abundance of the different particle groups, which makes it difficult to compare to previous results.

We added to page 6 line 17: *"Classification criteria and possible sources are given in table 1"*.

- We changed the sentence (ref. comment. Page 15, line 15-17): *"The relative abundance of alumina particles in IR samples is higher in our campaign compared to two previous campaigns at Jungfraujoch using the same instrumentation but without the Ni coating of the Ice-CVI (Ebert et al., 2011; Worringen et al., 2015). This might be explained by the fact that we only focused on sub-micrometer particles and/ or the difference in meteorology, sample time and particle load all influencing the relative composition of contamination particles."*

Table 1: Classification criteria and possible sources/ explanation for particle groups for both, total aerosol and ice particle residuals.

Group	**Major elements**	**Morphology/ beam stability**	***Source/ particle explanation***
Soot	C	Chain-like or more compact agglomerates of primary particles	*Combustion, black carbon*
C-rich	C	No soot morphology	*Organic aerosol, biomass burning**, biological***
Complex secondary particles	No X-ray spectra or S-peak	Most particles evaporating, some relatively stable	*Sulphur rich secondary organic aerosol, might also contain a substantial fraction of nitrates and other organics*
Aged – sea salt	Na, S (sometimes small amount of Cl and Mg)	Relatively stable	*Marine aerosol, sea spray, might contain organics*
Mixed –sea salt	Na, S (sometimes small amount of Cl and Mg) + mineral composition		*Marine aerosol mixed with mineral particles. Might contain organics.*
Ca-rich	Ca, C, O		*Mineral particles, calcium carbonates e.g. calcite*
Ca-sulphate	Ca, S,O		*Mineral particles, e.g. gypsum and anhydrite*
Silica	Si, O		*Mineral particles, e.g. quartz*
Alumosilicate	Al, Si, O		*Mineral particles, e.g. kaolinite*
Fe- alumosilicate	Al, Si, Fe, O		*Mineral particles, e.g. almandine*
Other-alumosilicates	Variable amounts of Na, K, Ca, Si, Al, O, Ti and Fe		*Mineral particles, e.g. feldspars, illite and smectite (montmorillonite)*
Metal/ metal oxides	Fe, O or Ti, O or Fe, Cr, Mn	Fly ash was detected as spherical particles	*Mineral particles like hematite, magnetite and rutile, or steel particles (alloys)*
Pb-rich	Pb, or Pb, Cl	Single particle or inclusions within particle	*Helicopters and small aircrafts, previously reported at Jungfraujoch*
Other	Particles which do not meet the classification criteria above		
Alumina*	Al, O		*Artefact, Ice-CVI*
Ni-rich*	Ni		*Artefact, Ice-CVI*
Cu-rich*	Cu		*Artefact, particle substrate*
Pure salt*	Na, Cl		*Artefact, hypothesised from secondary ice processes e.g. crystal break-up, marine origin***

*Most likely contamination. **Uncertain origin because the chemical characterisation and/or morphology was not typical for this particle group.

Page 7, line 5: This seems to require a statement that the cloud sampling temperatures were considered as appropriate as the ice crystal formation temperature. Could satellite data say anything about coldest cloud top temperatures at these times? Or do you also assume that the limited ice crystal size range sampled restricts this condition?

- We don't know the ice nucleation temperature, therefore, we can only give the site temperatures.
- We changed the sentence to: *"During seven days, ten Ice-CVI samples were taken in clouds at the site temperatures between -10 and -18°C. Sampling day, time and site temperatures are presented in Fig.2, and as table in the electronic supplement (table S1)".*
- We moved this sentence about site temperature to the method section (Ref. comment Page 18, lines 14-15) *"Temperatures was measured at the station, and can differ to the onset ice nucleation temperature of the particles depending on where in the mixed phase cloud nucleation occurred".*

Results:

Page 12: A general comment - it might be nice to show both a representative particle image and elemental spectra for each of the different particle composition categories. This could go in the supplement in addition to the single example given.

- We added particle examples to the supplement (see the supplement section below the comments).

Page 12: General comment 2 – It is only if one goes immediately to look at Fig. S5 at this point that one realizes that the vast majority of particles were categorized as artifacts. Surely this needs to be mentioned upfront. Greater that 50.

- We moved the artefact discussion to methods and added the relative amount of alumina particles accordingly to reviewer 1. We added the following sentences at the beginning of the paragraph: "*The IR samples are heavily loaded with artefacts (40-78% of the particles – alumina, Ni-rich and pure salt) easily characterised and removed in further analysis. The Cu-rich particles are a part of the substrates and can in principle be found in both IR samples and total aerosol samples".*

Page 12, line 7: I wonder if in the basic analysis performed if a mineral particle could be distinguished as being from desert or from other soils? I assume this would remain unresolved, since the soil particle could have multiple potential actual ice nucleation sources, including trace organics.

- Indeed an interesting question, but SEM-EDX is not suited for this analysis.

Page 12, line 10: When the authors say "sea salt", what is meant? Is it only NaCl, or does this refer to aerosols of sea spray origin, with a more complex mixing state? There are only two categories, aged and (aged-) mixed, and by mixed are also included mixtures with other aerosols such as minerals. This makes attribution specifically to "sea salt" nebulous, and yet statements are subsequently made in the results about the ice activity of "sea salt". This is problematic.

- We agree with the reviewer and changed the name of these particles to *sea salt-containing particles* – as commented later (Page 15, line 1). The particle groups are put together for statistical reasoning, with the assumption that they originate or at least both contain some material from the sea. We cannot say with our method what part of the particles that make them ice active.

Page 12, line 14: I assume that aluminum oxides are omitted from the metal oxide category because of the alumina contamination that is not really discussed?

- This is right. As we added a column to table 1 explaining the origin of the different particle groups, this point should be clear now.

Discussion:

Page 15, line 1: Sea salt is similarly ice active as aluminosilicates? Is it the sea salt, the organic content of marine aerosols, or the particles they are mixed with? Hence my earlier question. Perhaps these should be stated to be sea salt-containing particles, and a statement is needed about how this does not identify the "salt" as the ice nucleating component.

- We cannot identify with our method the main component for ice nucleation, and have to leave this as an open question. The pure salt is not present in the total aerosol samples and are hence regarded as contamination.
- We changed the name of sea salt (aged and mixed sea salt) accordingly to *"sea salt-containing particles*".

Page 15, lines 15-17: A focus on fine particles is mentioned as an explanation for the occurrence of more alumina in this study, apparently from crystals etching this from the CVI walls (nowhere stated clearly). This is the first mention of any different focus in this study. What is meant be a focus on fine particles? Why would there be so much less Ni and so much more Al? Was the coating quickly destroyed? Ineffective? Also on line 15, "but" is misspelled.

- Most IR particles (>90 %) in our study are smaller than 1 µm (equivalent projected area diameter). Worringen et al. 2015 and Ebert et al. 2011 sampled with two stages, and one of them had a larger particle cut off (1 µm). The size distribution in Worringen et al. 2015 showed that one stage sampling is sufficient, and our size distribution is comparable to their size distribution in terms of IRs. One stage of the sampler had a 50 % cut off at 1 µm in the previous studies, which might exclude some of the alumina particles leading to a lower relative abundance of this group.
- Also the meteorology is different to previous campaigns.

- We corrected *"but"* accordingly.
- We rewrote the explanation to: *"The relative abundance of alumina particles in IR samples is higher in our campaign compared to two previous campaigns at Jungfraujoch using the same instrumentation but without the Ni coating of the Ice-CVI (Ebert et al., 2011; Worringen et al., 2015). This might be explained by the fact that we only focused on the sub-micrometer particles and/ or the difference in meteorology, sample time and particle load all influencing the relative composition of contamination particles."*

Page 15, lines 24-26: If pure or "fresh" salt is an artefactual reflection of secondary ice formation contributions, how is this reliably distinguished from sea spray aerosols? Would aging of sea salt always occur for marine particles reaching the site? Relatively unaged marine aerosols are found at other remote locations.

- We agree, we cannot exclude that this is of marine source. We have added marine as possible source in the new table 1.

Page 16, line 12: By "concentration of the total inlet" do you mean the accumulated particle number concentrations sampled from the total particle inlet (after dilution)?

- There were CPCs operating behind the total inlet, interstitial inlet and Ice-CVI during the campaign.
- We changed the sentence to*: "Three of the total aerosol samples (S-3b, S-4b and S-6b) are sampled under conditions where the concentration (measured with condensation particle counters) of the total inlet was lower than the interstitial inlet."*

Page 17, lines 8-10: This might well be the third mention of the sample that was exposed to high vacuum in the electron microscope for too long. Please edit.

- Changed to: *"The high soot and C-rich particle abundance of the first sample may be explained by footprint plots showing that the air-mass had a longer surface residence time over Po Valley (Italy) which is an urban/industrial area with abundant sources of carbonaceous particles. The potential artefact in the second sample does not influence the enrichment factor all other particle groups."*

Page 17, line 23: "section 4.3"

- Changed as suggested

Page 18, lines 14-15: This statement regarding the association of sampling temperatures with actual ice nucleation temperatures should preface measurements in the discussion of methods.

- Moved to method section as suggested.

Page 18, line 21: The reason that the authors believe that the current results are correct in regard to the lack of contribution of complex secondary particles and soot as IPRs (and thus INPs), and why the previous studies erred, should be summarized.

- Changed to: *"Complex secondary aerosol particles and soot were not found in the IR fraction, in contrast to previous work at Jungfraujoch (Cozic et al., 2008a;Ebert et al., 2011;Worringen et al., 2015;Schmidt et al., 2017), even though these groups dominate the total aerosol fraction. Thus, their ice nucleating ability under the conditions of our campaign, can be assumed to be very low. One explanation for this difference might be the higher site temperatures during our campaign."*

Page 18, lines 24-25: This statement regarding the composition of the secondary particle category also belongs in the methods material, which was painfully short in describing the different categories and their justification.

- We fully agree, a more descriptive table can now be found in the new table 1.
- We added a reference to table 1 in the sentence: "*It must be emphasised here that this particle group most likely also consists of a substantial fraction of organics and nitrates (Vester et al., 2007), see table 1.*"

Page 18, line 28: Are the studies herein and those summarized in Knopf et al. (2018) for cloud activation temperatures in the same range?

- Changed to: "*C-rich particles are reported in previous studies of mixed phase clouds at Jungfraujoch (S.Mertes et al. 2007; Cozic et al. 2008; Kamphus et al. 2010; Ebert et al 2011; Worringen et al. 2015; Schmidt et al. 2017). Our results are also in agreement with findings of many cirrus cloud field studies (see recent review by Knopf et al. (2018) and references therein) which show that organic aerosol is found in the IR fraction, but is depleted relative to total aerosol.*"

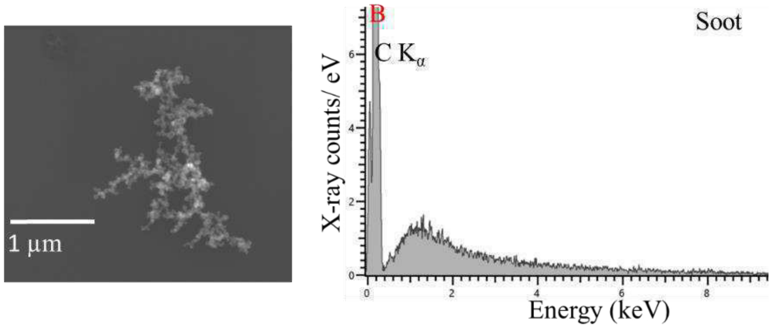
Page 20, first paragraph discussion of "sea salt": This discussion was odd. I could take argument with the authors about the supposedly "controversial" nature of ice nucleation involving marine aerosols overall, but let me focus on lines 6-8. Unless the authors wish to reject clear evidence in the papers mentioned or in papers published since involving specific sampling of sea spray particles (none referenced here), the ice activity is clearly if not definitively associated with contained organics in many instances. It is not really a hypothesis that the salt itself is not the INP, so it is good that the authors will not "exclude" this fact.

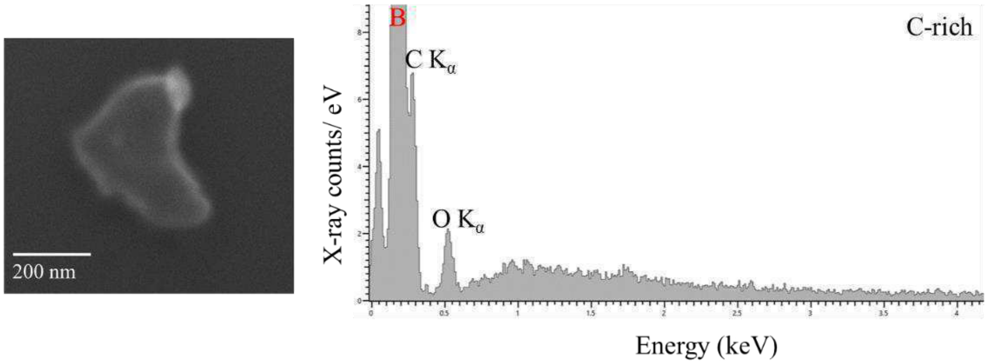
- We agree with the reviewer. Our intention was not to reject the evidence published in papers regarding ice nucleation of sea salt/ sea spray particles. Our intention was only to express that we cannot say with our method where the nucleation occurred.
- We now write: *"Sea salt containing particles may act as an INP due to the presence of organics (Wilson et a. 2015; DeMott et al. 2016; Iwata and Matsuki, 2018). However, we cannot define with our measurement technique where the ice nucleation occur in a particle, i.e. pores or thin coating."*

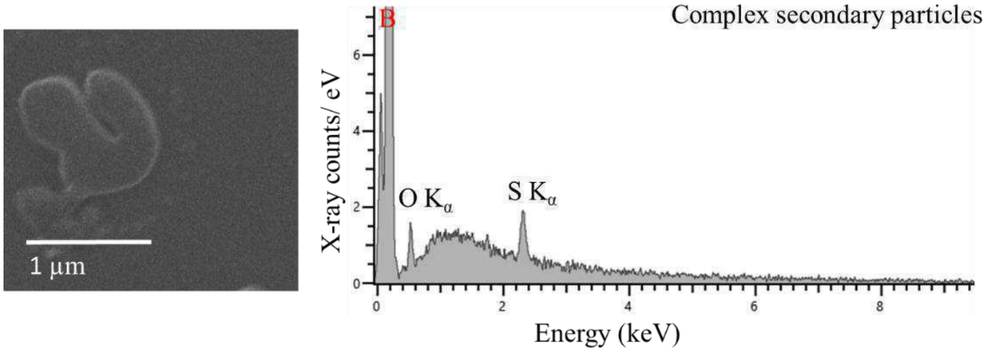
Supplement:

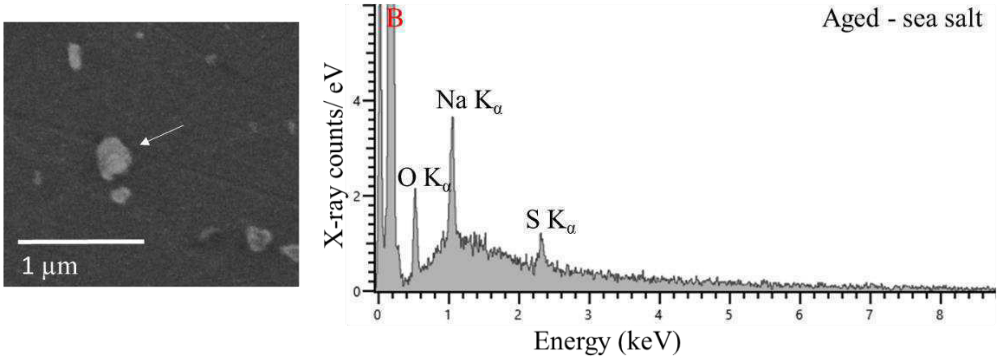
Examples of each particle group

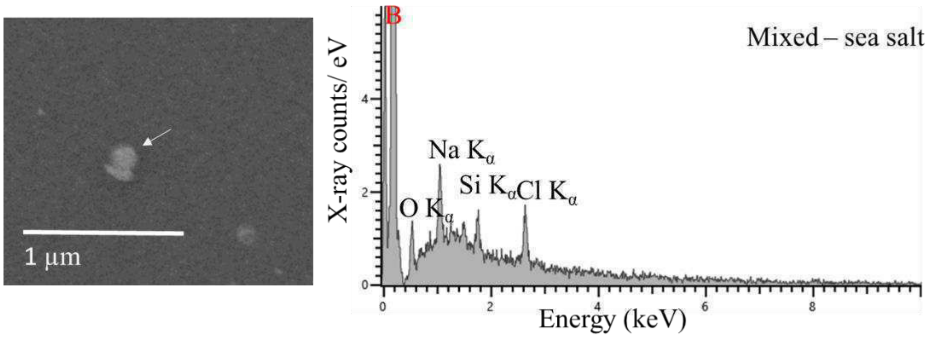
Secondary electron image and corresponding energy dispersive X-ray spectrum for a typical particle of each group are presented under. B indicates the X-ray peak from the boron substrate.

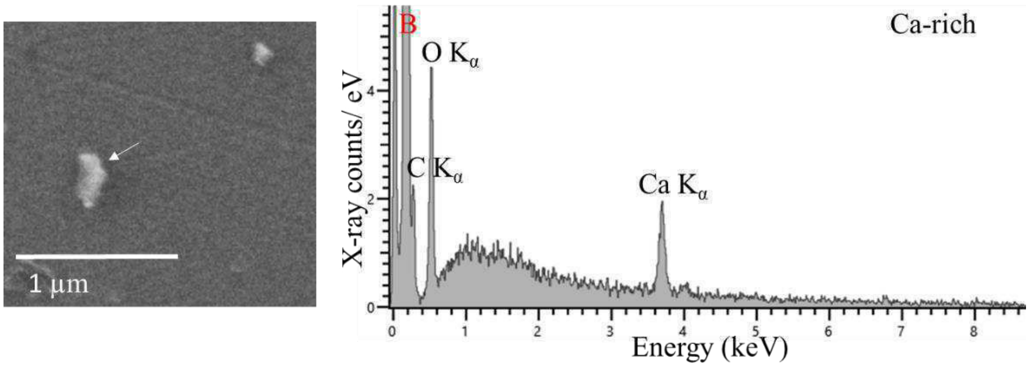


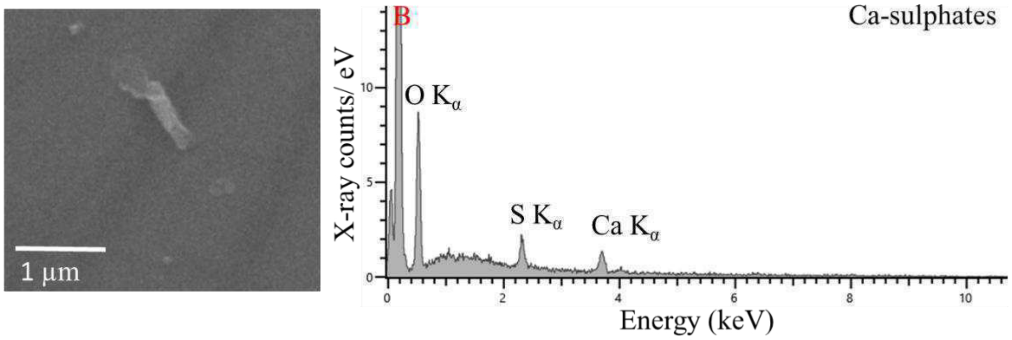


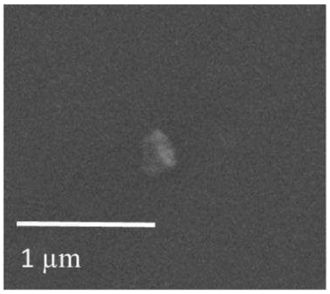


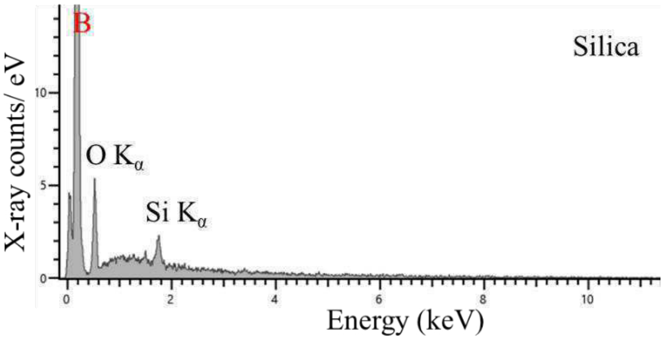

1 μm
B
Aged - sea salt
Na K_α
O K_α
S K_α
X-ray counts/ eV
0
2
4
Energy (keV)
0
1
2
3
4
5
6
7
8

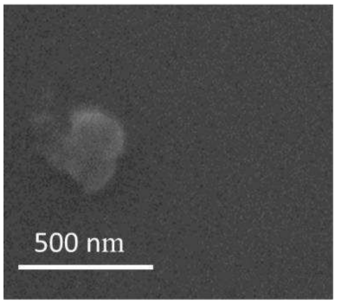

1 μm
B
Mixed – sea salt
Na K_α
Si K_α
Cl K_α
O K_α
X-ray counts/ eV
0
2
4
Energy (keV)
0
2
4
6
8

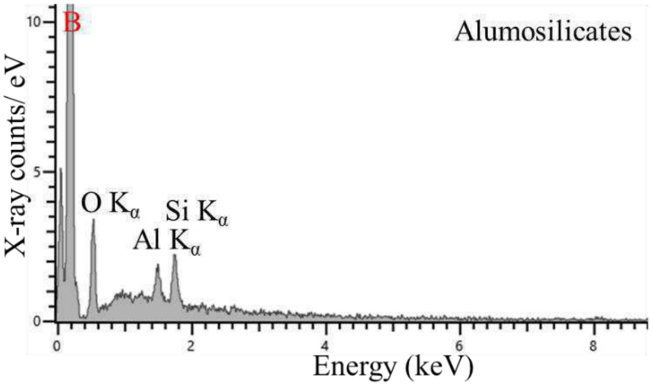

1 μm
B
Ca-rich
O K_α
C K_α
Ca K_α
X-ray counts/ eV
0
2
4
Energy (keV)
0
1
2
3
4
5
6
7
8

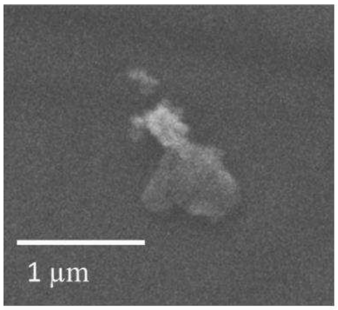

1 μm
B
Ca-sulphates
O K_α
S K_α
Ca K_α
X-ray counts/ eV
0
5
10
Energy (keV)
0
2
4
6
8
10

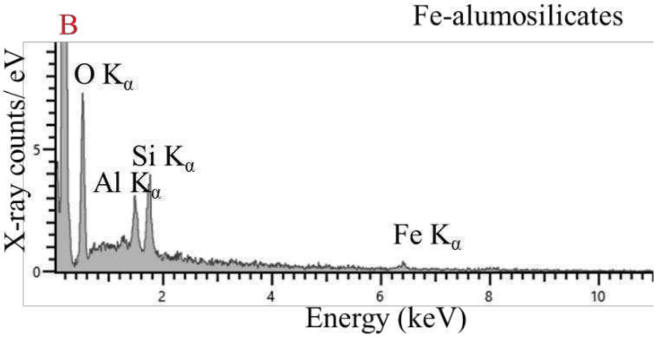

1 μm

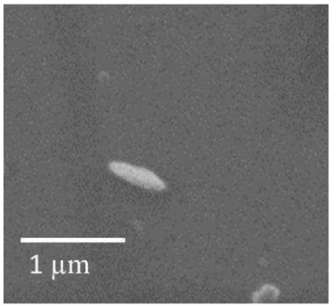

Silica
B
O Kα
Si Kα
X-ray counts/ eV
0
5
10
0
2
4
6
8
10
Energy (keV)

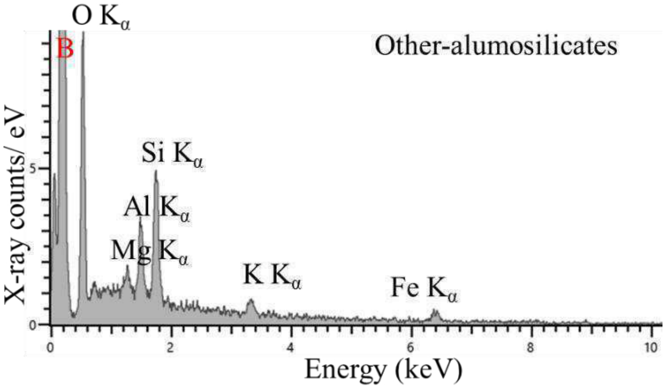

500 nm

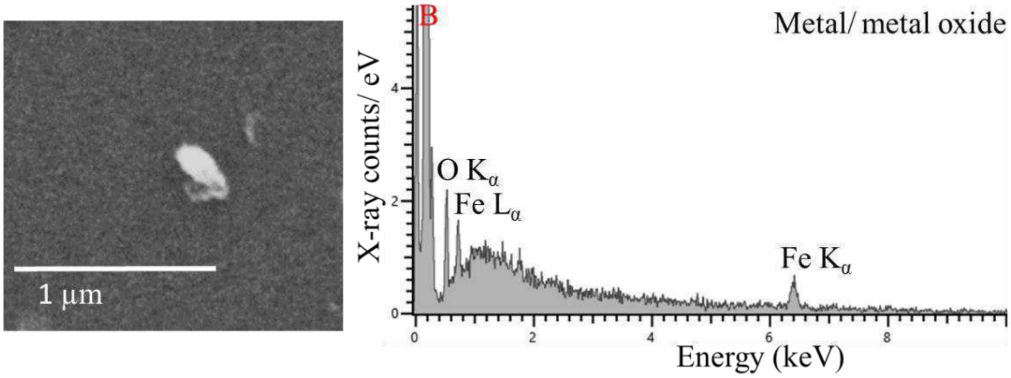

Alumosilicates
B
O Kα
Si Kα
Al Kα
X-ray counts/ eV
0
5
10
0
2
4
6
8
Energy (keV)

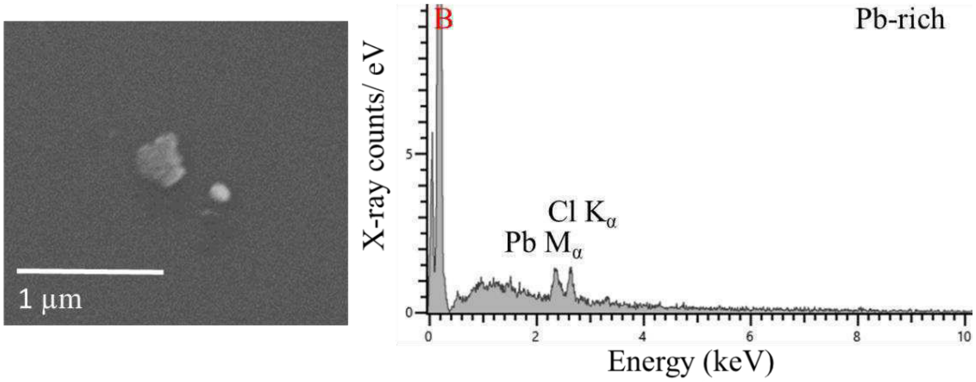

1 μm

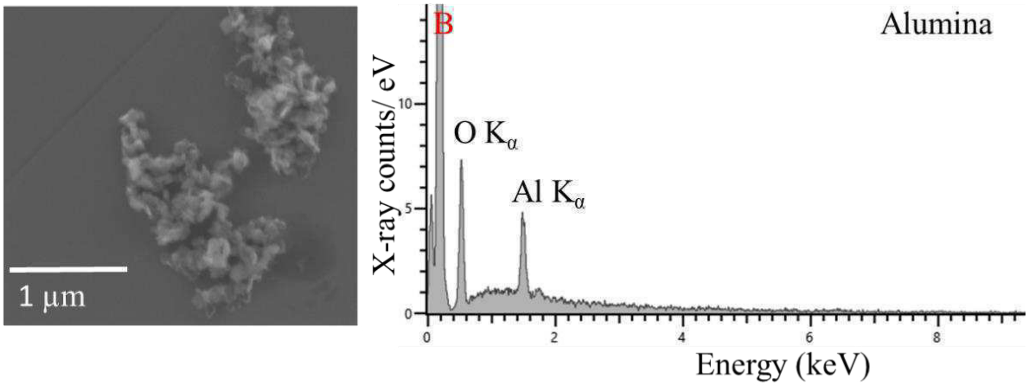

Fe-alumosilicates
B
O Kα
Si Kα
Al Kα
Fe Kα
X-ray counts/ eV
0
5
2
4
6
8
10
Energy (keV)

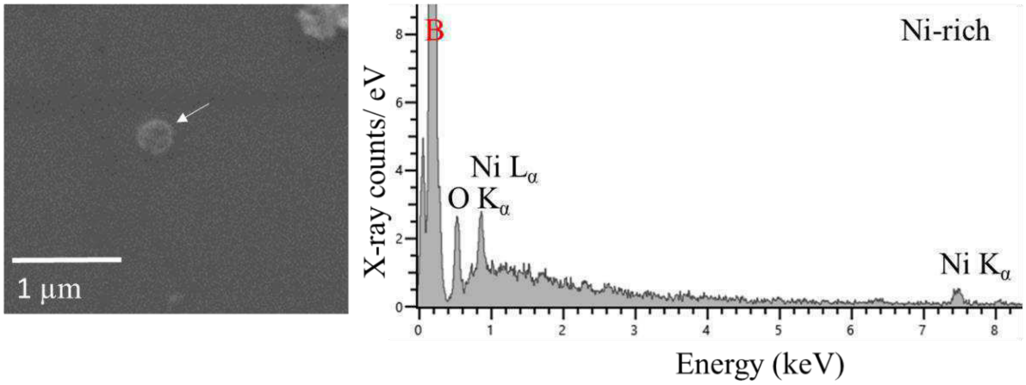

1 μm

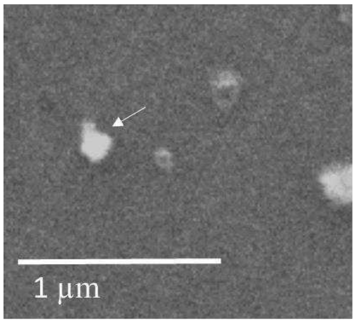

O Kα
B
Other-alumosilicates
Si Kα
Al Kα
Mg Kα
K Kα
Fe Kα
X-ray counts/ eV
0
5
0
2
4
6
8
10
Energy (keV)

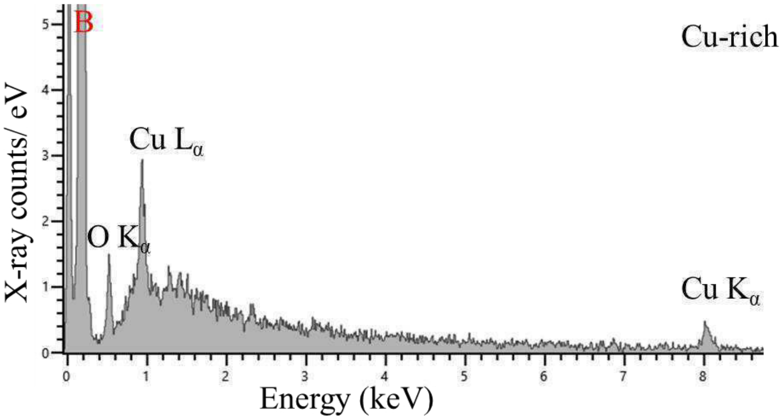

1 μm
B
Metal/ metal oxide
X-ray counts/ eV
O K_α
Fe L_α
Fe K_α
0
2
4
0
2
4
6
8
Energy (keV)


1 μm
B
Pb-rich
X-ray counts/ eV
Cl K_α
Pb M_α
0
5
0
2
4
6
8
10
Energy (keV)


1 μm
B
Alumina
X-ray counts/ eV
O K_α
Al K_α
0
5
10
0
2
4
6
8
Energy (keV)


1 μm
B
Ni-rich
X-ray counts/ eV
Ni L_α
O K_α
Ni K_α
0
2
4
6
8
0
1
2
3
4
5
6
7
8
Energy (keV)


1 μm


B
Cu-rich
Cu L_α
O K_α
Cu K_α
X-ray counts/ eV
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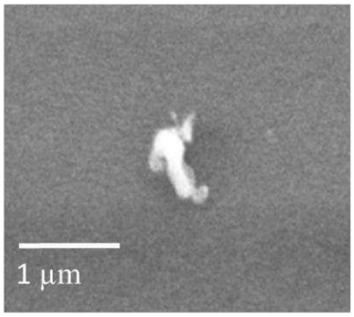
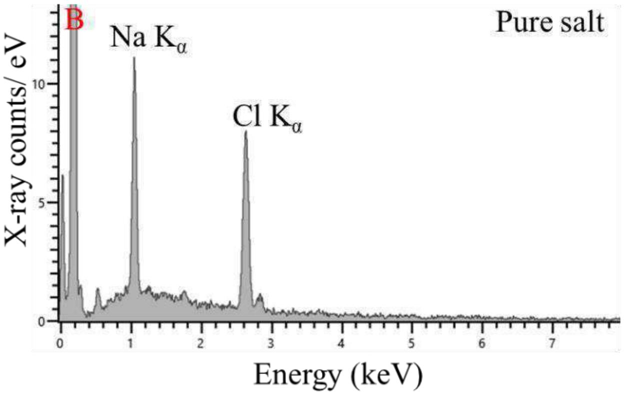
1
2
3
4
5
0
1
2
3
4
5
6
7
8
Energy (keV)


1 μm


B
Pure salt
Na K_α
Cl K_α
X-ray counts/ eV
0
5
10
0
1
2
3
4
5
6
7
Energy (keV)

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Composition of ice particle residuals in mixed phase clouds at Jungfraujoch (Switzerland): Enrichment and depletion of particle groups relative to total aerosol

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Abstract

Ice particle residuals (IRs) and the total aerosol particle population were sampled in parallel during mixed phase cloud events at the high altitude research station Jungfraujoch in January/February 2017. Particles were sampled behind an ice selective counterflow impactor (Ice-CVI) for IRs and a heated total inlet for the total aerosol particles. A dilution setup was used to collect total particles with the same sampling duration as for IRs to prevent overloading of the substrates. About 4000 particles from ten Ice-CVI samples (from seven days of cloud events at temperatures at the site between -10 °C and -18°C) were analysed and classified with operator controlled scanning electron microscopy. Contamination particles (identified by their chemical composition) most likely originating from abrasion in the Ice-CVI and collection of secondary ice, were excluded from the further analysis. Approximately 3000 total aerosol particles (IRs and interstitial particles) from five days in clouds were also analysed. Enrichment and depletion of the different particle groups (within the IR fraction relative to total aerosol reservoir) are presented as odds ratio relative to alumosilicate (particles only consisting of Al, Si and O), which was chosen as reference due to the large enrichment of this group relative to total aerosol and the relatively high number concentration of this group in both total aerosol and the IR samples. Complex secondary particles and soot are the major particle groups in the total aerosol samples, but are not found in the IR fraction and are hence strongly depleted. C-rich particles (most likely organic particles) showed a smaller enrichment compared to alumosilicates by a factor of ~20. The particle groups with similar enrichment as alumosilicate are silica, Fe-alumosilicates, Ca-rich, Ca-sulphates, sea salt-containing particles and metal/ metal oxide. Other-alumosilicates – consisting of variable amounts of Na, K, Ca, Si, Al, O, Ti and Fe- are somewhat more (factor ~2) and Pb-rich more (factor ~8) enriched than alumosilicates. None of the sampled IR groups showed a temperature or size dependence in respect to ice activity, which might be due to the limited sampling temperature interval and the similar size of the particles. Footprint plots and wind roses could explain the different total aerosol composition in one sample (carbonaceous particle emission from the urban/industrial area of Po Valley), but this did not affect the IR composition. Taken into account the relative abundance of the particle groups in total aerosol and the ice nucleation ability, we found that silica, alumosilicates and other-alumosilicates were the most important ice particle residuals at Jungfraujoch during the mixed phase cloud events in winter 2017.

1. Introduction

Mixed phase clouds are important because they have an impact on the hydrological cycle, cloud electrification, and because they influence the atmospheric radiation balance (Storelvmo, 2017). Ice nucleating particles (INPs) can initiate cloud glaciation which may cause precipitation (Myhre et al., 2013). The order of magnitude of the effect from aerosol-cloud interaction on previously called "second indirect aerosol effect" and "semi-indirect effect" is still uncertain (Myhre et al., 2013;Flato et al., 2013;Korolev et al., 2017).

In nature, spontaneous freezing of supersaturated droplets occurs at temperatures below -38°C and a relative humidity (RH) with respect to ice > ~140 % (Kanji et al., 2017), termed homogeneous ice nucleation (Vali et al., 2015). At higher temperatures, a surface, like a particle surface, can lower the free energy and thereby assist the phase transition to ice when relative humidity allows for this, termed heterogeneous ice nucleation. Heterogeneous ice nucleation can occur in different hypothesized modes; (1) deposition nucleation, (2) immersion freezing, (3) contact freezing and (4) condensation freezing. A detailed description of the different modes are found elsewhere (Vali et al., 2015;Kanji et al., 2017). Mixed phase cloud temperature range between -40°C and 0°C (Storelvmo, 2017), with immersion and contact freezing as the dominating ice formation modes (Lohmann and Diehl, 2006).

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Ice nucleation ability was studied off-line and on-line in many laboratory and field experiments as well as by modelling (Hoose et al., 2010;Hoose and Möhler, 2012;Kanji et al., 2017), and references therein). Summarised from laboratory studies (Hoose and Möhler, 2012), biological particles seem to dominate the ice activity at higher temperature above -10 °C, whereas mineral dust is found mostly ice active below -10 °C, and organic particles and soot nucleate ice below -30 °C close to homogenous freezing. A model study of mixed phase clouds on a global scale by Hoose et al. (2010) shows that the main component of INPs are mineral dust particles. The findings of field experiments at different locations globally are presented by Kanji et al. (2017) as function of nucleation temperature. In this paper only broadly defined classes are given to characterise the ice nucleation efficiency from INP concentration in different environments. To summarise, biological particles from rural areas dominate at higher temperatures (-5 °C to -20 °C), marine particles from coastal areas show a lower ice activity in the higher temperature range than biological particles (-5 °C to -30 °C). Particles from Arctic and Antarctic locations seem to have relatively high INP abundance between -17 °C and -25 °C, and particles from areas with biomass burning show high INP concentration between -10 °C and -30 °C. Mineral dust rich regions show particles with the highest ice activity in the range of -10 °C to -40 °C, and these particles seem to be the most ice active component. Exact number concentration are found in Kanji et al. (2017) and references therein. Particle groups determined based on chemical composition in cirrus clouds are reported as sulphates, organics, sea salt, mineral dust or fly ash, metal particles, soot and biological material in the IR fraction (Heintzenberg et al., 1996;Cziczo et al., 2004;Cziczo et al., 2013). Twohy and Poellot (2005) found highest abundance of salts and industrial particles in cirrus, followed by crustal, organic and soot particles. In mixed phase clouds, at the high altitude research station Jungfraujoch in Switzerland, different IR groups were reported to act as ice nuclei. With the use of electron microscopy and looking at the enrichment relative to interstitial aerosol, Ebert et al. (2011) interpreted complex secondary aerosol, Pb-bearing particles, and complex mixtures as ice nuclei. In contrast, Worringen et al. (2015) considered only particle groups as ice nuclei which were found with three different techniques (FINCH + PCVI, Ice-CVI and ISI). These groups included silicates, Ca-rich particles, carbonaceous particles, metal/ metal oxide and soot. Using single particle mass spectrometry, Schmidt et al. (2017) considered all particles observed in the IR fraction as INP (biological, soil dust, minerals, sea salt/ cooking, aged material, engine exhaust, soot, lead-containing, industrial metals, Na- and K-dominated and others). Kamphus et al. (2010) report mineral dust and fly ash (with and without some volatiles), metallic particles and black carbon as the most ice active particles, measured with two different mass spectrometers behind the Ice-CVI. Cozic et al. (2008a) investigated black carbon enrichment with two PSAP simultaneously behind the Ice-CVI and a total inlet, and by aerosol mass spectrometry (AMS) and single particle mass spectrometer (measuring particles between 200 nm and 2 µm) behind the Ice- CVI during cloud events. They concluded, based on the enrichment, that black carbon is ice active.

In-situ cloud measurements of ice particle residuals (IRs) can be done with an aircraft for pure ice clouds, like for cirrus clouds, with the use of a counter flow virtual impactor (CVI) (Ogren et al., 1985;Heintzenberg et al., 1996;Ström and Ohlsson, 1998;Twohy et al., 2003;Froyd et al., 2010;Cziczo and Froyd, 2014;Cziczo et al., 2017), and references therein). In-situ IR sampling in mixed phase cloud requires an extra step to separate ice crystals from droplets and is, therefore, up to now restricted to ground based measurements. A dedicated inlet system (Ice-CVI) was developed by Mertes et al. (2007) to sample freshly produced ice particles in mixed phase clouds and, after sublimating the ice, deliver the residuals (IRs) to connected sampling or analysing instruments. As described in Mertes et al. (2007), a residual particle can be interpreted as their original INP only when sampling small ice crystals. There are three reasons for this size restriction leading to sampling of rather young ice particles. The first reason is that only the small ice particles grows by water vapour diffusion, in contrast, larger ice particles could further grow by riming. Moreover, larger and older ice particles experience impaction scavenging by interstitial particles. Both processes add more aerosol particles to the ice crystal and thus the original INP cannot be identified any more after ice sublimation in the Ice-CVI. Last is a technical reason that larger ice particles would shatter and break-up at the inner surfaces of the Ice-CVI sampling system.

The major aims of our paper are to improve the sampling approach and to study the variation of IRs in mixed phase clouds. In contrast to previous work (Worringen et al., 2015;Ebert et al., 2011;Kamphus et al., 2010;Schmidt et al., 2017), IR and total aerosol were collected in parallel. This allows us to examine the ice nucleation efficiency of the various particle groups, and to investigate the dependence on temperature, particle size and air mass history.

2. Experimental

2.1. Sampling

In January/February 2017 an extensive field campaign was conducted by INUIT (Ice Nucleation Research Unit funded by the German Research Foundation DFG) at the high altitude research station Jungfraujoch in Switzerland (3580m asl). The campaign lasted for five weeks with the aim to investigate IRs from mixed phase clouds which are considered as the original true INPs. During mixed phase cloud events, IRs where separated from other cloud constituents like interstitial aerosol particles, supercooled droplets and large ice aggregates by use of the Ice-CVI (Mertes et al., 2007). Total aerosol particles (interstitial particles and IRs) were sampled in parallel. Particles where sampled by the use of multi MINI cascade impactors with the same design as described in Ebert et al. (2016) and Schütze et al. (2017), but with the use of only one stage with a lower 50% cut-off diameter of approximately 0.1 µm (aerodynamic). The multi MINI cascade impactor is equipped with purge flow and 5 min flushing of the system was always performed prior to sampling to avoid carryover of particles from previous samples. The particles were collected on boron substrates to allow detection of light elements including carbon (Choël et al., 2005;Ebert et al., 2016).

2.2. Total aerosol sampling

Total aerosol particles were sampled in parallel to IRs behind a heated inlet (Weingartner et al., 1999) to study IR enrichment and depletion, identify contaminants and characterise the air-masses present. Total aerosol samples were collected with a dilution setup (Fig. 1) to match the longer sampling time (up to 5 hours) of the Ice-CVI. The dilution unit is build up by two valves to control the air stream in and out of the system, making it possible to send air through two filters

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In-situ cloud measurements of ice particle residuals (IPRs) can be done with an aircraft for pure ice clouds, like for cirrus clouds, with the use of a counter flow virtual impactor (CVI) (Ogren et al., 1985). In-situ IPR sampling in mixed phase cloud requires an extra step to separate ice crystals from droplets and is, therefore, up to now restricted to ground based measurements. A dedicated inlet system (Ice-CVI) was developed by Mertes et al. (2007) to sample freshly produced ice particles in mixed phase clouds and, after sublimating the ice, deliver the residuals (IPRs) to connected sampling or analysing instruments. Knowledge on particle groups acting as ice nuclei in mixed phase clouds is contradictory. IPRs are the residuals ice crystals formed on real INPs after they have been activated in the environmen ...

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to dilute the incoming aerosol flow. Without this dilution, due to the much higher concentration of total particles, these samples would be overloaded and not suited for single particle analysis.

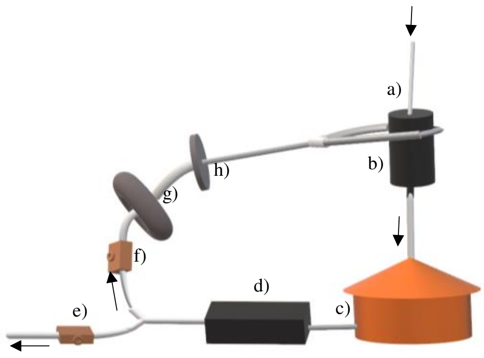

Figure 1: Illustration of the dilution unit behind the heated total inlet. A) An inlet tube attached to the total inlet, b) diluter, c) multi MINI impactor, d) pump, e) valve to control out flow, f) valve to control air going back in the system, g) pre-filter (Whatman, Sigma-Aldrich), h) main filter (Millipore, Sigma-Aldrich). Arrows indicate the air flow direction.

2.3. Ice-CVI

The Ice-CVI is a modified counterflow virtual impactor which can separate freshly formed ice particles in mixed phase clouds, for details see Mertes et al. (2007). The inlet consists of several components to separate: (a) large precipitating ice crystals > 50 µm by the 90° inlet, (b) large ice particles > 20 µm with a virtual impactor, (c) supercooled droplets > 5 µm with two cold impaction plates where the droplets freeze and the ice crystals bounce off, and (d) interstitial particles < 5 µm which are removed by a counter flow virtual impactor.

2.4. Scanning electron microscopy

Size, morphology, chemical composition and mixing state of IRs and total aerosol particles were investigated by scanning electron microscopy using a FEI Quanta 400 ESEM FEG instrument (FEI, Eindhoven, The Netherlands) equipped with an energy-dispersive X-ray detector (Oxford, Oxfordshire, United Kingdom). All analyses were carried out manually, referred to as operator controlled SEM, using an acceleration voltage of 15 kV and a sample chamber pressure around $1x10^{-5}$ mbar. The multipoint feature "point&ID" in the Oxford software Aztec (version 3.3 SP1) was used for the operator controlled single particle analysis. On each sample, about 500 particles were measured with 5 seconds counting time for X-ray microanalysis. To ensure unbiased results all particles in an image frame with an equivalent projected area diameter ≥ 100 nm were investigated. The particles were classified based on chemical composition, mixing state, morphology and stability under the electron beam. Classification criteria and possible sources are given in table 1. Particles that could not be assigned to any of the defined classes were grouped as "other". This group contains for example Mg-rich, Zn-rich and Ag containing particles. Four groups are interpreted as contamination particles: pure salt, alumina, Cu-rich and Ni-rich particles.

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Table 1: Classification criteria and possible sources/ explanation for particle groups for both, total aerosol and ice particle residuals.

Group	**Major elements**	**Morphology/ beam stability**	**Source/ particle explanation**
Soot	C	Chain-like or more compact agglomerates of primary particles	Combustion, black carbon
C-rich	C	No soot morphology	Organic aerosol, biomass burning**, biological**
Complex secondary particles	No X-ray spectra or S-peak	Most particles evaporating, some relatively stable	Sulphur rich secondary organic aerosol, might also contain a substantial fraction of nitrates and other organics
Aged – sea salt	Na, S (sometimes small amount of Cl and Mg)	Relatively stable	Marine aerosol, sea spray, might contain organics
Mixed –sea salt	Na, S (sometimes small amount of Cl and Mg) + mineral composition		Marine aerosol mixed with mineral particles. Might contain organics.
Ca-rich	Ca, C, O		Mineral particles, calcium carbonates e.g. calcite
Ca-sulphate	Ca, S,O		Mineral particles, e.g. gypsum and anhydrite
Silica	Si, O		Mineral particles, e.g. quartz
Alumosilicate	Al, Si, O		Mineral particles, e.g. kaolinite
Fe- alumosilicate	Al, Si, Fe, O		Mineral particles, e.g. almandine
Other-alumosilicates	Variable amounts of Na, K, Ca, Si, Al, O, Ti and Fe		Mineral particles, e.g. feldspars, illite and smectite (montmorillonite)
Metal/ metal oxides	Fe, O or Ti, O or Fe, Cr, Mn	Fly ash was detected as spherical particles	Mineral particles like hematite, magnetite and rutile, or steel particles (alloys)
Pb-rich	Pb, or Pb, Cl	Single particle or inclusions within particle	Helicopters and small aircrafts, previously reported at Jungfraujoch
Other	Particles which do not meet the classification criteria above		
Alumina*	Al, O		Artefact, Ice-CVI
Ni-rich*	Ni		Artefact, Ice-CVI
Cu-rich*	Cu		Artefact, particle substrate
Pure salt*	Na, Cl		Artefact, hypothesised from secondary ice processes e.g. crystal break-up, marine origin**

*Most likely contamination. **Uncertain origin because the chemical characterisation and/or morphology was not typical for this particle group.

2.5. Sampling days, meteorology and footprint plots

During seven days, ten Ice-CVI samples were taken in clouds at the site temperatures between -10 and -18°C. Sampling day, time and site temperatures are presented in Fig.2, and as table in the electronic supplement (table S1). Temperatures was measured at the station, and can differ to the onset ice nucleation temperature of the particles depending on where in the mixed phase cloud nucleation occurred. Six parallel total aerosol samples were successfully collected. The other four total samples are either overloaded or do not have enough particles on the substrate.

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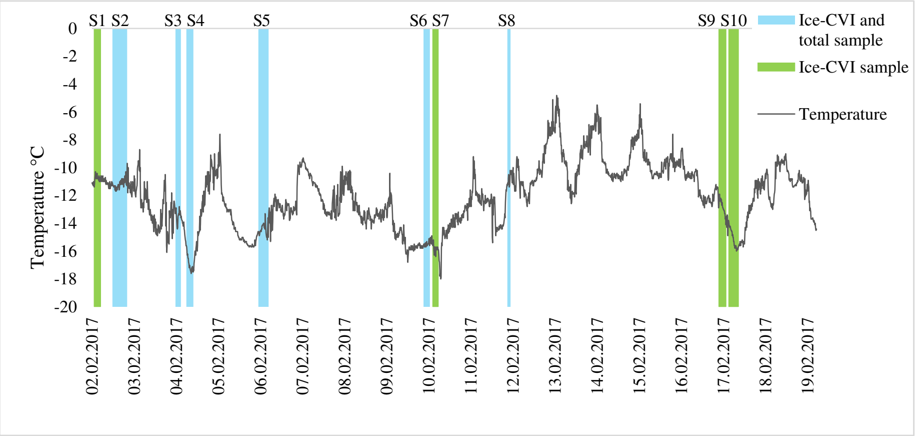

Figure 2: Temperature (°C) and sampling times in February 2017 behind Ice-CVI and total inlet. Sample numbers are given above the bars. Blue bars indicate sampling periods with parallel samples, green bars periods for which only IR samples could be analysed. Temperature data were received from the Federal Office of Meteorology and Climatology (MeteoSwiss; www.meteoswiss.admin.ch).

During the whole campaign, north-easterly and south-westerly winds were the dominating local wind directions in accordance with the topography at Jungfraujoch. Footprint plots, showing the probable air-mass residence time at the surface, were calculated with the FLEXPART model (Stohl et al., 1998;Stohl and Thomson, 1999;Stohl et al., 2005;Seibert and Frank, 2004). These plots are calculated with 10 days back trajectories and a potential emission sensitivity to determine the probable emission region of the particles arriving at Jungfraujoch. Wind roses and footprint plots are presented in Fig. 3.

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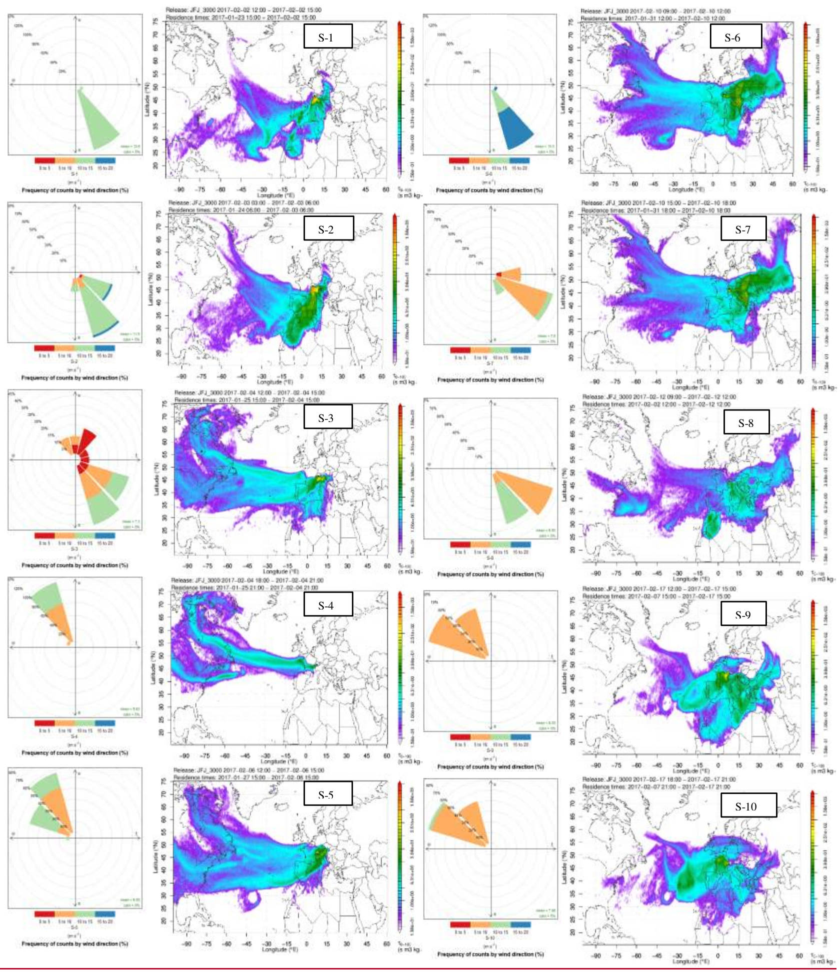

Figure 3: Wind rose (left) and footprint plots (right) calculated with the FLEXPART model, http://lagrange.empa.ch/FLEXPART_browser/ (Stohl et al., 1998;Stohl and Thomson, 1999;Stohl et al., 2005;Seibert and Frank, 2004). Horizontal wind direction and speed were received from the Federal Office of Meteorology and Climatology (MeteoSwiss; www.meteoswiss.admin.ch)

2.6. Methodological problems

2.6.1. Sampling artefacts

The observed alumina, pure salt, Ni-rich and Cu-rich particles are regarded as sampling artefacts. *The IR samples are heavily loaded with artefacts (40-78% of the particles – alumina, Ni-rich and pure salt) easily characterised and removed in further analysis. The Cu-rich particles are a part of the substrates and can in principle be found in both IR samples and total aerosol samples.* Alumina particles are found in all IPR samples at relative high number abundances between 25 and 70 %, despite the fact that the Ice-CVI was coated before the present campaign with Ni to avoid this contamination. The relative abundance of alumina particles in IPR samples is higher in our campaign compared to two previous campaigns at

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Jungfraujoch using the same instrumentation nut without the Ni coating of the Ice-CVI (Ebert et al., 2011;Worringen et al., 2015). *This might be explained by the fact that we only focused on the sub-micrometer particles and/ or the difference in meteorology, sample time and particle load all influencing the relative composition of contamination particles.* In contrast to previous work, we sampled IPR and total aerosol in parallel to be able to clearly distinguish instrumental artefacts from IPRs. As we did not detect a single alumina particle in total aerosol samples, this particle group is regarded as contamination. Alumina particles are easily recognised and were subtracted from the real IPRs. Nevertheless, their presence helped substantially to locate the impaction spot on the boron substrates.

Secondary ice processes can produce ice crystals in the critical size range selected by the Ice-CVI. The low temperature during sampling does not support the Hallett-Mossop process (Hallett and Mossop, 1974) regarding rime splintering, but other secondary processes producing ice crystals like ice-crystal break up, blown snow or crystal-crystal collisions in the critical size range are plausible (Mertes et al., 2007). We hypothesise that pure salt is an artefact due to sampling of the mentioned secondary ice production processes in clouds. The presence of sodium and chloride in ice crystals previously acting as cloud condensation nuclei can later form solid NaCl in line or on the substrate after evaporation of water. This hypothesis is inconclusive because pure salt is not observed in the total aerosol fraction, where only aged and mixed salt are present. This might be explained by evaporation of ice crystals in the heated inlet and the longer sampling line, and the relatively low number concentration of these particles compared to the dominating groups (soot and complex secondary particles) in the total aerosol samples. It should be mentioned here that sea salt was considered to be an artefact in the IPR fraction by Worringen et al. (2015).

A few Ni-rich particles (1-7% relative by numbers) were encountered in the IPR fraction but not in the total aerosol. The Ni-rich particles most likely stem from the Ni coating of some parts of the Ice-CVI. The few Cu-rich particles found, in both total aerosol and the IPR samples, are from the boron substrate where boron is embedded in cupper.

2.6.2. Accuracy of particle group abundance

Accuracy of the particle group abundance depends on three different factors: (1) separation of IPR from the rest of the aerosol particles by the Ice-CVI and deposition losses behind both inlets, (2) detection of particles in SEM, and (3) the classification procedure. Sampling issues like abrasion, deposition losses and ice crystal breakup may occur in the Ice-CVI (Mertes et al., 2007). Abrasion particles were easily recognised as discussed in the previous paragraph. Sampling of secondary ice may have led to the relative high abundance (~2 – 28 %) of pure salt particles in the IPR fraction discussed in the previous paragraph. As we regard pure salt particles as artefact, they are not included in the sea salt-containing particles group. Deposition loss can generally not be excluded. Three of the total aerosol samples (S-3b, S-4b and S-6b) are sampled under conditions where the concentration (measured with condensation particle counters) of the total inlet was lower than the interstitial inlet. There are two possible explanations for this: deposition loss in the total aerosol inlet and/or a leak in the interstitial inlet. The relative abundance of the different particle groups in these samples is however comparable to previous findings at Jungfraujoch (Cozic et al., 2008b;Kamphus et al., 2010;Fröhlich et al., 2015). A possible deposition loss leading to systematic bias in the concentration measurements does not seem to change the relative abundance of the different particle groups. Our conclusions are thus not affected as we do not discuss number concentrations.

For most particle groups we do not expect to have significant detection artefacts in SEM. These particle groups are detected with high efficiency, in both the total aerosol as well as the IPR fraction. However, C-rich particles and soot may be interchanged in total aerosol samples because the image quality can be reduced by evaporating complex secondary particles leading to less efficient detection of carbonaceous species which have a low contrast in SEM images. Usually, evaporation of complex secondary particles is not a problem because the particles are observed at the start of analysis. Nevertheless, in one sample, complex secondary particles were lost prior to observation because this sample was erroneously left in the

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chamber for a longer time before it was analysed. However, these effects seem to be small because we have observed a comparable abundance of carbonaceous particles and complex secondary aerosol particles (in total aerosol) as in previous work (Cozic et al., 2008b).

The classification criteria used (table 1) may lead to problems for small (below approximately 150 nm equivalent projected area diameter) carbonaceous particles. Due to the limited lateral resolution of the instrument, the typical morphology of soot may not be recognised for small particles. In this case, soot would be misclassified as C-rich particles. Still, the sum of both particle groups should be accurate. However, this problem is only significant for the total aerosol samples because evaporating secondary aerosol in these samples leads to deterioration of the image quality. Misclassification of soot as C-rich particle would imply that soot is even more depleted in the IPR fraction.

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2.7 Statistical analysis

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To calculate enrichment and depletion of the different particle groups in the IR fraction relative to total aerosol all particle group abundances are normalised to the abundance of the alumosilicate group. We have chosen this group as reference as it has the highest relative abundance in both, the IR samples and the total aerosol. We do not show a simple ratio of proportions (e.g., proportion of alumosilicates in IRs divided by proportion of this group in total aerosol) because the proportion is constrained to values between 0 and 1. This is generally referred to as closed data (Aitchison, 2003;Van den Boogaart and Tolosana-Delgado, 2013) and implies that only ratios of two groups can be interpreted (i.e., not the proportion of one group alone). Furthermore, we do not discuss differences in proportions between IR and total aerosol as it was done by Ebert et al. (2011), as this difference is strongly dependent on the relative abundance of a particle group. To overcome these problems, only alumosilicate normalised particle group abundances are used to quantify enrichment/ depletion of a particle group in the IR fraction. This measure is termed odds ratio in the statistical literature.

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The odds ratios (OR) is calculated in the following way:

$$\mathrm{OR}_i = \frac{\left(\frac{n_i}{n_{AlSi}}\right)_{IR}}{\left(\frac{n_i}{n_{AlSi}}\right)_{total}}, \qquad (1)$$

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with n_i the absolute number of particles in particle group i, n_{AlSi} the absolute number of particles in the group of alumosilicates in both IR and the total aerosol fraction. For particle groups which did not contain a single particle, one particle (which is the detection limit) was added to the respective group in order to calculate an odds ratio. For these groups the odds ratios shown in (Fig.8) represent an upper or lower limit, respectively. The odds ratios represent enrichment/depletion of a particle group normalised to alumosilicates when the IR fraction is compared to the total aerosol. Enrichment relative to alumosilicates is discussed for each group which is present in the IR. The two groups of complex secondary particles and soot are interpreted as depleted because these particles are not found in the IR fraction. These two particle groups are hence depleted compared to alumosilicates and absolutely compared to total aerosol.

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The Fisher test was applied to estimate confidence intervals for the odds ratio and was calculated with RStudio (RStudioTeam, 2015). Figure 5, Fig. 7 and Fig.8 are plotted in RStudio with the package “ggplot2” (Wickham, 2009). Wind roses (Fig.3) were plotted with the RStudio package “openair” (Carlslaw and Ropkins, 2012).

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3. Results

3.1. Total aerosol

Particle groups observed in the total aerosol samples include complex secondary particles, soot, C-rich, Ca-rich, Ca-sulphates, silica, alumosilicates, Fe-alumosilicates, other-alumosilicates, metal/metal oxide, sea salt-containing particles (aged and mixed) and other particles (Fig. 4).

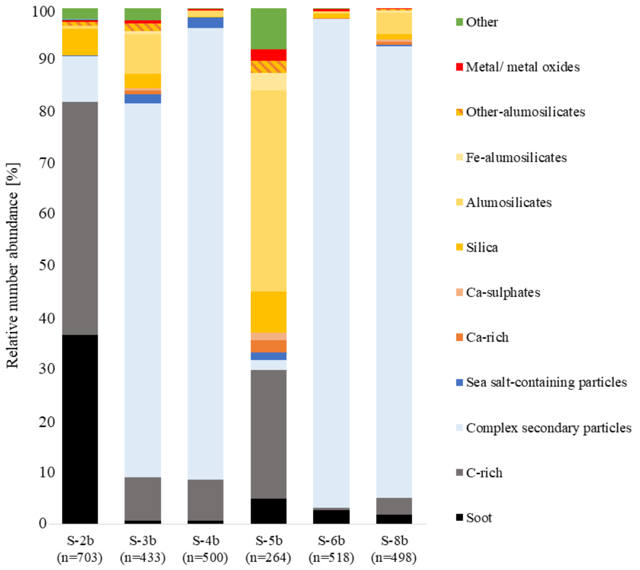

Figure 4: Relative number abundance of the different particle groups within total aerosol samples. Sample S-2b shows a combustion event with air mass history form the Po Valley, and sample S-5b is influenced by an analytical artefact from particle loss of volatile particles.

A few fly ash particles were detected in the metal/ metal oxides group. In addition, one group of artefact particles (Cu-rich) originating from the substrate was found and excluded from further analysis. Four of the six samples are dominated by secondary aerosol, which consists of sulphates and highly instable particles (under vacuum and/or electron bombardment) for which no X-ray spectrum could be obtained. Still, remains of these particles are easily seen in the secondary electron images. The highly instable particles are classified based on the fact that they evaporated during the operator controlled X-ray analysis. In contrast to the IR fraction, we observed two groups of carbonaceous particles. Carbon dominated particles without typical morphology are classified as C-rich particles (Fig. S1). Chain like or more compacted agglomerates of spherical primary carbonaceous particles are interpreted as soot in accordance with previous literature e.g.,Wentzel et al. (2003);Buseck et al. (2014);Weinbruch et al. (2018). Sample S-2b is taken during night time and consists of two separate samples directly taken one after the other (for 3 hours each). The unusual high abundance of carbonaceous particles within this sample most likely result from urban/industrial sources of the Po Valley seen in the footprint plot (Fig. 3). Sample S-5b shows a high relative abundance of mineral particles which may be the result of having lost complex secondary particles in the instrument, as this sample was exposed to the vacuum of the electron microscope for a much longer time than the other samples.

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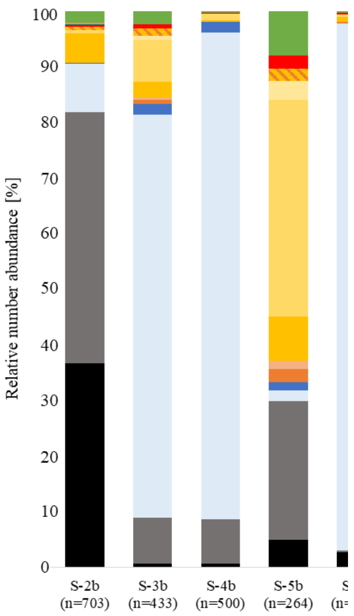

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Most of the total aerosol particles have geometric diameter below 500nm (Fig. 5). The mineral groups of alumosilicates, Fe-alumosilicates and other-alumosilicates are somewhat larger than the rest of the particle groups. The size distribution (dNdlogD$_p$ vs. particle diameter) is shown in the electronic supplement (Fig. S3).

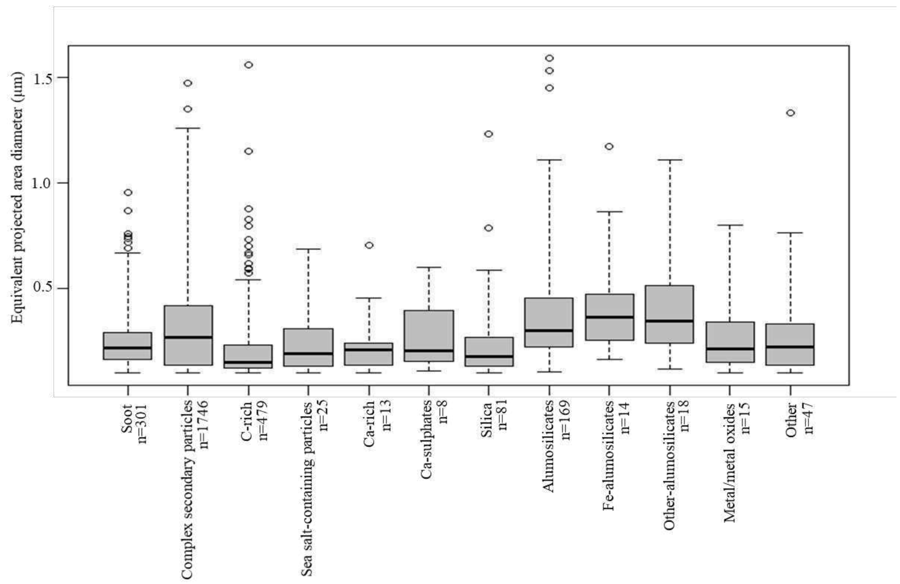

Figure 5: Size of total aerosol particles.

3.2. Ice particle residuals

The following particle groups were observed in the IR samples (Fig.6): minerals (silica, alumosilicates, Fe-alumosilicates, other-alumosilicates, Ca-sulphates and Ca-rich), sea salt-containing particles (aged and mixed salt), C-rich, Pb-rich, metal/ metal oxide and other particles. In addition, four groups of sampling artefacts were found: pure salt, alumina, Ni-rich and Cu-rich particles. The sampling artefacts are regarded as contamination (see section 2.6.), and are, thus not included in the figures. Composition including contamination particles is given in the electronic supplement (Fig.S5).

Mineral particles are of highest relative abundance (between 60 – 90 % by number) in all samples (Fig.6), and mainly consist of silica, alumosilicates and other-alumosilicates, as well as smaller fractions of Fe-alumosilicates, Ca-sulphates and Ca-rich particles. A small percentage (≤ 7 % by number) of Pb-rich particles – PbCl or particles containing heterogeneous Pb inclusions – is found in eight of the samples. Sea salt- containing particles is present in all samples in variable amounts up to 12 %. The C-rich particles observed in the IR fraction can be excluded to be soot because they do not show the typical morphology of chain-like or more compacted agglomerates of primary particles (see supplement Fig.S1). Instead, these particles are most probably organic particles. The group of metal/ metal oxide particles includes Fe-oxides/hydroxides, Ti-oxides, and steel particles (Fe, Cr, Mn alloys).

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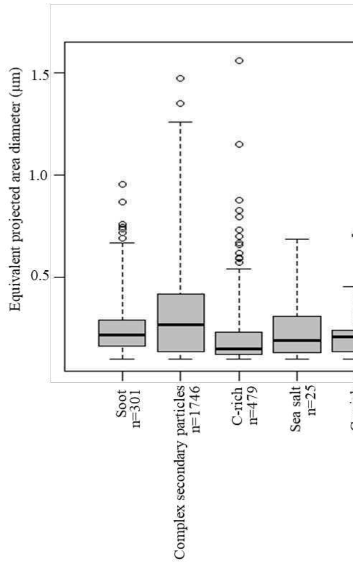

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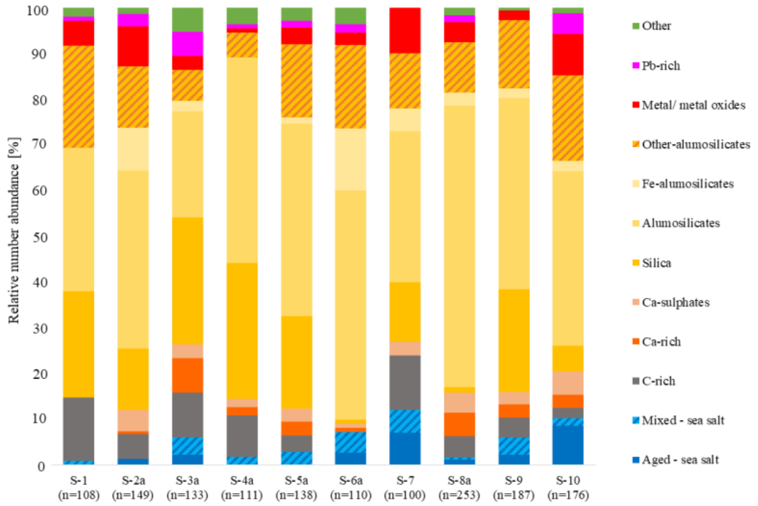

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Figure 6: Relative number abundance of the different particle groups of IR sampled in mixed phase clouds at site temperatures between -10°C and -18°C. Sampling artefacts (pure salt, alumina, Ni-rich and Cu-rich particles) are not shown.

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Most IRs have an equivalent projected area diameter below 500 nm (Fig.7). The groups of Fe-alumosilicates and other-alumosilicates are somewhat larger and show a higher variation than the rest of the particle groups. The size distribution (dNdlogD_p vs. particle diameter) is shown in the electronic supplement Fig.S4.

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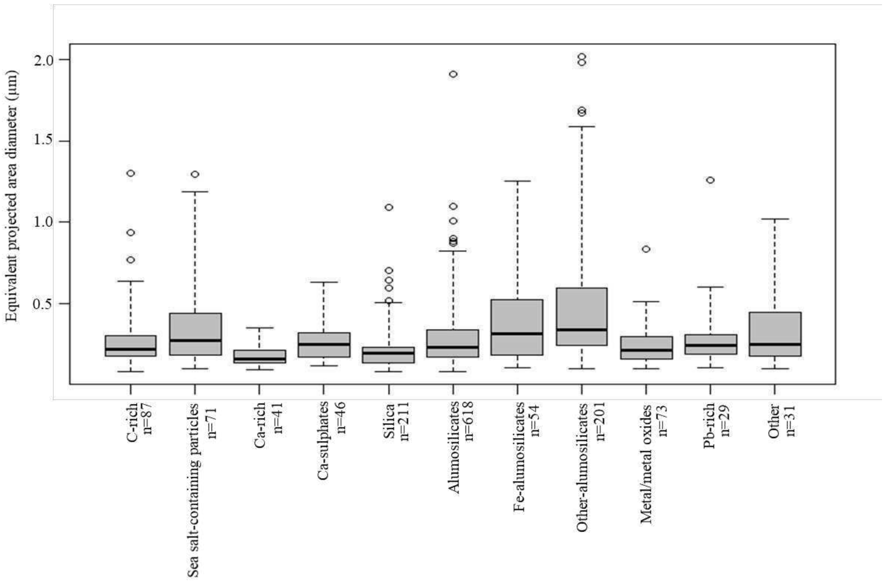

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Figure 7: Size of IRs. Three outliers of other-alumosilicates are shown presented (2.7 µm, 2.9 µm and 3.4 µm).

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3.3. IR versus total aerosol

For six sample pairs (simultaneous sampling of total aerosol and IR) the enrichment/depletion of the particle groups compared to alumosilicates is shown in Fig. 8 as odds ratio. Complex secondary particles and soot are always strongly depleted in the IR fraction, as not a single particle of both groups was observed as IR. An upper limit for the depletion relative to alumosilicates can be obtained by setting the number of particles in the IR fraction for both groups equal to one (the detection limit). With this assumption it can be seen that soot is depleted in the IR fraction relative to alumosilicates by at least a factor 700, and secondary aerosol particles by a factor of at least 4200. Both particle groups are also depleted in the IR fraction relative to total aerosol. C-rich particles are less enriched in the IR fraction than alumosilicates by a factor of approximately 20.

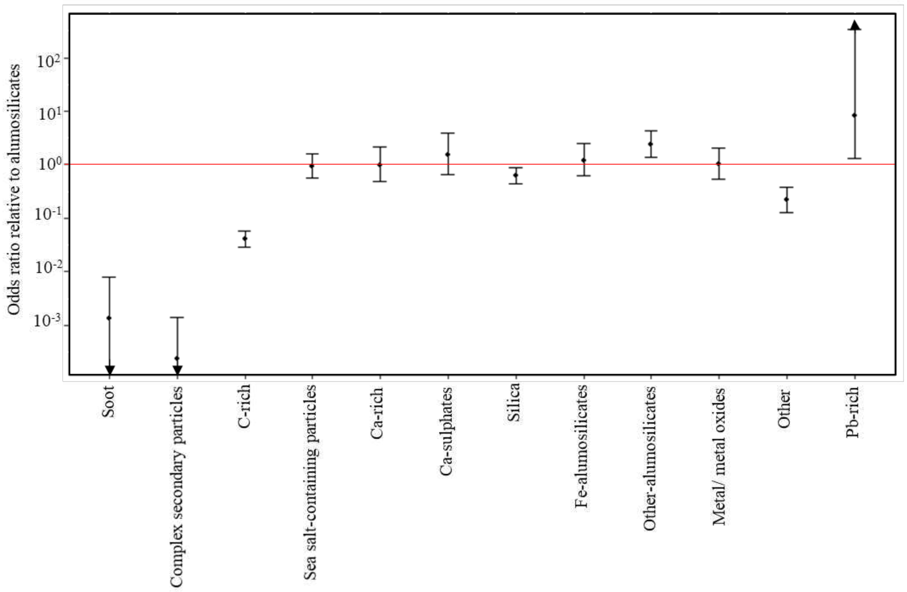

Figure 8: Enrichment/depletion of the different particle groups within the IR fraction expressed as odds ratio (see text for details). The 95 % confidence interval (CI) of the odds ratio is shown as error bars. For soot and complex secondary particles the lower limit of the CI, and for Pb-rich particle the upper limit of the CI cannot be defined precisely due to counting statistics. Thus they are marked by arrows.

Pb-rich particles and other-alumosilicates are enriched (relative to alumosilicates) within the IR fraction. However, the enrichment factor has large uncertainties due to counting statistics. The remaining particle groups are within counting error similar enriched in the IR fraction as alumosilicates (for this latter group the odd ratio is one per definition).

4. Discussion

The major finding of our paper is that sea salt-containing particles, Ca-rich particles, Ca-sulphates, silica, Fe-alumosilicates and metal/ metal oxides are similar ice active as alumosilicates at Jungfraujoch in warm mixed phase clouds (-10 °C to -18 °C). Other-alumosilicates and the Pb-rich particles seem to be even more ice-active as alumosilicates. In contrast, soot

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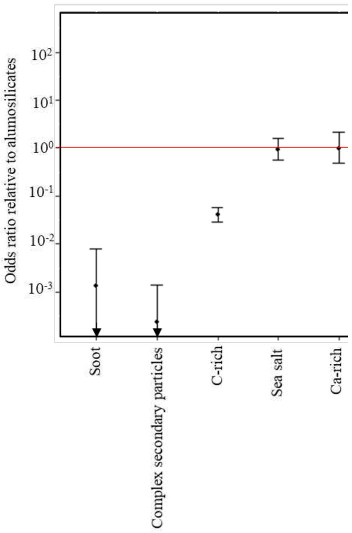

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and complex secondary particles are strongly depleted (compared to alumosilicates and absolutely compared to total aerosol) in the ice residuals. C-rich particles are less enriched than alumosilicates by a factor of approximately 20. Thus, it is concluded that their ice nucleation ability under these conditions is significantly lower. The ice nucleation activities of the different particle groups are discussed intensely in section 4.2.

4.1. Composition of total aerosol

Four of the six total aerosol samples are dominated by complex secondary particles (Fig.4), which seems to be typical for Jungfraujoch (Cozic et al., 2008b;Fröhlich et al., 2015). Two samples (S-2b and S-5b) have a different composition (Fig.4). The first sample (S-2b) shows a higher carbonaceous fraction, the second sample (S-5b) a higher fraction of mineral particles and C-rich particles. The high soot and C-rich particle abundance of the first sample may be explained by footprint plots showing that the air-mass had a longer surface residence time over Po Valley (Italy) which is an urban/industrial area with abundant sources of carbonaceous particles. The potential artefact in the second sample does not influence the enrichment factor all other particle groups. Merely, the odds ratio of complex secondary particles shown in Fig.8 will be somewhat lower. Our general conclusion that complex secondary particles are inefficient ice nuclei under the investigated conditions is not changed.

Most particles of the total aerosol have sizes below approximately 1 µm which is in good agreement with Herrmann et al. (2015).

Overall, our total aerosol samples consist of complex secondary particles (60 % by number) and C-rich particles (16 %), soot (10 %) and mineral particles (14 %). This composition is similar to previous findings at Jungfraujoch during winter. According to Cozic et al. (2008b) the total aerosol is dominated by organic matter and secondary aerosol (87 % by mass), and smaller contributions of black carbon (4 %) and a "non-determined mass" (reported as *"assumed to be composed of insoluble compounds such as silicate from mineral dust"*) fraction (9%). It was also shown by Kamphus et al. (2010) that the main components of the ambient aerosol at Jungfraujoch in winter (2007) are sulphate and organics, and only a small fraction (between 1% and 17%) is classified as mineral particles.

With respect to ice nucleation, mineral dust particles are of most importance (see section 4.2.). Alumosilicates are the most abundant group of mineral particles in the total aerosol with almost twice the amount of silica. This fits well to the distribution of different minerals in soils presented by Hoose et al. (2008) where kaolinite and illite show a higher abundance than calcite and quartz in the clay fraction worldwide. Other-alumosilicates and Ca-rich particles are present in four of the six samples at low number concentration (1-2 %). Ca-containing particles at Jungfraujoch were also found by Cozic et al. (2008b), albeit mainly in the coarse mode.

The footprint plots (Fig.3) were quite similar with high particle residence time over the North Atlantic Ocean. None of the samples are taken during mineral dust events, which normally occur in spring at Jungfraujoch (Coen et al., 2007). One total aerosol sample with higher fraction of carbonaceous particles had a higher surface residence time over Po Valley than the rest.

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Moved up [2]: <#>Methodological problems¶ Sampling artefacts ¶ The observed alumina, pure salt, Ni-rich and Cu-rich particles are regarded as sampling artefacts. Alumina particles are found in all IPR samples at relative high number abundances between 25 and 70 %, despite the fact that the Ice-CVI was coated before the present campaign with Ni to avoid this contamination. The relative abundance of alumina particles in IPR samples is higher in our campaign compared to two previous campaigns at Jungfraujoch using the same instrumentation nut without the Ni coating of the Ice-CVI (Ebert et al., 2011;Worringen et al., 2015), but this might be explained by the fact that we only focused on fine particles. In contrast to previous work, we sampled IPR and total aerosol in parallel to be able to clearly distinguish instrumental artefacts from IPRs. As we did not detect a single alumina particle in total aerosol samples, this particle group is regarded as contamination. Alumina particles are easily recognised and were subtracted from the real IPRs. Nevertheless, their presence helped substantially to locate the impaction spot on the boron substrates.¶ Secondary ice processes can produce ice crystals in the critical size range selected by the Ice-CVI. The low temperature during sampling does not support the Hallett-Mossop process (Hallett and Mossop, 1974) regarding rime splintering, but other secondary processes producing ice crystals like ice-crystal break up, blown snow or crystal-crystal collisions in the critical size range are plausible (Mertes et al., 2007). We hypothesise that pure salt is an artefact due to sampling of the mentioned secondary ice production processes in clouds. The presence of sodium and chloride in ice crystals previously acting as cloud condensation nuclei can later form solid NaCl in line or on the substrate after evaporation of water. This hypothesis is inconclusive because pure salt is not observed in the total aerosol fraction, where only aged and mixed salt are present. This might be explained by evaporation of ice crystals in the heated inlet and the longer sampling line, and the relatively low number concentration of these particles compared to the dominating groups (soot and complex secondary particles) in the total aerosol samples. It should be mentioned here that sea salt was considered to be an

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4.2. Ice nucleation activity of different particle groups

Ice particle residuals mainly consist of mineral particles (Fig.6). The classes of Fe-alumosilicates, Ca-sulphates, Ca-rich, silica, sea salt*-containing particles* and metal/ metal oxides are similar enriched as alumosilicates (odds ratio ~1). Other-alumosilicates are more enriched than alumosilicates by a factor of ~2. The mineral particles abundance between 60-85% in the IR fraction is in good agreement with previous findings for mixed phase clouds at Jungfraujoch (Kamphus et al., 2010;Ebert et al., 2011;Worringen et al., 2015). Mineral particles are also reported as ice active in cirrus clouds (DeMott et al., 2003;Cziczo and Froyd, 2014). Studies of IRs in cirrus clouds are mentioned sometimes in the discussion to show which kind of IRs are found in the environment, independent on the cloud regime. It has to be emphasised here that this is not meant as direct comparison as the temperature and freezing regimes are quite different, note that deposition nucleation dominates in cirrus clouds (Cziczo et al., 2013).

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The size of IRs varies between the detection limit (100 nm) and 3.4 µm (Fig.7). The size distribution is comparable to previous findings by Worringen et al. (2015) showing a maximum around 300 nm. We did not find a relationship between the size of the particles and the enrichment factor (odds ratio) presumably because the particles size did not differ much.

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The sampling temperature at the site varied between -10°C and -18°C (Fig.2). Temperature was measured at the station, and can differ to the onset ice nucleation temperature of the particles depending on where in the mixed phase cloud nucleation occurred. None of the particle group abundances in the IR fraction showed a systematic temperature dependence. However, based on the limited number of samples and the relatively small temperature range, no definite conclusion regarding the temperature dependence can be drawn.

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The importance of a given particle group for ice nucleation in the atmosphere depends on the ice nucleation ability and the abundance of this group in the total aerosol. Both parameters will be discussed in the following. Complex secondary aerosol particles and soot were not found in the IPR fraction, in contrast to previous work at Jungfraujoch (Cozic et al., 2008a;Ebert et al., 2011;Worringen et al., 2015;Schmidt et al., 2017), even though these groups dominate the total aerosol fraction. Thus, their ice nucleating ability under the conditions of our campaign, can be assumed to be very low. One explanation for this difference might be the higher site temperatures during our campaign. In the present study, complex secondary particles are defined by the presence of a S-peak in the X-ray spectrum and/or the instability under electron bombardment. It must be emphasised here that this particle group most likely also consists of a substantial fraction of organics and nitrates (Vester et al., 2007), see table 1.

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C-rich particles were observed in the total aerosol and the IR fraction, but are less ice active than alumosilicates (odds ratio ~ 0.04). C-rich particles are reported in previous studies of mixed phase clouds at Jungfraujoch (S.Mertes et al. 2007; Cozic et al. 2008; Kamphus et al. 2010; Ebert et al 2011; Worringen et al. 2015; Schmidt et al. 2017). Our results are also in agreement with findings of many cirrus cloud field studies (see recent review by Knopf et al. (2018) and references therein) which show that organic aerosol is found in the IR fraction, but is depleted relative to total aerosol.

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Alumosilicates are enriched in all samples and have the highest relative number abundance in the IR fraction. Alumosilicates are also found to be efficient ice nuclei in other field experiments (Cziczo et al., 2013;Worringen et al., 2015;Iwata and Matsuki, 2018). Among alumosilicates, kaolinite is reported as efficient ice nucleus in laboratory studies (Zimmermann et al., 2007;Murray et al., 2011;Wex et al., 2014;Freedman, 2015). As alumosilicates often have a high abundance in the total aerosol and in the IR samples, they are the most important particle group for ice nucleation. Therefore the enrichment/depletion of the particle groups was normalised to this group.

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Silica is the second most abundant mineral particle group in the IR samples and the only mineral group which seems to have a somewhat lower ice activity than alumosilicates (upper limit of 95 % confidence interval of the odds ratio <1).

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However, keeping in mind the counting error for alumosilicates, silica is statistically similar enriched. This observation is in agreement with Atkinson et al. (2013) but in contradiction to Eastwood et al. (2008) who concluded that quartz is less ice active than kaolinite and montmorillonite. The silica fraction in the IR samples varies between 1 and 30 %. Boose et al. (2016) point out that quartz is always present in atmospheric dust in all size ranges, even in the smallest size fraction which is dominated by clay minerals. They conclude that quartz is an important atmospheric INP component because it is present in the size fraction with the longest atmospheric residence time. Despite the fact that the enrichment of silica is somewhat lower than alumosilicate, the relative high abundance in the IR fraction in our samples confirms this conclusion.

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Fe-alumosilicates are similar enriched in the IR fraction as alumosilicates. Fe-alumosilicates were reported as cloud residual by Matsuki et al. (2010). As these authors did not differentiate between droplet and ice crystals, nothing can be said about the ice nucleation ability of Fe-alumosilicates. This mineral group is not present at high relative abundance at Jungfraujoch, thus, it will not contribute much to ice nucleation at this location.

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The group of other-alumosilicates most likely consists of different minerals like for example feldspars, illite and smectite. Laboratory studies (Atkinson et al., 2013;Iwata and Matsuki, 2018) showed that K-feldspar and clay minerals (Zimmermann et al., 2008;Hiranuma et al., 2015;Boose et al., 2016) have a high ice nucleation ability compared to other minerals. A high ice nucleation ability of clay minerals is also reported from field experiments (Targino et al., 2006;Worringen et al., 2015). Also our field study shows an enrichment of other-alumosilicates in the IR fraction indicating a high ice nucleation ability. However, as feldspar is less common in the smallest dust fraction, it was concluded by Boose et al. (2016) that at least the feldspar group is generally of minor importance.

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Ca-rich and Ca-sulphate particles are relatively low in number concentration, both in total aerosol and IR samples. Similar to quartz, calcium containing particles showed different ice nucleation ability in previously laboratory studies (Zimmermann et al., 2008;Atkinson et al., 2013). In field experiments, however, Ca-rich particles and Ca-sulphates were observed in the IR fraction (Ebert et al., 2011;Worringen et al., 2015;Iwata and Matsuki, 2018).

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Based on chemistry, three subgroups of salt can be distinguished in the IR samples: pure salt, aged-sea salt and mixed-sea salt. The pure salt is regarded as artefact (see section 2.6.1.) and, thus, excluded from the further analysis. Due to their low number abundance, the two other salt subgroups are combined into the sea salt-containing particles group. Sea salt-containing particles is similar enriched as alumosilicates. The ice activity of salt and sea salt is still controversial due to discrepancies between different laboratory studies (Wise et al., 2012;Niehaus and Cantrell, 2015;Ladino et al., 2016). Kanji et al. (2017) assign these differences to the experimental setup, i.e. different size, composition and particle generation methods. In field experiments, however, salts are present in the IR fraction of both, cirrus and mixed phase clouds (Targino et al., 2006;Ebert et al., 2011;Cziczo et al., 2013;Worringen et al., 2015;Iwata and Matsuki, 2018). It is advocated by Iwata and Matsuki (2018) that pure NaCl is not ice active due to molar depression of the freezing point. Sea salt-containing particles may act as an INP due to the presence of organics (Wilson et a. 2015; DeMott et al. 2016; Iwata and Matsuki, 2018). However, we cannot define with our measurement technique where the ice nucleation occur in a particle, i.e. pores or thin coating.

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The enrichment of metal and metal oxides is similar to alumosilicates. The ice activity of different metal and metal oxide particles varies with their chemical composition (Kanji et al., 2017). Our samples are dominated by FeCrMn (steel), Ti-oxide, Fe-oxide. Literature regarding the metal/ metal oxide group is ambiguous. Hematite was reported as ice active by Zimmermann et al. (2008). In contrast, hematite, magnetite and rutile were found not to be very ice active in deposition mode by Yakobi-Hancock et al. (2013). Even so, metal and metal oxides are often found in IR samples from cirrus and mixed phase clouds (Kamphus et al., 2010;DeMott et al., 2003;Ebert et al., 2011;Worringen et al., 2015;Schmidt et al., 2017).

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Pb-containing particles are present in the IR fraction as already reported in previous work at Jungfraujoch (Cziczo et al., 2009;Kamphus et al., 2010;Ebert et al., 2011;Worringen et al., 2015;Schmidt et al., 2017). In the present study, Pb-rich particles are the most enriched particle group. A high enrichment of Pb-rich particles among IRs was also reported by Ebert et al. (2011). In addition, laboratory work showed that Pb can increase the ice activity of mineral particles considerably (Cziczo et al., 2009;Yakobi-Hancock et al., 2013). Helicopters and small aircrafts were discussed as local sources of Pb at Jungfraujoch by Kamphus et al. (2010) and Ebert et al. (2011). As the samples were collected during in-cloud conditions, we do not expect freshly on-site emitted Pb-rich particles from the mentioned sources. A time delay between emission and sampling results in relatively low concentrations of Pb in the ambient air in clouds at Jungfraujoch. However, Kamphus et al. (2010) and Schmidt et al. (2017) detected Pb-bearing particles with mass spectrometry in both ambient air and IRs. Keeping in mind the better counting statistics of mass spectrometry, it seems plausible that the total aerosol contains a small amount of Pb-rich particles which were missed in our total samples.

To summarise, the two particle groups of complex secondary particles and soot are strongly depleted compared to alumosilicates as well as absolutely to the total aerosol. Despite an uncertainty due to potential misclassification, the C-rich group is less enriched compared to alumosilicates. Other-alumosilicates and Pb-rich particles are enriched compared to alumosilicates. A high enrichment of Pb-rich particles indicates that this group is more ice active than the rest of groups present in the IR fraction. All other particle groups (silica, Fe-alumosilicates, Ca-sulphates, Ca-rich, sea salt-containing particles and metal/metal oxides) are similar enriched as alumosilicate. The relative high abundance of artefacts was identified by comparing the IR and total aerosol fraction, showing how important parallel sampling is for identification of IRs. Taken into account the relative abundance of the particle groups in total aerosol and the ice nucleation ability, we conclude that silica, alumosilicates and other-alumosilicates were the most important ice nucleating particles in mixed phase clouds site temperatures between -10 °C and -18 °C during the campaign at Jungfraujoch in winter 2017.

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Data availability: The data set is available for the community and can be accessed by request to Stine Eriksen Hammer (sehammer@geo.tu-darmstadt.de) of the Technical University Darmstadt.

Competing interests: The authors declare that they have no conflict of interest.

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Author contributions

Stine Eriksen Hammer collected the samples, analysed the particles by electron microscopy, performed data analysis and prepared the manuscript. Martin Ebert contributed to electron microscopy and data analysis. Konrad Kandler designed the dilution unit and contributed to data analysis. Stephan Mertes designed, improved and operated the Ice-CVI during the campaign. Johannes Schneider organized the field campaign at Jungfraujoch and contributed to data analysis. Stephan Weinbruch contributed to data analysis and manuscript preparation.

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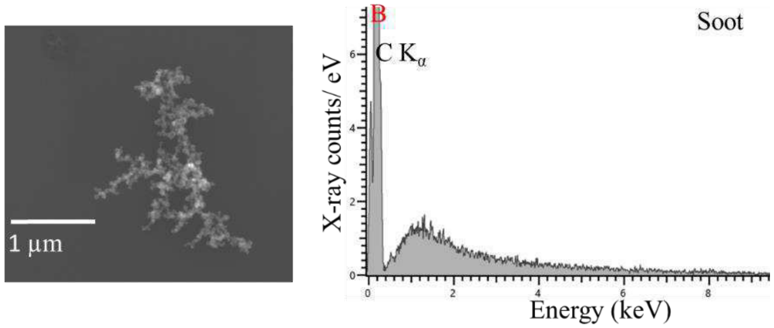
S1: Sample information

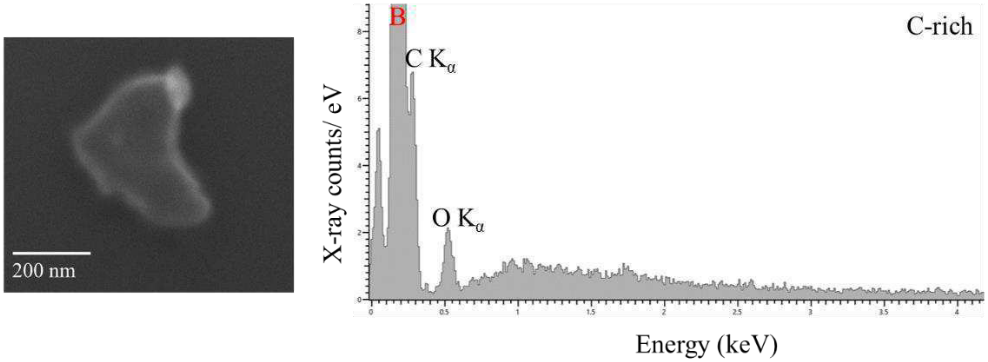
Table S1: Sampling time, average temperature and sample number

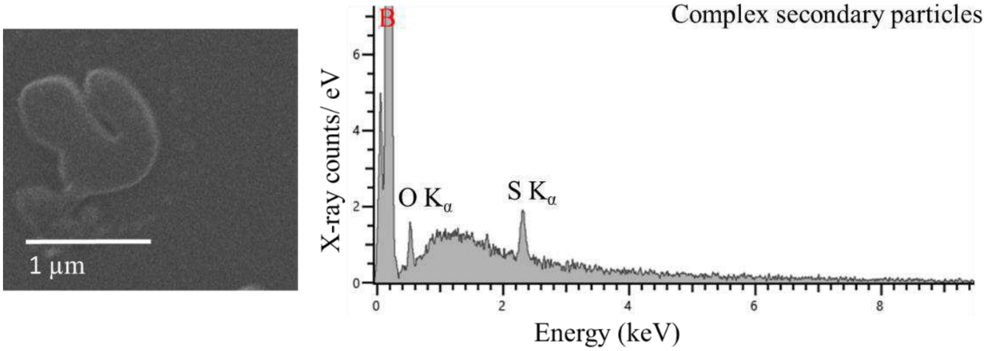
Date and time (UTC+1)	Temperature*(ºC)	Sample number
02.02.2017 (11:08-15:00)	-11	1
02-03.02.2017 (21:51-5:57)	-11	2a+b
04.02.2017 (10:02-13:37)	-13	3a+b
04.02.2017 (16:16-20:06)	-16	4a+b
06.02.2017 (09:29-15:16)	-15	5a+b
10.02.2017 (08:31-12:03)	-16	6a+b
10.02.2017 (13:40-16:46)	-16	7
12.02.2017 (08:32-10:12)	-11	8a+b
17.02.2017 (10:06-14:06)	-12	9
17.02.2017 (15:41-21:14)	-15	10

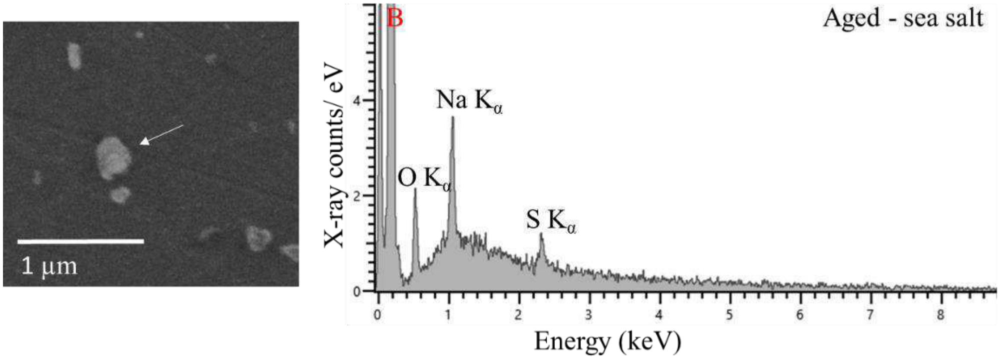
*mean value for sampling period

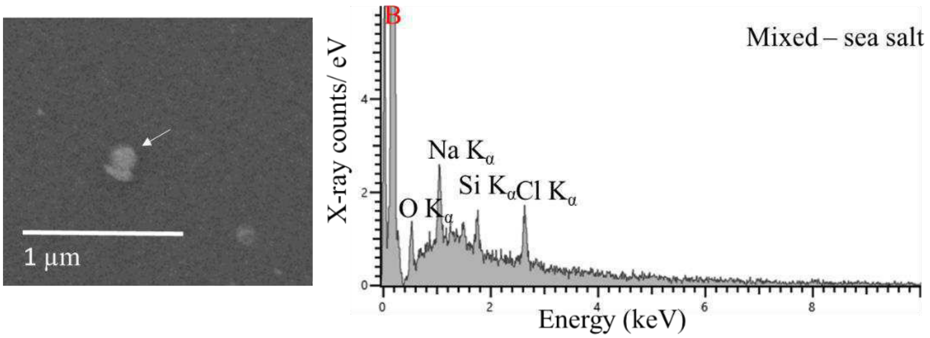
Examples of each particle group. Secondary electron image and corresponding energy dispersive X-ray spectrum for a typical particle of each group are presented under. B indicates the X-ray peak from the boron substrate.

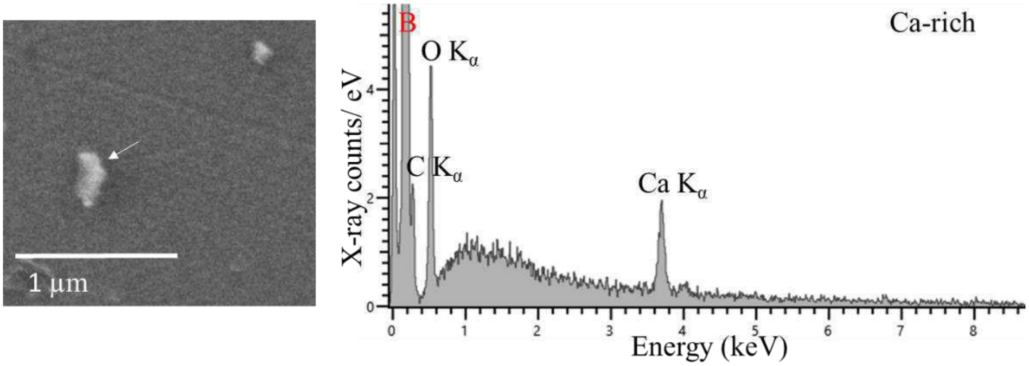


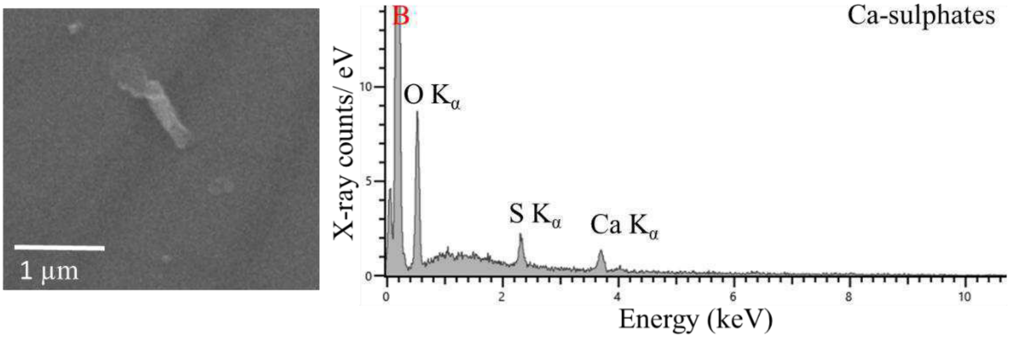

200 nm
B
C-rich
C Kα
O Kα
X-ray counts/ eV
Energy (keV)
0
2
4
6
8
0
0.5
1
1.5
2
2.5
3
3.5
4

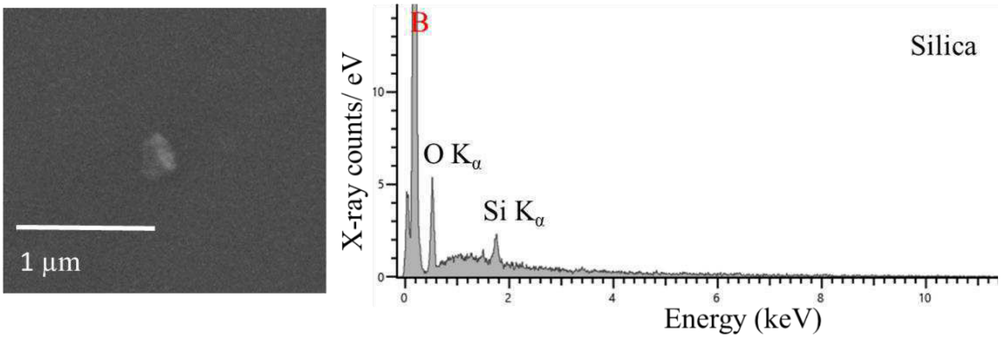

1 μm
B
Complex secondary particles
O Kα
S Kα
X-ray counts/ eV
Energy (keV)
0
2
4
6
0
2
4
6
8

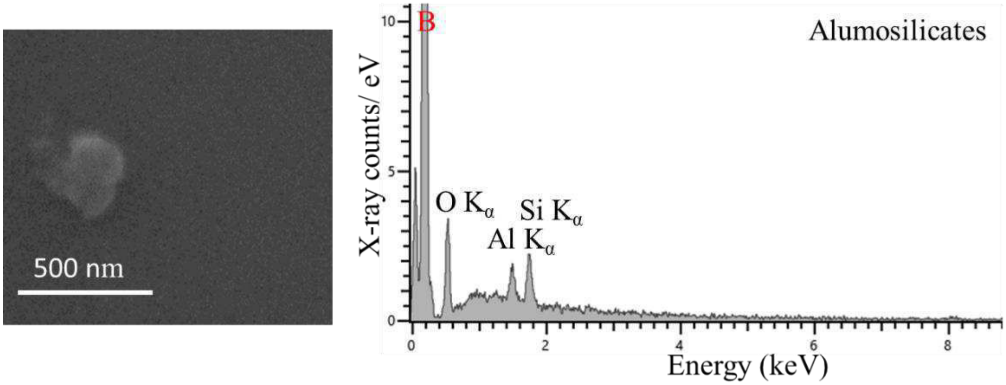

1 μm
B
Aged - sea salt
Na Kα
O Kα
S Kα
X-ray counts/ eV
Energy (keV)
0
2
4
0
1
2
3
4
5
6
7
8

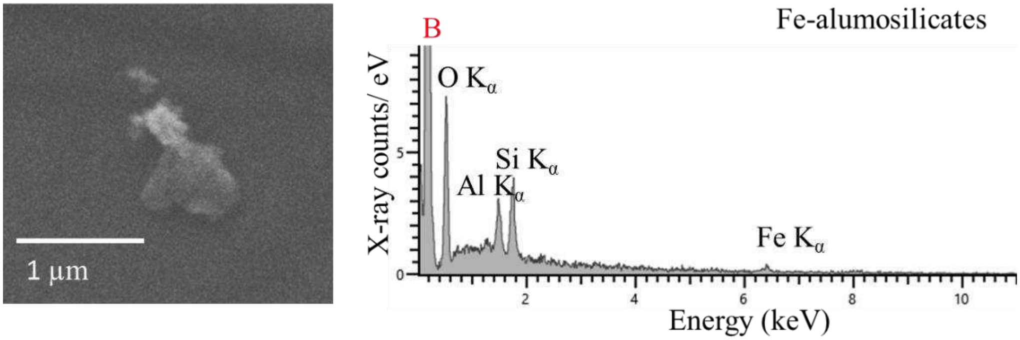

1 μm
B
Mixed – sea salt
X-ray counts/ eV
Na K_α
Si K_α
Cl K_α
O K_α
0
2
4
6
8
Energy (keV)

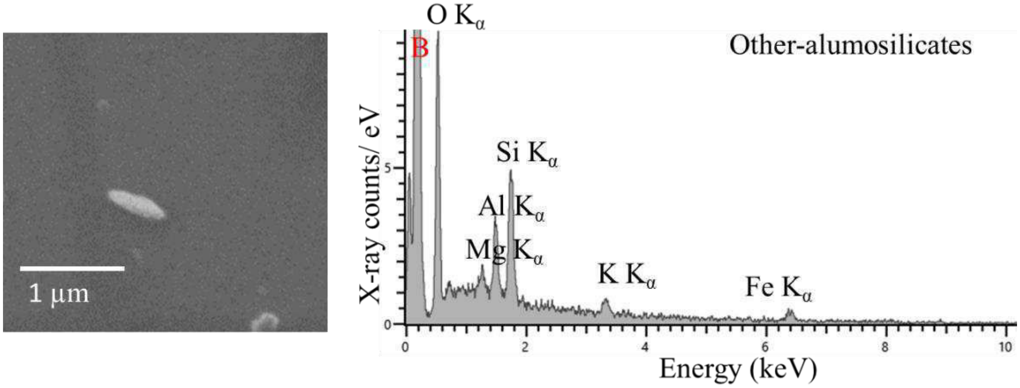

1 μm
B
Ca-rich
O K_α
C K_α
Ca K_α
X-ray counts/ eV
0
2
4
1
3
5
6
7
8
Energy (keV)

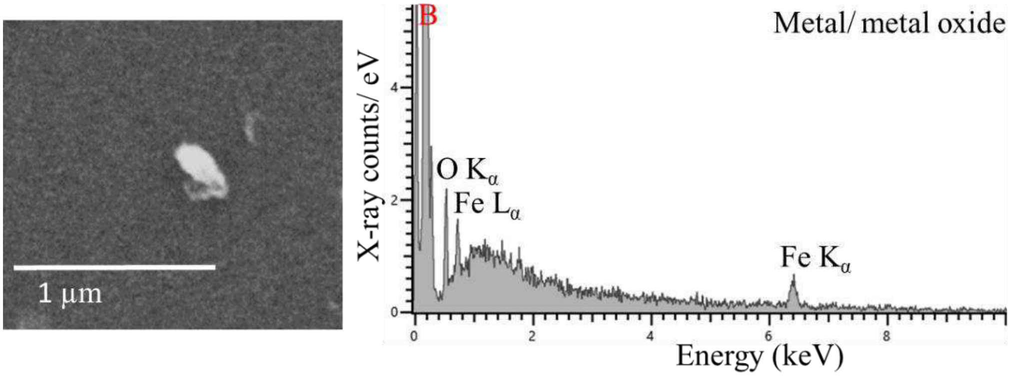

1 μm
B
Ca-sulphates
O K_α
S K_α
Ca K_α
X-ray counts/ eV
0
5
10
2
4
6
8
10
Energy (keV)

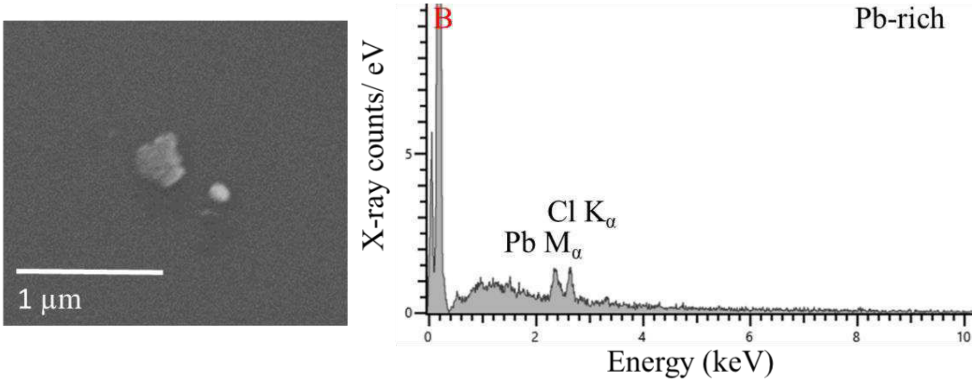

1 μm
B
Silica
O K_α
Si K_α
X-ray counts/ eV
0
5
10
2
4
6
8
10
Energy (keV)

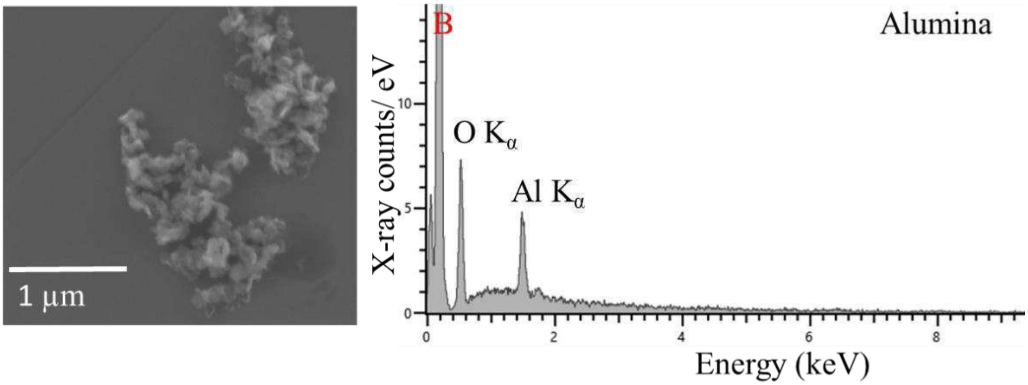

500 nm
Alumosilicates
B
O Kα
Al Kα
Si Kα
X-ray counts/ eV
10
5
0
0
2
4
6
8
Energy (keV)


1 µm
Fe-alumosilicates
B
O Kα
Al Kα
Si Kα
Fe Kα
X-ray counts/ eV
5
0
2
4
6
8
10
Energy (keV)


1 µm
O Kα
B
Other-alumosilicates
Si Kα
Al Kα
Mg Kα
K Kα
Fe Kα
X-ray counts/ eV
5
0
0
2
4
6
8
10
Energy (keV)


1 μm
B
Metal/ metal oxide
X-ray counts/ eV
O K$_\alpha$
Fe L$_\alpha$
Fe K$_\alpha$
Energy (keV)
0
2
4
6
8


1 μm
B
Pb-rich
X-ray counts/ eV
Cl K$_\alpha$
Pb M$_\alpha$
Energy (keV)
0
5
0
2
4
6
8
10


1 μm
B
Alumina
X-ray counts/ eV
O K$_\alpha$
Al K$_\alpha$
Energy (keV)
0
5
10
0
2
4
6
8

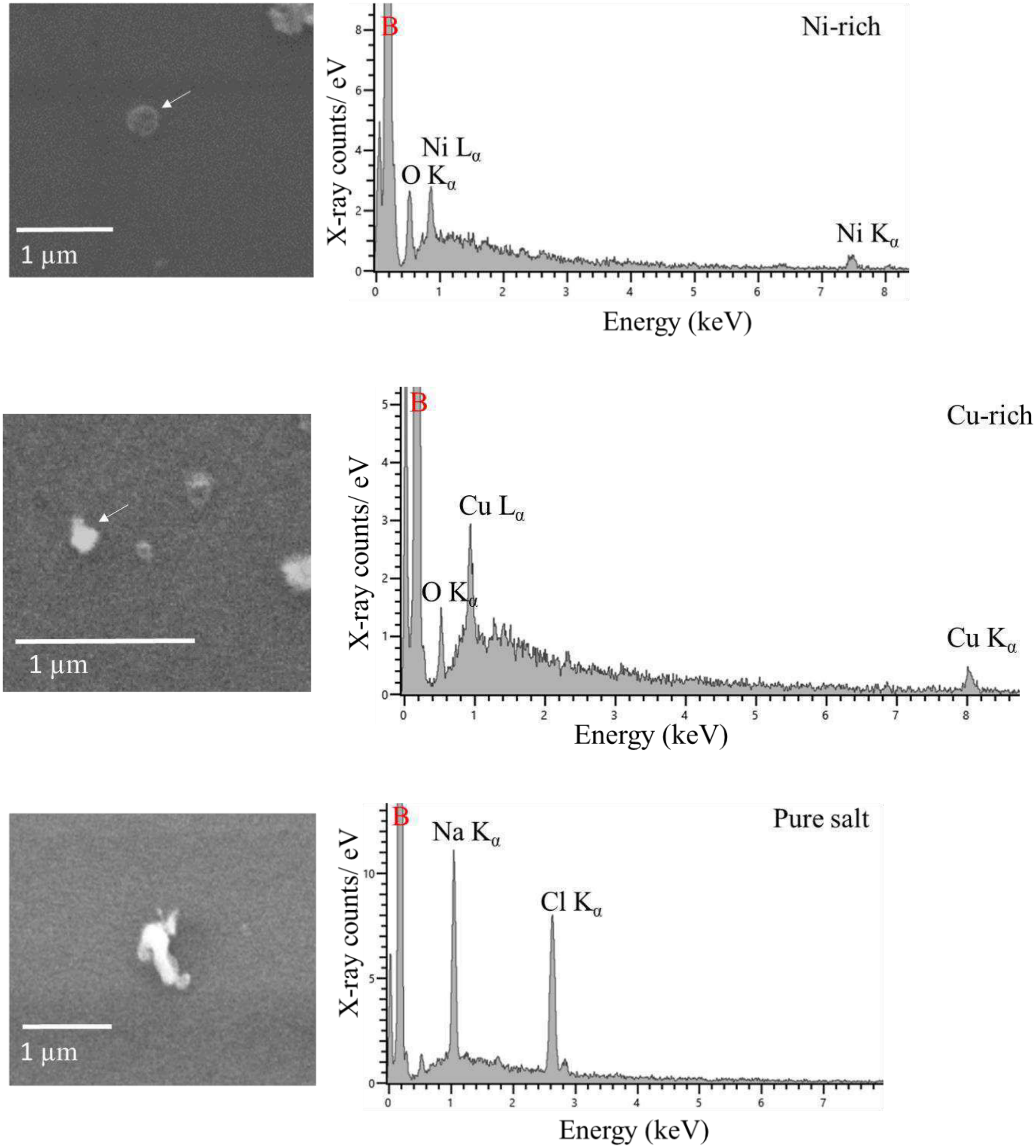


Figure S1**:** Secondary electron images and corresponding energy dispersive X-ray spectrum for typical particles in the IR and total aerosol fraction. B indicates the X-ray peak from the boron substrate

S2: Size distribution

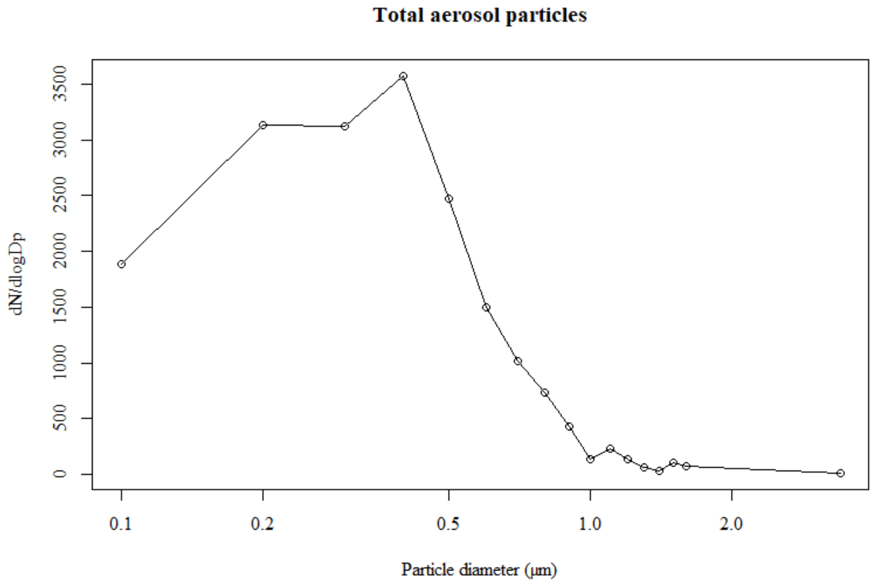


Figure S2: Size distribution of total aerosol, all groups and samples combined.

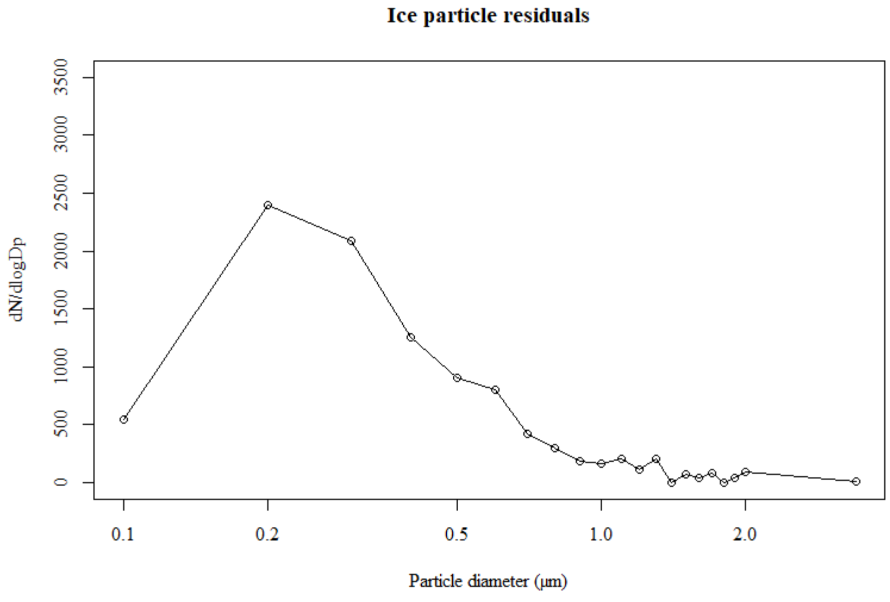


Figure S3: Size distribution of ice particle residual, all groups and samples combined.

S3: All particle groups found in the IR samples

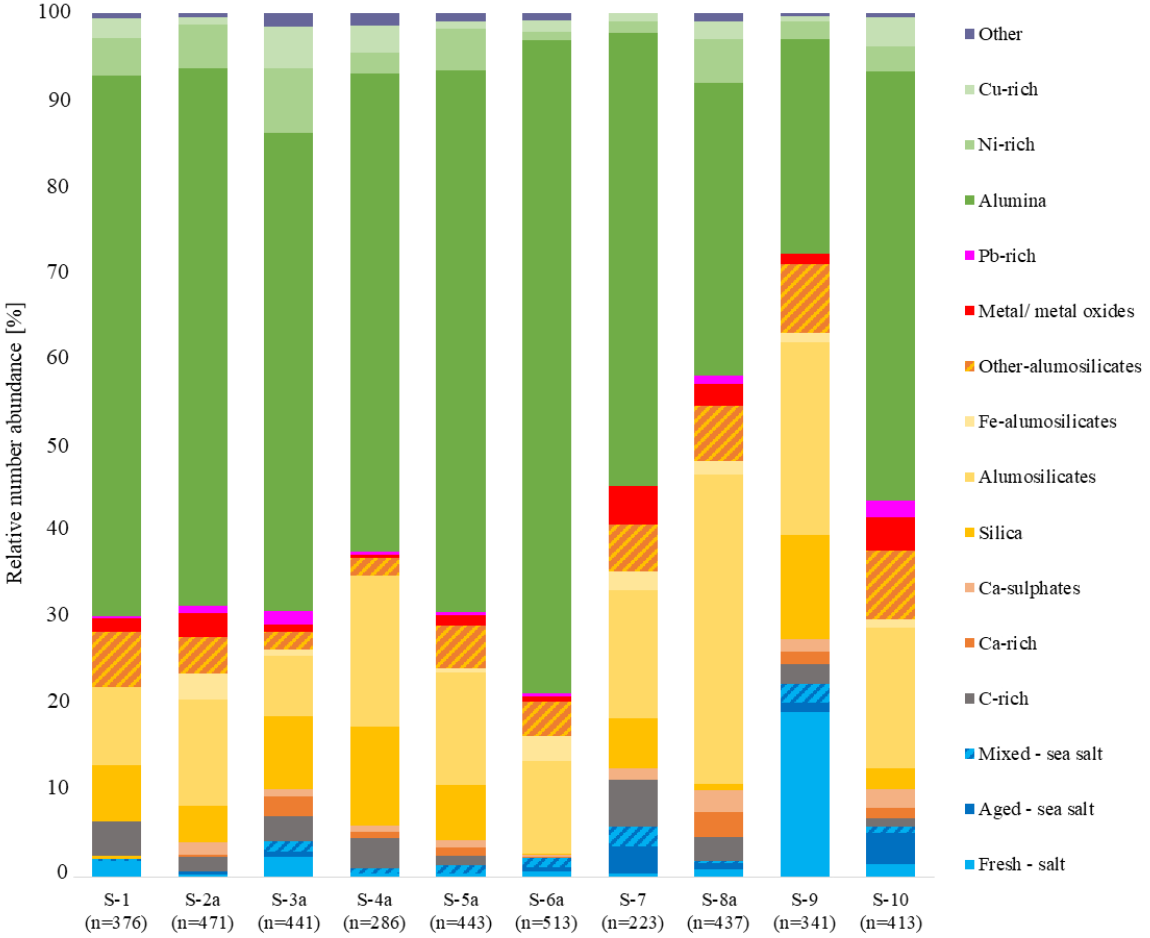


Figure S4: Relative number abundance of the different particle groups of IR sampled in mixed phase clouds at temperatures between -10°C and -18°C including sampling artefacts (pure salt, alumina, Ni-rich and Cu-rich particles).