

This study presents results from a campaign at the high alpine station in Jungfraujoch studying the composition of ice particle residuals as sampled from two different inlets. A single particle mass spectrometer was used to probe composition of the ice particle residuals in conjunction with several auxiliary measurements and inferences were made concerning the source and history based on back trajectory analysis. The study adds to a growing list of IPR analysis studies which provide the potential to expand our understanding of ice formation in the atmosphere.

However, the current manuscript contains numerous typographical errors as well as sentences that often obscure the intended meaning of the results or interpretations. In addition, the manuscript provides information that is not necessarily relevant to the current study while providing key information regarding methodology that might shed light on interpretation of the results. Finally, this paper suffers from a lack of insight and often reads as a simple recitation of observations. It is not clear that the content in this paper is currently suitable for publication given more fundamental issues concerning methodology.

Changes in the manuscript are highlighted as follows:

Referee#1 → yellow

Referee#2 → green

Referee#3 → red

Additional changes → blue

Major issues

Particle Transmission and Size Distributions

In section 2.2, the authors discuss briefly transmission efficiencies through the sampling system concluding on pg. 4684, lines 1-2, that the efficiency is between 45 to 90% for particles of 3 μm . This in and of itself is a fairly broad range and the authors never go on to explain why this wide range exists. And, on pg. 4683, line 28, they state that the transmission efficiency for particles in the range of 200 to 500 nm is $\approx 99\%$. The authors never explain exactly why this range is important. And this gets to the larger issue concerning particle transmission – no where in the paper do they discuss instrument response as a function of diameter. This has a large impact on the interpretation of results. As the size distributions measured with the ALABAMA are used to draw major conclusions, it is important to explicitly state the transmission efficiency of particles as a function of diameter through the mass spectrometer inlet.

The ALABAMA covers a size diameter range from 100 – 3000 nm but with the most efficient size diameter range from 200 – 900 nm. Particles with approximately 400 nm size range were ionized best (detection and ablation efficiency have already been shown in Brands et al. (2011)). To sample different particle types the ALABAMA was connected to three different inlets. The tubes between the inlets and the ALABAMA had different lengths (ISI = 370 cm; Ice-CVI = 126 cm; total = 261 cm). The larger the particles and the longer the tubes, the higher are the losses inside the tubes. In the size range between 200 and 500 nm the transmission efficiency is about 99% for all three inlets. But for particles with a size range of

3000 nm the transmission efficiency varies between 45% for the particles sampled through the ISI (longest sampling line) and 90 % for the particles sampled with the Ice-CVI (shortest sampling line).

Page 5 line 33 – page 6 line 2 and page 6 line 11 – 13.

Section 3.5 provides extended discussion of size distributions drawn from three different instruments: the Sky-OPC, ALABAMA and ESEM analysis. Aside from the lack of a interpretable statement regarding transmission efficiencies, the analysis runs into several fundamental issues. First, as pointed out by a previous referee, the analysis of size seems to extend below the range defined pg.4683, line 23, of 250 nm. Second, the authors attempt to compare size distributions from instruments measuring three different properties: optical size, aerodynamic size and geometric size. Finally, although the authors state that the maxima of the detected IPR appears to occur between 300 and 650 nm for both the Sky-OPC and ALABAMA for all three inlets (pg. 4697, line 8), Figure 10 shows that this is clearly not the case and the authors acknowledge this on pg 4697, lines 19-21. The authors attribute this differences to the detection efficiency of ALABAMA and ESEM (pg 4697 lines 21-22) but once again do not explicitly state this efficiency is. But, they do not acknowledge that differences might also be influenced by the different diameters measured.

The lower size range limit 250 nm refers only to the OPC, not to the ALABAMA. This was clarified in the manuscript.

Page 6 line 3 – 4.

For the revised version, we converted the diameter inferred from the ESEM analysis to the vacuum aerodynamic diameter measured by the ALABAMA. The vacuum aerodynamic diameter was calculated according to DeCarlo et al. (2004) with the assumption that the projected area diameter from the electron microscopy analysis equals the volume-equivalent diameter. Furthermore, an average dynamic shape factor of 1.2 was used for the calculations. This seems to be justified, as most non-extremely shaped particles show low variation in shape factor (Zelenyuk et al., 2006; Schneider et al., 2006), except for soot with high fractal dimension (Slowik et al., 2004), which was not commonly encountered in the present work. The density ratios required for the calculation were estimated from the major composition of the particle according to the values from Weinbruch et al. (2014) (Table S2).

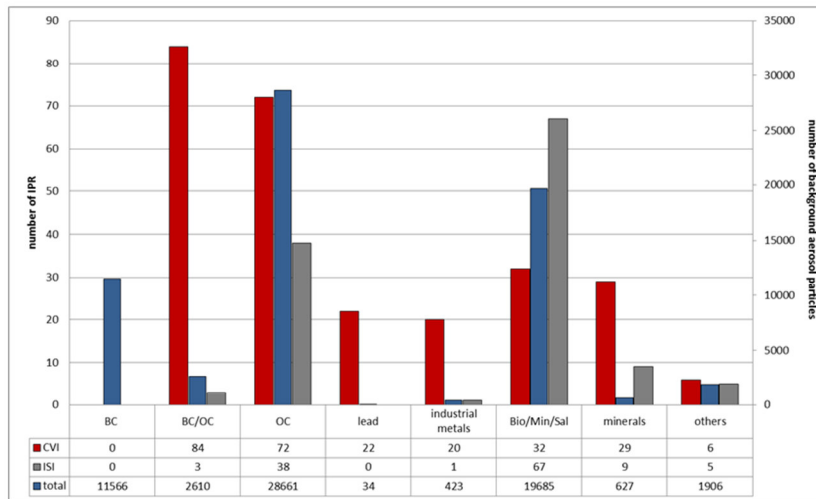
Conversion of the optical size to vacuum aerodynamic diameter, however, appears to be uncertain. Still, the OPC data give important insight into the IPR size distribution, while the size distribution of ALABAMA and ESEM show the impact of the instruments' response as a function of diameter. We therefore prefer to keep this figure in the paper. We revised the discussion of the figure in the manuscript (Section 3.5 Page 18 – 20).

Additionally, we analyzed the ALABAMA data for < 1000 nm and > 1000 nm separately. The Figure below shows the chemical composition of the particles smaller than 1000 nm. For particles larger than 1000 nm, these data are already included in the paper (Fig. 11). No significant differences are found (also due to the low number of particles > 1000 nm that were analyzed), and therefore we think that this additional figure would not improve the paper.

Page 21 line 3 – 6.

On page 4723, a typo was corrected in the caption of Figure 10: It must be “200 nm – 30 μm in (b, d, f)” instead of “3 μm ”.

a) Particles smaller 1000 nm



I would recommend removing any attempt to compare the distributions and remove discussion of ESEM results altogether as this is the only place where they have any impact. Limit discussion to particle composition as a function of size and the impact of this relation on potential ice formation paths. Remove Figure 10 altogether as this seems to not be relevant to the discussion and replace with a comparison of IPR composition for particles less than and larger 1 μm .

See reply to comment above.

IPR as IN

In the introduction, the authors consume some space discussing ice nucleation (pp. 4680-4681), attempting to make the connection that the IPR are dominated by ice nuclei (IN). The identification of IPR with IN requires significant assumptions regarding the formation of the ice crystals sampled. This extrapolation continues on pg. 4693 where the the authors infer that organic containing particles serve as better IN at warmer temperatures than mineral containing particles. The problem with this conclusion is two-fold: 1) that all IPR are not IN and 2) that the ice formation did not necessarily occur within the immediate vicinity of the laboratory, and therefore the average local temperature may not be a good approximation of the ice formation temperature.

We agree in principle that not all IPR are IN. Therefore the Ice-CVI and the ISI were designed such that only small, freshly formed ice particles are sampled. Ice particles with a size range of 20 μm and smaller grow only by water vapour diffusion and there is a negligible probability that they scavenge aerosol particles by impaction and riming. The released residual particles by the Ice-CVI can be interpreted as the original ice nuclei. This is discussed in detail in Mertes et al. (2007) and references therein. According to the data of Fukuta and Takahashi (1999), an ice crystal of 20 μm diameter is clearly in the diffusion growth regime and has been growing for about 20 seconds. Thus the assumption that the ice formation has occurred in the vicinity of the laboratory is well justified.

Page 4/5 line 31 – 2.

It would be better if the authors did not readily presume that the ice formation was due to ice nucleation, but rather discuss possible ice formation and particle inclusion pathways. Remove the extended discussion of ice nucleation mechanisms in the introduction as this is beyond the scope of the current study. Rather, state two main pathways for ice formation from single particles (heterogeneous nucleation and homogeneous freezing) and focus on how composition affects these two paths. The finding that organics may dominate heterogeneous nucleation at warmer temperatures is an interesting finding and is consistent with the finding of Tobo et al. (2014) which discusses the role of soil organic matter in ice nucleation. It would be worthwhile to include this in the discussion.

In our opinion the discussion of the ice nucleation mechanisms is not “extended”. We only mentioned the four different ice formation modes. Homogeneous freezing does not play a role in mixed-phase clouds in our case, because of the “high” temperatures during the campaign. Homogeneous freezing starts at temperatures about -37°C. During the measurement campaign the ambient temperatures were not lower than -30°C.

The finding of Tobo et al. (2014) is very interesting and will be included in the discussion.

Page 15 line 30 – 33.

Finally, given the issues with measuring size distribution and the unnecessary assumption that all IPR are IN, remove the discussion of ice active sites on pp. 4698-4699. This discussion seems tangential to the focus of the study, has no impact on the conclusions (this is not even mentioned) and is purely speculative.

We removed the discussion about the ice active sites.

Compositional Analysis

In section 2.2 line 18, the authors state clearly that the analysis using the ALABAMA mass spectrometer excludes negative ions. This is an important fact and it is good that the authors provided this information. However, this fact seems to play an important role in the clustering algorithms as the particle classification of BioMinSal is broad and ambiguous, potentially covering a range of different types of particles central to heterogeneous ice nucleation.

Yes, it is true that the classification of the BioMinSal-type is broad. The spectra we assigned to this type contain only metal cations, but the source of these ions is unclear. For example, some spectra contain large peaks at m/z 39 (K^+) and m/z 23 (Na^+). Our (and other) lab studies show that these two ions (or even just one large potassium peak) can present spectra from soil and dessert dust, minerals, biological particles, cigarette smoke particles and biomass burning particles. Without anion mass spectra, this particle type cannot be classified in more detail.

In section 2.6.3 covering the classification of industrial metals, the authors state that the signature of the particles may in fact be due to contamination from the stainless steel tubes, but “due to not clear evidence”, these particles were not excluded (pg. 4688, lines 18-19). This statement is vague at best; the authors should include clear rationale for including these

particles, stating exactly what “clear evidence” would be and how these spectra did not exhibit contamination.

Due to the low flow speed and laminar flow conditions in our sampling tubes we can exclude abrasion of material by collision with aerosol particles and the flow tubes wall. Possible sources for steel contamination particles are only opening and closing of the valves. Thus, detection of such “industrial metal” particles within a few seconds after opening/closing the valves can be seen as “clear evidence” for contamination. However, during these time periods no particles were found in the industrial metal cluster and therefore no particles were excluded as contamination.

Page 11 line 3 – 9.

Finally, the authors make the statement in the ALABAMA data evaluation section that the “error limits of the number of mass spectra per particle types was estimated using counting statistics.” This statement in and of itself is ambiguous such that it appears to be quite meaningless. Are the authors implying that the results are quantifiable in the sense that the number of particles measured with a particular mass spectra is representative of the ambient population? According to Murphy (2007), what is measured will be heavily dependent on a number of factors related to particles sampled as well as the instrument itself. If the authors intend to suggest that the relative fractions observed by the mass spectrometer are representative of the relative fractions in the IPR, then they should state clearly why the “counting statistics” matter and how they came about the uncertainties. But, I would suggest that it is sufficient to simply state how many particles of a particular cluster type were observed.

The number of particles referring to each bar was already given in the table above the figure. Counting statistics in our case refers to the Poisson statistics of small numbers, such that the uncertainty equals \sqrt{N} . Such an error estimation is important to show significant statistic differences between, e.g., relative composition of IPR and of out-of-cloud aerosol. But we exclude the error bars from the figures.

Meteorology

Although meteorology will play an important role in the interpretation of results, there is little space given to a discussion of the meteorology at the lab during this campaign. The classification of meteorology during sampling into ++ and +- events is broad and should be further refined. The statement on pg. 4690, lines 14 and 15 that ++ events measured mainly ice nuclei is purely speculative. And the observation during +- events, samples could be contaminated by fragmentation (line 16) is quite disconcerting as this can have a large impact on the observations downstream. In fact, the larger portion of sampling periods appear to occur in this +- regime and therefore calls into question the disproportionate influence of these artifacts on total observations.

Indeed, the indicated text passage is somewhat misleading. The intention was to say that the (++)-events are mainly free from precipitation and blown snow, so that the sampling of small secondary ice particles (Ice-CVI sampling range 5 to 20 μm) from crystal-crystal collisions

that do not contain the original INP is negligible. As a consequence primary ice particles are mainly sampled that have grown only by water vapor diffusion in this size range, which means that the residual particle can be attributed to the original INP.

For the (+-)-events the presence of small secondary ice cannot be totally ruled out, since higher wind speeds for the production of blown snow and precipitation occurred. Sampled small secondary ice particles do also release a residual particle during the evaporation inside the CVI, which has nothing to do with the INP (scavenged interstitial particles or condensation of CCN substances that were solved inside supercooled drops before freezing or riming). Thus, these residual collections and analysis has to be treated with more caution in the interpretation. However, these residuals are mostly smaller than 100 nm and can therefore be separated from the original INPs, which are known to be much larger.

These definitions of (++)- and (+-)-events is now better described in the revised manuscript. Page 12 line 16 – 26.

Due to closer consideration of the (++)- and (+-)-events and taking into account that the ALABAMA did not measure the whole cloud event at the Ice-CVI we get a new classification with more (++)-events which are now called (++)/(+-)-sampling-periods (Table 1).

Meteorological data (average temperature, wind direction, wind speed and cloud formation) are given in Table 1.

Further, one aspect related to the location of the laboratory is never even broached. At the altitude of Jungfraujoch, it seems likely that the laboratory will be in different portions of the atmosphere during different periods (i.e. boundary layer or free troposphere). Yet, the authors never discuss this and the impact the location has on the results.

The origin of the air masses was investigated by back-trajectory analysis. Figure 5 clearly shows that during the same cloud event air masses arrived both from the boundary layer as from the free troposphere. However, the low number of IPR per cloud event does not allow for a more detailed analysis of IPR composition as a function of origin.

For out-of-cloud aerosol the situation is different: A comparison for out-of-cloud aerosol is shown in Figure 9. Here during one event the air masses have a clear boundary layer origin, while during the other event the air is mainly from free tropospheric origin. We added some discussion on this point to the manuscript in section 3.4.

Page 18 line 4 – 16.

Minor Concerns

- The authors use the acronym INP for ice nucleating particles. To be consistent with the existing literature, this should be ice nuclei, or IN.

In the INUIT community it was decided to follow the nomenclature suggested by Vali et al. (2014). Vali et al. (2014) clearly favor the use of INP for “ice nucleating particles” instead of IN for “ice nucleus”. (“Since ice nucleation is more complicated than condensation, due to the different modes it can follow, using “ice nuclei” in the

general sense similar to “condensation nuclei” is overly ambiguous and can misleading.”)

- Pg. 4681, line 1 – “replace have good ice nucleating capabilities” with “are ice nuclei”
It was replaced
Page 3 line 23
- Pg. 4682, line 25 – “critical nozzle” should be “critical orifice” to maintain consistency with references within the manuscript as well as the literature.
“critical nozzle” was changed to “critical orifice”.
Page 5 line 13.
- Pg. 4685, line 7 – typo, line should read “in order to prevent”
It was changed.
Page 7 line 18.
- Pg 4685, lines 10-12 – Expand on how the WBF process is used to remove supercooled drops. Also, provide more detail concerning the “custom built chamber”.
The WBF process is used by deploying a chamber with ice-coated inner walls within the ISI, thus providing an environment in which there is saturation with respect to ice. This in turn means that there is sub-saturation with respect to water (due to the difference in saturation vapour pressures over water and ice), which leads to evaporation of liquid droplets inside the chamber and transfer of water vapour from the droplets to the ice-coated walls of the chamber. The design of the chamber is described in detail in Sect. 2.2 of Kupiszewski et al. (2014). This is now explained in the manuscript. Page 7 line 24 – 30.
- Pg 4685, lines 23-24 – Provide references for the PPD and WELAS.
References for the PPD and WELAS are included.
Page 8 line 7 and 8.
- Pg 4688, line 23 – typo; should read “unambiguously”.
It was changed to “unambiguously”
Page 11 line 12.
- Pg 4690, lines 13-14 – Mentions “sampling efficiency and properties of the Ice-CVI”, but this not discussed in detail anywhere in the manuscript.
This remark of the reviewer is not only justified, moreover the wording in this text passage is unfavorably chosen. The sampling properties or better sampling methodology is now explained in much more detail in section 2.3 and the meaning of the cloud event classification, which is related to the Ice-CVI sampling method is now discussed in the text passage indicated by the reviewer.
Page 6 line 24 – 32.

- Pg 4691, lines 26-29 – The manuscript states that back trajectories “were calculated with CRISP”, but section 2.6 states CRISP is used to retrieve information concerning single particles, so the authors need to explain exactly what they mean by this given that the HYSPLIT code actually generates the back trajectories using particular meteorological data set.

The software package CRISP was used to evaluate the data and to compile backward trajectories with access to HYSPLIT. In CRISP the start parameter of the trajectories were given and printed in a map. The backward trajectory itself was calculated with HYSPLIT. To clarify we replace “calculated” with “compile”.

Page 13 line 30.

- Pg 4691, line 24 – typo; “such that also...” should read “such that...”
“Also” was removed.
- Pg. 4692, line 17 – typo; “is one of the ...” should be “are two of the...”
It was changed.
Page 14 line 17.
- Pg. 4694, lines 17-20 – This sentence is a mess and it is difficult to determine what exactly the authors are trying to say. Reword for clarity.
To make it more clearly we rearranged this paragraph.
Page 16 line 16 – 27.
- Pg. 4697, line 3 – typo; sentence should start “In Figure 10c...”
We added an “in”
Page 17 line 19.
- Pg. 4699 line 25 – typo; The meaning of this sentence is unclear. What does it mean to have results that “comply with previous investigations”?
We mean that the results agree with previous measurements. We changed “comply” to “agree”
Page 21 line 9.

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In-situ single submicron particle composition analysis of ice residuals from mountain-top mixed-phase clouds in Central Europe

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Abstract

Ice nucleating particles have a high impact on ice crystal formation in clouds and thereby on precipitation and the global radiation budget. Because the chemical composition of these particles plays an important role at the nucleating processes, investigation of the chemical composition of ice nucleating particles is a topic of current research. This paper presents results from the “INUIT/CLACE 2013” (Cloud and Aerosol Characterization Experiment) field campaign at the high alpine research station Jungfraujoch in January/February 2013. The chemical composition of ice particle residuals (IPR) was measured in orographic, convective and non-convective clouds. The submicron particles were analyzed by a single particle mass

1 spectrometer (ALABAMA) under ambient conditions characterized by temperatures between
2 $-28\text{ }^{\circ}\text{C}$ and $-4\text{ }^{\circ}\text{C}$ and wind speed from 0.1 m s^{-1} to 21 m s^{-1} . Additionally, background aerosol
3 particles in cloud free air were investigated. The IPR were sampled from mixed-phase clouds
4 with two inlets which selectively extract small ice crystals in-cloud, namely the Counterflow
5 Virtual Impactor (Ice-CVI) and the Ice Selective Inlet (ISI). The IPR as well as the aerosol
6 particles were classified into seven different particle types: (1) black carbon, (2) organic
7 carbon, (3) black carbon internally mixed with organic carbon, (4) minerals, (5) one particle
8 group (termed “Bio/Min/Sal”) that may contain biological particles, minerals, or salts, (6)
9 industrial metals, and (7) lead containing particles. For any sampled particle population it was
10 determined by means of single particle mass spectrometer how many of the analyzed particles
11 belonged to each of these categories. Accordingly, about 30 % of the IPR and roughly 43 %
12 of the background particles contained organic carbon. The measured fractions of minerals in
13 the IPR composition varied from 10 % to 14 %, while the values for the “Bio/Min/Sal” group
14 were between 20 % and 54 %. Two percent to 20 % of the IPR contained organic carbon
15 mixed with black carbon. Both inlets delivered similar results of the chemical composition
16 and of the particle size distribution, although lead was found only in the IPR sampled by the
17 Ice-CVI. The results show that the ice particle residual composition varies substantially
18 between different cloud events, which indicates the influence of different meteorological
19 conditions, such as origin of the air masses, temperature and wind speed.

20

21 1 Introduction

22 Ice formation in clouds influences the life-time of clouds, the formation of precipitation, and
23 the Earth’s solar and thermal radiation budget (Lohmann and Feichter, 2005). There are two
24 major pathways by which ice is formed in the atmosphere: homogeneous and heterogeneous
25 freezing. The spontaneous formation of ice inside droplets at temperatures of lower $-37\text{ }^{\circ}\text{C}$
26 and without any catalysts is called homogenous freezing (Cantrell and Heymsfield, 2005) and
27 occurs in high clouds at a saturation similar to that of liquid water (Koop et al., 2000).
28 Heterogeneous freezing needs particulate catalysts to initiate freezing at temperatures higher
29 than $-37\text{ }^{\circ}\text{C}$ in mixed-phase clouds. These catalysts are called ice nucleating particles (INP).
30 There are four different heterogeneous ice formation modes (Pruppacher and Klett, 2010):
31 deposition nucleation, condensation freezing, immersion freezing and contact freezing.
32 Because heterogeneous freezing starts at higher temperatures than homogeneous freezing, ice
33 crystals, which are formed by ice nucleating particles grow faster (by diffusion) and perhaps
34 precipitate first (DeMott et al., 1998). Another reason for faster formation of precipitation is

1 the Wegener-Bergeron-Findeisen process, which plays an important role on cloud formation
2 and precipitation, especially in mixed-phase clouds. In mixed-phase clouds, where
3 supercooled droplets and ice crystals exist, the supercooled droplets evaporate and the water
4 vapor freezes on the ice crystals. Because of the lower saturation vapor pressure over ice than
5 over water the ice crystals will grow at the expense of cloud droplets. This results in a quick
6 freezing of the supercooled water cloud. These iced clouds have a shorter lifetime than
7 supercooled water clouds, because the precipitation formation via the ice phase is more
8 efficient than in warm clouds (Lohmann and Feichter, 2005).

9 Ice formation is very selective because of the low number concentration of particles that can
10 act as INP. Roughly about one in 10^5 atmospheric particles can act as INP (Rogers et al.,
11 1998; DeMott et al., 2010). The ice nucleation is induced at some point on the surface of the
12 nucleating particle and the ice nucleation ability of different types of aerosol particles is
13 usually described either by an ice active-site density approach or by classical nucleation
14 theory involving a contact angle (see e.g. Steinke et al., 2015, and references therein). Several
15 laboratory, field and model studies (DeMott et al., 2003a; DeMott et al., 2003b; Cantrell and
16 Heymsfield, 2005; Kamphus et al., 2010; Hoose et al., 2010; Hartmann et al., 2011; Murray et
17 al., 2011; Hoose and Möhler, 2012; Murray et al., 2012; Atkinson et al., 2013; Diehl et al.,
18 2014) have shown that certain mineral dusts belong to the most important ice nucleators in the
19 atmosphere because of their high abundance. On the other hand, biological particles like
20 bacteria, pollen and spores (e.g. Diehl et al., 2001; von Blohn et al., 2005; Möhler et al., 2007;
21 Pratt et al., 2009; Prenni et al., 2009; Diehl and Wurzler, 2010) are the most efficient ice
22 nuclei (Hoose et al., 2010). Also soot (e.g. Cozic et al., 2008a; Pratt and Prather, 2010; Pratt et
23 al., 2010) and effloresced salts (Abbatt et al., 2006; Wise et al., 2012) have been found to act
24 as ice nuclei. There is also some evidence that glassy organics (Froyd et al., 2010; Murray et
25 al., 2010), porous particles (Adler et al., 2013) and lead-containing particles (Cziczo et al.,
26 2009; Ebert et al., 2011) have favorable ice nucleation qualities.

27 Direct measurements of the chemical composition of single INP or IPR (Ice particle residuals
28 = particles remaining after the ice of cloud ice particles is evaporated) are important to better
29 understand ice formation in mixed-phase clouds, to improve the prediction of precipitation,
30 and to evaluate the influence of anthropogenic aerosol on these processes. Measurements of
31 INP/IPR require instrumentation that can separate the INP/IPR from the background or
32 interstitial aerosol particles and supercooled drops and measure the chemical composition on-
33 line. In several field studies a combination of a CFDC (Continuous Flow Diffusion Chamber;

1 Chen et al., 1998), a CVI (Counterflow Virtual Impactor; Cziczo et al., 2003; Mertes et al.,
2 2007) which separates the ice crystals from background aerosol and a Single Particle Mass
3 Spectrometer (SPMS; DeMott et al., 2003a; Cziczo et al., 2003; Cziczo et al., 2004a; Cziczo
4 et al., 2004b; Pratt et al., 2009; Corbin et al., 2012) to measure ice nucleating particles were
5 deployed. Previous measurements of INP and IPR (on-line and off-line) conducted at the
6 Jungfraujoch showed that particles consisting of mineral components dominate the ice
7 particles number (Kamphus et al., 2010), but also particles containing black carbon (Mertes et
8 al., 2007; Cozic et al., 2008a) and lead (Cziczo et al., 2009; Ebert et al., 2011) were found to
9 be enriched in IPR.

10 Here we report on measurements conducted with the single particle instrument ALABAMA
11 (Aircraft-based Laser Ablation Aerosol Mass Spectrometer; Brands et al., 2011) to analyze
12 the chemical composition of IPR sampled by two unique different ice sampling inlets. The
13 goal of these measurements was to investigate the chemical composition of IPR in ambient
14 mixed-phase clouds in upward transported boundary layer air and free tropospheric air at the
15 high-alpine research station Jungfraujoch (JFJ; 3580 m asl) in Central Europe. Additionally,
16 background aerosol was measured by the use of a total inlet during cloud free conditions.

17

18 **2 Experimental**

19 **2.1 Measurement location and meteorological conditions**

20 The intensive field campaign INUIT-JFJ/CLACE 2013 in January/February 2013 at the High
21 Alpine Research Station Jungfraujoch (JFJ, Swiss Alps; Sphinx Laboratory, 3580 m asl;
22 7°59'2''E, 46°32'53''N) took place in the framework of the DFG (Deutsche
23 Forschungsgemeinschaft)-funded research unit INUIT (Ice Nuclei research UnIT) and the
24 Swiss National Science Foundation-funded *Interaction of aerosols with Clouds and Radiation*
25 *project* (see also overview paper by Schneider et al., this issue). The IPR were sampled out of
26 mixed-phase clouds by the Ice-CVI (Ice Counterflow Virtual Impactor; Mertes et al., 2007)
27 and the ISI (Ice Selective Inlet; Kupiszewski et al., 2014) and fed into the ALABAMA single
28 particle mass spectrometer (Brands et al., 2011). During cloud free times the ALABAMA was
29 connected to the heated total inlet (20 °C; Weingartner et al., 1999) to sample the background
30 aerosol particles. The Ice-CVI and the total inlet were located in a central position on the roof
31 of the Sphinx Laboratory and the ISI was located at the railing at the eastern edge of the roof.
32 A short description of the instruments is given in Sections 2.2 to 2.5. Both the Ice-CVI and
33 ISI sample only ice crystals smaller than 20 μm. Such small ice crystals have grown only by

1 water vapor diffusion and have an age of less than about 20 seconds (Fukuta and Takahashi,
2 1999). It is therefore very likely that these ice crystals have formed in the vicinity of the inlets
3 and that the IPR extracted from such fresh ice crystals corresponds to the original IPN. The
4 meteorological conditions during the campaign along with basic information on the
5 encountered cloud types are summarized in Table 1.

7 **2.2 ALABAMA (Aircraft-based Laser Ablation Aerosol MAss spectrometer)**

8 The ALABAMA (Brands et al., 2011) consist of three sections: aerosol inlet, sizing region
9 and desorption/ionization region. The aerosol inlet is an aerodynamic lens (Liu-type; Liu et
10 al., 1995b; Liu et al., 1995a; Liu et al., 2007; Kamphus et al., 2008) which focuses aerosol
11 particles to a narrow beam by utilizing 6 apertures with decreasing diameter. The particles are
12 separated from ambient air and accelerated to $50 - 100 \text{ m s}^{-1}$, while entering the vacuum-
13 system. For optimal sampling conditions the pressure in front of the aerodynamic lens should
14 be between 0.5 hPa and 5 hPa. For this, a critical orifice is used, which limits the flow to
15 $80 \text{ cm}^3/\text{min}$ under standard working conditions and which reduces the pre-pressure of the lens
16 to 3.8 hPa. During this campaign, the critical orifice was constructed by a constricted O-ring
17 such that also under Jungfraujoch conditions (ambient pressure around 630 hPa) the lens
18 pressure was regulated to best operating conditions. A skimmer separates the first and the
19 second pumping stages. Two continuous wave detection lasers, which are orthogonal to the
20 particle beam, are located in the second pumping stage. As a modification of the instrument
21 described in Brands et al. (2011), two UV laser diodes (Blu-Ray laser; InGaN, 405 nm) are
22 now used. The particles pass through the laser beams and the scattered light is reflected by an
23 elliptical mirror and detected by a photomultiplier tube (PMT). The vacuum aerodynamic
24 particle size (DeCarlo et al., 2004) can be determined from the velocity of the particles by
25 calibration with particles of known size. In this section the ablation laser (pulsed Nd-YAG-
26 Laser, 266 nm; 6 – 8 mJ per pulse, 5.2 ns per pulse, max. 21 Hz) is triggered. If one particle
27 passes through both laser beams, the in-house designed and built electronic control system
28 sends out a trigger signal to the ablation laser, the laser shoots and ionizes the particles. The
29 ions are separated in the Z-shaped bipolar time-of-flight mass spectrometer (TOFWERK AG,
30 Switzerland) by their mass-to-charge ratio. In principle both signals (for positive and negative
31 ions) can be detected using a multichannel plate (MCP). However, for this study only positive
32 ions were available due to technical issues. The average mass resolution $m/\Delta m$ of the Z-ToF
33 mass spectrometer ranges between 100 for low m/z values and 200 for larger ions (Brands et
34 al., 2011). The ALABAMA covers a size diameter range from 100 to 3000 nm (see Fig. 10)

1 with the most efficient size diameter range being between 200 nm and 900 nm. Particles in the
2 size diameter range of approximately 400 nm were ionized at best.

3 Additionally the particle size distribution was measured by a Sky-OPC (Optical Particle
4 Counter; Grimm 1.129) with size diameter range from 0.25 to 52 μm . The Sky-OPC is
5 integrated into the ALABAMA instrument upstream of the aerodynamic lens. Due to the size
6 limitation by the inlet system a maximum particle size of approximately 3 μm was measured.
7 Both instruments sampled through ¼" stainless steel tubes with different lengths (ISI =
8 370 cm; Ice-CVI = 126 cm; total = 261 cm). Particle losses inside the sampling tube were
9 calculated with the Particle Loss Calculator (von der Weiden et al., 2009). In the size range
10 between 200 nm and 500 nm the transmission efficiency is about 99 % for all three inlets. The
11 larger the particles and the longer the tubes, the higher are the losses inside the tubes. For a
12 size of 3 μm the transmission efficiency is between 90 % (tube to the Ice-CVI with a length of
13 126 cm) and 45 % (tube to the ISI with a length of 370 cm). The switching between the three
14 different inlets was performed manually.

16 2.3 Ice-CVI (Ice Counterflow Virtual Impactor)

17 The Ice-CVI is designed to sample IPR from mixed-phase clouds. A detailed description and
18 instrumental characterization is provided in Mertes et al. (2007) thus it is only briefly
19 described here. The Ice-CVI uses an omnidirectional inlet, which removes particles larger
20 than 20 μm from the aspired air. The separation of the particles larger than 20 μm out of the
21 sample flow is done with a virtual impactor (VI) downstream of the inlet. After that the
22 supercooled droplets ($> 5 \mu\text{m}$) are removed by a pre-impactor (PI). The PI consists of
23 impaction plates colder than 0 °C. The supercooled droplets freeze on these plates upon
24 contact while the ice crystals bounce off and remain in the sample flow. Subsequently, a
25 counterflow virtual impactor (CVI, Mertes et al., 2005) rejects interstitial aerosol particles,
26 and potentially remaining supercooled drops and ice particles smaller than 5 μm . Thus, all
27 supercooled drops are pre-segregated by the cut-off behavior of PI and CVI and only small ice
28 crystals, i.e. those with aerodynamic size diameters between 5 μm and 20 μm (cut-off
29 properties of VI and CVI) remain in the sample flow. A transmission efficiency of the PI
30 concerning supercooled drops and ice particles of about 0 % and 100 %, respectively, as
31 expected from Tenberken-Pötzsch et al. (2000) and Murphy et al. (2004), was shown by
32 Mertes et al. (2007).

1 For complete sublimation, the small ice particles are injected into particle-free and dry carrier
2 air inside the CVI. The aerosol particles that remain after evaporation/sublimation of the ice
3 are termed IPR. The walls of the evaporation tube as well as the carrier air are at room
4 temperature. The IPR can be transferred to different aerosol instruments for physico-chemical
5 characterization. The sampling principle of the CVI leads to an enrichment of the collected
6 particles. This enrichment (factors between 5 and 10) is given by the ratio of the velocity
7 upstream and downstream the CVI inlet tip.

8 A CPC (Condensation Particle Counter, model 3010, TSI Inc.) was connected downstream of
9 the Ice-CVI at a suitable position for measuring to determine the total particle number
10 concentration of the IPR. Significant non-zero particle number concentrations indicate the
11 presence of ice particles in mixed-phase clouds.

12

13 **2.4 ISI (Ice Selective Inlet)**

14 Extracting IPR from mixed-phase clouds was also possible with the ISI (detailed description
15 in Kupiszewski et al., 2014). Small ice crystals (the IPR within are assumed to be
16 representative of the original ice nuclei) are segregated from larger ice crystals, supercooled
17 droplets and interstitial aerosol particles by a combination of four inlet components. The first
18 component is the omnidirectional inlet, which is shielded from above **in order to prevent** large
19 precipitating particles entering the inlet. Subsequently, a custom-made cyclone (BGI Inc.)
20 removes ice crystals, with aerodynamic diameters of ca. 20 μm (D_{50} cut size, i.e., the particle
21 diameter at which 50 % of incoming particles are removed from the sample flow) and larger.
22 Further downstream the removal of supercooled droplets takes place in a custom built ice-
23 coated droplet evaporation chamber using the Wegener-Bergeron-Findeisen (WBF) process.
24 **The WBF process is used by deploying a chamber with ice-coated inner walls within the ISI,**
25 **thus providing an environment in which there is saturation with respect to ice. This in turn**
26 **means that there is sub-saturation with respect to water (due to the difference in saturation**
27 **vapour pressures over water and ice), which leads to evaporation of liquid droplets inside the**
28 **chamber and transfer of water vapour from the droplets to the ice-coated walls of the**
29 **chamber. The design of the chamber is described in detail in Sect. 2.2 of Kupiszewski et al.**
30 **(2014).** The key difference to the Ice-CVI is that here the separation of supercooled droplets
31 from ice crystals is conducted in the airborne state via evaporation. Finally, the interstitial
32 aerosol and the cloud condensation nuclei (CCN) released during droplet evaporation are
33 removed by a pumped counterflow virtual impactor ($D_{50} \approx 5 \mu\text{m}$). The extracted ice crystals

1 with aerodynamic diameter between 5 μm and 20 μm are heated and the released IPR are
2 transferred into the laboratory for physical and chemical characterization using state of the art
3 single particle aerosol instrumentation (single particle soot photometer (SP2), ALABAMA
4 single particle mass spectrometer, Wideband Integrated Bioaerosol Sensor (WIBS) and a
5 Grimm optical particle counter). The ISI additionally allows for simultaneous counting, sizing
6 and imaging of the hydrometers contained in the cloud with the use of two WELAS (white
7 light aerosol spectrometer; Heim et al., 2008; Rosati et al., 2015) aerosol sensor system (Palas
8 GmbH) and a Particle Phase Discriminator (PPD; Kaye et al., 2008; Vochezer et al., 2015).
9 These are placed behind the cyclone (first WELAS OPSS) as well as behind the droplet
10 evaporation unit (second WELAS OPSS and PPD). The ISI, together with the downstream
11 aerosol instrumentation, thus provides number size distribution of sampled hydrometers and
12 aerosol particles, information on ice crystal shape and surface roughness, as well as number
13 size distribution and chemical composition of ice residual particles.
14 The ISI enriches the collected particles inside the pumped counterflow virtual impactor with
15 an enrichment factor between 1 and 10.

16

17 **2.5 Supplement instruments**

18 **Particle Volume Monitor (PVM; Gerber, 1996):** The PVM measured the liquid water
19 content (LWC = total liquid water present in a cloud) and the surface area of cloud droplets
20 (e.g., Wendisch, 1998). Cloud droplets cross a laser beam and the scattered light is measured.
21 Elevated LWC values are used to identify cloud events, using a threshold value of 20 mg m^{-3} .
22 During the measurement campaign two PVMs were operated by PSI (Paul Scherrer Institute)
23 and the University of Manchester.

24

25 **Cloud Droplet Probe (CDP):** The CDP is a forward-scattering spectrometer for
26 determination of particles sizes and concentrations of cloud droplets. Counting and sizing of
27 the particles is done by detecting light scattered by the particles (for more details see for
28 example Lance et al., 2010).

29

30 **Scanning electron microscopy (SEM):** Ice particle residuals (IPR) were collected by a two
31 stage impactor system (50 % cut-off aerodynamic diameters 1.0 and 0.1 μm , respectively) on
32 transmission electron microscopy grids and elemental boron substrates and analyzed by
33 scanning electron microscopy (SEM, FEI Quanta 200 FEG, FEI Eindhoven, the Netherlands)
34 and energy-dispersive X-ray fluorescence (EDX, EDAX, Tilburg, The Netherlands) to

1 characterize the particles with regard to their chemical composition, morphology, size,
2 internal mixing state and electron beam stability (volatility). (For further details see Kandler
3 et al., 2011). Here we only present the size distribution of IPR measured by SEM and
4 compare them to the IPR sizes obtained by the ALABAMA and the Sky-OPC. Detailed
5 results on the chemical composition analysis of IPR, INP, and background aerosol by SEM
6 are given in Worringer et al., 2015.

7

8 **2.6 ALABAMA data evaluation**

9 The data evaluation was done with the software package CRISP (Concise Retrieval of
10 Information from Single Particles; Klimach, 2012) based on the software IGOR Pro (Version
11 6, WaveMetrics) and following the procedure described in Roth (2014). This software
12 package includes mass calibration, conversion of the mass spectra into ‘stick’ spectra by
13 integration over the peak width, and various procedures to sort the mass spectra into groups or
14 clusters of similar spectra. This sorting can be done manually, by means of cluster algorithms
15 (*fuzzy c-means* or *k-means*), or by searching for certain parameters (e.g., ion signals at a
16 certain m/z ratio).

17 The Clustering depends to some degree on the interstitial settings of the algorithm and its
18 parameters. The start parameters are *Normalization type and time*, *Preprocessing type*,
19 *Initialisation type*, the *number of clusters* and the *start cluster difference*. Using the *fuzzy c-*
20 *means* algorithm (e.g. Bezdek et al., 1984; Hinz et al., 1999; Huang et al., 2013) the
21 parameters *fuzzifier* and *fuzzy abort* have to be set accordingly. The cluster parameters are
22 explained in detail in the appendix.

23 As only the cations were detected during the INUIT-JFJ/CLACE 2013 campaign the grouping
24 of the clusters into different particle types by using certain marker peaks was difficult in some
25 cases. At the end, seven different particles types were extracted: black carbon (BC), organic
26 carbon (OC), internal mixture of black carbon and organic carbon (BC/OC), lead containing
27 particles, industrial metals, **Bio/Min/Sal** (containing possibly bioparticles, minerals or salts),
28 and minerals. The average mass spectra of each particle type are shown in Figure 1. The
29 association of the mass spectra to the individual particle types is explained in detail below.
30 The error limits of the number of mass spectra per particle types was estimated using counting
31 statistics.

32 *Organic fraction: Black carbon (BC) and organic carbon (OC)*

1 The clusters categorized as BC are due to the presence of the typical fragmentation of C_n^+
2 (Dall'Osto et al., 2004; Pratt and Prather, 2010) of higher mass-to-charge ratios (see Fig. 1a).
3 In comparison to the black carbon, the organic carbon cluster (Fig. 1b) shows different
4 fragmentations of aromatics ($[C_4H_3]^+$ (m/z 51); $[C_5H_3]^+$ (m/z 63); $[C_6H_5]^+$ (m/z 77); $[C_7H_7]^+$
5 (m/z 91) (Dall'Osto and Harrison, 2006; Pratt and Prather, 2010)), amines ($[CHN]^+$ (m/z 27);
6 $[C_3H_8N]^+$ (m/z 58) (Pratt and Prather, 2010)) or other organic material ($[C_2H_3]^+$ (m/z 27);
7 $[C_3H]^+$ (m/z 37); $[CH_3O/CHNO]^+$ (m/z 43); $[C_4H_2/C_3N]^+$ (m/z 50); $[C_3H_7O]^+$ (m/z 59);
8 $[C_{11}H_{10}/C_8H_{16}NO]^+$ (m/z 142) (Pratt and Prather, 2010)). Black carbon internally mixed with
9 organic (BC/OC) shows both fragmentation types of $[C_n]^+$ and $[C_nH_mNO]^+$ (Corbin et al.,
10 2012; Fig. 1c).

11 Closer consideration of the three different carbon clusters (BC, BC/OC, OC) shows that
12 potassium is present in nearly every mass spectrum in the background aerosol. In the
13 background aerosol 45282 mass spectra including black or organic carbon were measured:
14 92 % of all these mass spectra show potassium. The BC-type includes the mass spectra
15 without potassium (20 %; only 1 % in the OC/BC-type and 6 % in the OC-type). The same
16 observation holds for the IPR composition measured using the Ice-CVI (Section 3.1): The
17 particle types including organic carbon show more spectra including potassium (91 % of all
18 OC and OC/BC). In contrast to that the particle type including organic carbon measured while
19 using the ISI show more spectra without a high potassium peak (77 %). Previous
20 investigations show that the presence of high potassium peak in the mass spectra in
21 combination with organic carbon is a marker for biomass burning (e.g. Pratt and Prather,
22 2010; Twohy et al., 2010; Corbin et al., 2012) or biogenic aerosol (e.g. Trimborn et al., 2002;
23 Pratt and Prather, 2010). However, because only cations were measured during this
24 experiment, spectra with a potassium peak mixed with BC and OC cannot clearly assigned to
25 biomass burning or biological particles.

26 *Lead containing particles*

27 Previous measurements at the Jungfraujoch showed that lead-containing particles can be
28 found in IPR (Cziczo et al., 2009; Ebert et al., 2011). The cluster of lead containing particles
29 shows the typical isotope pattern of lead (m/z 208, 207, 206, 204; Fig. 1d).

30 *Industrial metals*

31 The cluster classified as 'industrial metals' (Fig. 1e) shows metal signals from anthropogenic
32 (urban/industrial) emissions like $[Cr]^+$ (m/z 52, 53, 54, 50), $[Co]^+$ (m/z 59), $[V]/[VO]^+$ (m/z

1 51/67), [Fe]⁺ (m/z 54, 56), [Mn]⁺ (m/z 55), [Ni]⁺ (m/z 58, 60, 61, 62) and [Zn]⁺ (m/z 64, 66,
2 68) (de Foy et al., 2012). Chromium and nickel containing particles might also be due to
3 contamination from stainless steel tubes. However, due to the low flow speed and laminar
4 flow conditions in our sampling tubes we can exclude abrasion of material by collision of
5 aerosol particles with the flow tube walls. Possible sources for steel contaminations particles
6 are only opening and closing of the valves. Thus, detection of such “industrial metals”
7 particles within a few seconds after opening/closing of a valve indicates contamination
8 artifacts. However, during these time periods no particles of the type “industrial metals” were
9 detected and therefore no particles were excluded as contamination.

10 *Bio/Min/Sal cluster*

11 The spectra in this cluster type contain only metal cations and can therefore not be
12 unambiguously be assigned to a certain particle type. The spectra in the *Bio/Min/Sal* cluster
13 show a mixture or single signals of [Na]⁺ (m/z 23), [Al]⁺ (m/z 27), [K]⁺ (m/z 39, 40), [Ca]⁺
14 (m/z 40) and/or [Fe]⁺ (m/z 54, 56). An example of an average spectrum of this particle type is
15 shown in Figure 1f.

16 The interpretation of this particle cluster is difficult. The signals are most likely cations of
17 different kinds of salts (K₂SO₄ or KNO₃ are more conceivable than sea salt), minerals or
18 primary biological particles, but without corresponding anion an unambiguously assignment
19 to one particle type is not possible. Previous investigations of biological aerosol have shown
20 that metal signals like [Na]⁺ (m/z 23), [K]⁺ (m/z 39) or [Ca]⁺ (m/z 40) dominate the cation
21 spectra (e.g. Frank et al., 2011; Pratt and Prather, 2010; Ferguson et al., 2004). During
22 laboratory studies with test aerosol we also observed mainly single metal signals of sodium
23 and potassium in biological particles, but as well in mineral dust particles. Also iron (Fe⁺ m/z
24 54, 56), which is a typical marker for mineral dust, was observed to occur in some biological
25 particles (maybe due to hemoglobin or due to other ions with an m/z of 56). For these reasons
26 the cluster “*Bio/Min/Sal*” cannot be further differentiated in this study.

27 *Minerals*

28 Typically marker peaks of minerals are: [Li]⁺ (m/z 6, 7), [Mg]⁺ (m/z 24, 25), [Al]⁺ (m/z 27),
29 [Si]/[SiO]⁺ (m/z 28, 29, 30/44), [Ca]⁺ (m/z 40), [Ti]/[TiO]⁺ (m/z 48, 46, 47, 49, 50/64) and/or
30 [Fe]⁺ (m/z 54, 56) (Trimborn et al., 2002; Dall'Osto et al., 2004; Dall'Osto et al., 2010)
31 Clusters containing at least three of the above marker peaks were classified as *minerals* (Fig.
32 1g).

1 *Others*

2 The cluster *others* includes all particle mass spectra, which are very noisy or could not be
3 unambiguously assigned to any of the above cluster types.

4

5 **3 Results and Discussion**

6 During the INUIT-JFJ/CLACE 2013 campaign we measured 71064 background aerosol
7 particles during a measurement time of 217 h and 1803 ice particle residuals during a
8 measurement time of 342 h: 1659 spectra behind the Ice-CVI during 273 h and 144 spectra
9 behind the ISI during 69 h.

10 **3.1 Ice particle residual composition and potential aerosol sources**

11 The ALABAMA was used to analyze ice crystals extracted from mixed-phase clouds by two
12 different inlets: ISI and Ice-CVI. The times during which cloud particles were sampled by the
13 ISI were identified using the cloud liquid water content (LWC)-data measured with two PVM
14 instruments (PSI and University of Manchester) and a CDP (University of Manchester) while
15 the times when the Ice-CVI sampled cloud particles were identified using the ice residual
16 concentration measured with the CPC behind the Ice-CVI. According to the Ice-CVI sampling
17 capability, which is described in section 2.3, the cloud event periods where the ALABAMA
18 was coupled to the Ice-CVI were classified. This classification resulted in (++)-sampling-
19 periods, when there was hardly any precipitation or blown snow, so that small secondary ice
20 particles created by crystal-crystal collisions can be neglected and thus INP containing
21 primary ice particles are sampled. For (+)-sampling-periods, the sampling of small secondary
22 ice particles, that do not contain a particle that served as INP, cannot be excluded, since
23 precipitation and blown snow occurred. As a consequence, the ice particle residues analyzed
24 during (++)-sampling-periods are attributed to INP whereas for (+)-sampling-periods this
25 relation is not that clear and might be only valid for particles that are larger than at least
26 300 nm. Table 1 shows the identified cloud events along with sampling time, number of
27 acquired mass spectra, sampling-period classification, and weather conditions and cloud type.
28 The meteorological situation during the whole campaign was mainly influenced by low
29 pressure systems with low temperatures.

30 The occurrence of artifacts during the measurements using the Ice-CVI as well as the ISI is
31 described in Worringer et al. (2015). Aluminum oxide is an artifact of the measurements with
32 the Ice-CVI and silicon oxide is an artifact of the measurements with the ISI. The impaction

1 plates of the Ice-CVI contain aluminum. When the ice crystals bounce on the impactation plates
2 of the Ice-CVI, some aluminum oxide particles are removed from these plates and can be
3 carried with the air stream to the analysis instrument. The ISI was calibrated with silicon
4 oxide particles, which are remained in the system and occurred during the measurements as
5 artifacts. In our dataset it is difficult to distinguish between artifacts and a real component of a
6 particle. Therefore the peaks of m/z 27 (Al^+) and m/z 43 (AlO^+) with respect of the Ice-CVI
7 measurements and the peak of m/z 28 (Si^+) with respect to the ISI measurements were
8 ignored.

9 ~~In total, we measured 329 spectra during the (++) events (61 h measurement time) and 1335~~
10 ~~spectra during the (+-) events (160 h measurement time) by using the Ice-CVI. Behind the ISI~~
11 ~~we measured 144 spectra during 35 h measurement time.~~

12 Figure 2 shows the results of the clustering algorithm for all ice particle residual
13 measurements. The Ice-CVI data were analyzed separately for all **(++)-sampling-periods** (left
14 pie chart) and for all **(+)-sampling-periods** (middle pie chart). The right pie chart shows the
15 results for all ISI measurements. **This analysis shows that the metal containing particle groups**
16 **(Bio/Min/Sal, industrial metals, and minerals) are the dominating fractions in IPR**
17 **composition measured by using the Ice-CVI during the (+)-sampling-periods (49 %) and the**
18 **ISI (66 %).** Interestingly, during the **(++)-sampling-periods metal containing particles**
19 **represent only a smaller fraction (40 %).** We also detected lead containing particles, but only
20 while sampling through the Ice-CVI **(7 % in the (++) cases and 12 % in the (+-) cases).**
21 During the **(++)-sampling-periods** measured behind the Ice-CVI, black carbon internally
22 mixed with organic carbon (20 %) is one of the main fractions. Together with OC **(26 %)**,
23 these two particle types represent **46 %** of all IPR. It is worth noting that there are more
24 similarities between the Ice-CVI and ISI during **(+)-sampling-periods than the (++)-**
25 **sampling-periods.** A reason for that can be that the ISI measurements are also influenced by
26 secondary ice or incoming snowflakes. During the **(+)-sampling-periods** as well as during the
27 **ISI-sampling-periods** precipitation occurred. On the other hand, the measurements at the ISI
28 and the Ice-CVI were not done simultaneously, such that **also** differences in the air mass
29 origin could play a role here.

30 **Backward trajectories were compiled using CRISP (Klimach, 2012) with access to HYSPLIT**
31 **(Hybrid Single Particle Lagrangian Integrated Trajectory Model, National Oceanic and**
32 **Atmospheric Administration; Draxler and Rolph, 2012; Rolph, 2014), which was run using**
33 **GDAS (Global Data Assimilation System) meteorological dataset (starting altitude: 3580 m**

1 asl.; hours back: 72 h; initialize time: end of the current event). The geographical origin of the
2 air masses and change of altitude during the transport can be used to infer whether the air
3 masses are influenced by surface emissions or mainly characterized by free tropospheric air
4 and long distance transport. During all measurement episodes (total, Ice-CVI, ISI) the air
5 masses approached the measurement station from slightly different directions (Fig. 3). The air
6 masses during the (++)-sampling-periods came primarily from north-western directions from
7 North America over France, while during the (+)-sampling-periods the air masses arrived
8 more from the North, over Scandinavia and Germany. The origin of the air masses during the
9 measurements using the ISI are similar to those of the (++)-sampling-periods but with a
10 tendency towards southern directions (Fig. 3). During non-cloud episodes air masses
11 approached the measurement location from all directions.

12 Previous measurements at the JFJ showed that there is an enrichment of mineral dust and
13 black carbon in IPR composition (Mertes et al., 2007; Cozic et al., 2008b; Kamphus et al.,
14 2010). An enrichment of black carbon is not observed in our measurements. Cziczo et al.
15 (2009) found that lead-containing particles are also enriched in the IPR compared to the
16 background aerosol. Our measurements show also that mineral dust (measured behind the ISI
17 and during the (+) sampling periods) and lead (only measured behind the Ice-CVI) were two
18 of the dominating fractions in the IPR composition. Worringen et al. (2015) report on SEM
19 analyses of particles sampled during the same project behind the ISI and the Ice-CVI. They
20 found lead in two states, namely homogeneous lead-rich particles and small lead inclusions in
21 particles of other material. While the small lead inclusions are not considered as potential
22 artifacts, the large lead-rich particles might be artifacts from mechanical re-suspension of lead
23 containing particles from the surface of the impaction plates of the Ice-CVI. In our case the
24 lead-containing particles are internally mixed with organics, minerals or other metals,
25 therefore we interpret these particles as real atmospheric particles and not as artifacts.

26

27 **3.2 Event-to-event variability**

28 Figure 4 shows the IPR chemical composition measured during seven different events. These
29 sampling-periods were chosen, because these are (++)-sampling-periods and contamination of
30 e.g. incoming snowflakes are excluded and during these sampling-periods the most particles
31 were measured (except for the ISI measurements). Although the air masses sampled during all
32 seven events have very similar origin and history of altitude (Fig. 5a and 5b) the chemical
33 composition for each event is different from the others. All air masses during these events

1 arrived rising from a western direction to the measurement platform, such that the chemical
2 composition of these seven events was probably influenced by local emissions. During Event
3 3 and 4 the air masses arrived from a south-western direction. This is reflected in the chemical
4 composition: Both events show organic carbon as the main fraction and the amount of lead
5 containing particles is comparable (13 % Event 3 and 15 % Event 4). The differences between
6 Event 3 and 4 are the absence of BC in Event 4 and of minerals in Event 3. The chemical
7 composition of Event 12 is also comparable to Event 4 and Event 6. In this case also the
8 dominating fractions are OC and Bio/Min/Sal. The absence of lead containing particles (as
9 well as in Event 6) and the presence of 2 % BC/OC in Event 12 or 4 % in Event 6 are the
10 main differences between Event 12, 6 and Event 4.

11 Another reason for similarities and differences between these 7 events can be the temperature
12 (Fig. 6). Events 3, 4 and 6 have the highest fraction of OC (nearly 50 % of the particles) and
13 Event 6 additionally a high amount of metal containing particles (37 %; industrial metals,
14 minerals and Bio/Min/Sal). Event 3 and 4 have also the highest temperatures (Event 3:
15 average temperature $\bar{T} = -7.8$ °C; Event 4: $\bar{T} = -8.6$ °C). In contrast to that, Event 12 has the
16 highest amount of metal containing particles (65 %) and has an average temperature of about
17 $\bar{T} = -17$ °C. Event 6 has also a high amount of metal containing particles and the lowest
18 average temperature of about $\bar{T} = -21$ °C. Event 4 has also a high amount (41 %) of 'metal'
19 components but by closer consideration of the Bio/Min/Sal-type it can be shown that this type
20 consists mostly of metal ions together with organic ions in Event 4 and more single metal ion
21 signals during Event 12 and 6. This high amount of metal components measured at lower
22 temperatures is also comparable to Event 2 and 5. 62 % of the chemical composition of Event
23 2 and 51 % of Event 5 consist of metal components. Therefore the data indicate that organic
24 material dominates the IPR composition at higher temperatures and metal components from
25 mineral or salty origin dominate at lower temperatures. This finding is surprising, because
26 previous studies found that organics are ice active only at temperatures below -40 °C (Hoose
27 and Möhler, 2012). However, the organic signal in the mass spectra might also originate from
28 bioparticles, which would explain the ice formation at higher temperatures, because
29 bioparticles have been reported in the literature by many authors to be ice active at higher
30 temperatures (e.g. Möhler et al., 2008; Hoose and Möhler, 2012). Another source can be soil
31 organic matter. Tobo et al. (2014) shows that organic-rich particles are more important than
32 mineral particles for the ice-nucleating ability of agricultural soil dust at temperatures higher
33 than -36 °C. An exception is Event 1. During this event the second lowest temperatures ($\bar{T} = -$
34 19.2 °C) of all events prevailed, but a high relative amount of organic components was

1 measured (80 % BC/OC and OC). A reason for this high relative amount of organic material
2 can be local emissions. At this time the total particle concentration (measured inside the cloud
3 using the total inlet) shows a short period with high concentrations ($> 2000 \text{ cm}^{-3}$, see Fig. 7),
4 which indicates local emissions.

6 3.3 Comparison between background aerosol particle composition and IPR

7 During non-cloud phases the ALABAMA was connected to the total inlet to measure
8 background aerosol particles. Figure 8 shows the averaged composition of all background
9 aerosol particles along with the IPR composition measured behind the Ice-CVI during the
10 (++)-sampling-periods and behind the ISI. The temperature range during the background
11 aerosol measurements was between $-27 \text{ }^{\circ}\text{C}$ and $-6 \text{ }^{\circ}\text{C}$, which is comparable to the temperature
12 range of the cloud events. In comparison to the IPR composition, the measurements show a
13 high fraction of black carbon (17 %; Fig. 8) and only a minor fraction of BC/OC (4 %). The
14 fraction of the particle type ‘BC/OC’ in the background aerosol is comparable to that in the
15 IPR sampled by the ISI. However, also the aerosol particles are dominated by the particle
16 types ‘organic carbon’ (43 %) and ‘Bio/Min/Sal’ (30 %). ~~Previous high mountain-top~~
17 ~~measurements at the Storm Peak Laboratory (SPL; 3200 m asl.) in northern Colorado show~~
18 ~~also organic as the major component in the background aerosol (DeMott et al., 2003a ;Cziczo~~
19 ~~et al., 2004a).~~ The differences as compared to the IPR compositions are the negligibly small
20 amount ($< 0.1 \text{ %}$) of lead-containing particles and the much smaller amount of minerals
21 (about 1 %). This is partly in contrast to other measurements. Previous measurements with the
22 ATOFMS at the Jungfraujoch as well as airborne measurements over North America show 5
23 and 10 % lead-containing particles in the background aerosol (Murphy et al., 2007) but also
24 only a small amount of mineral dust or fly ash measured at the Storm Peak Laboratory (SPL;
25 3200 m asl.) in northern Colorado (DeMott et al., 2003a). Data from the SPL show also
26 organic as the major component in the background aerosol (DeMott et al., 2003a ;Cziczo et
27 al., 2004a). A part of the organic material detected in the IPR as well as in the background
28 aerosol may be due to could be local anthropogenic emissions. In the vicinity of the
29 measurement station is a large and popular skiing region. Additionally, cooking emissions,
30 diesel exhaust or residential heating may also play a role.

~~Previous investigations show that the presence of a high potassium peak in the mass spectra in~~
32 ~~combination with organic carbon is a marker for biomass burning (e.g. Pratt and Prather,~~
33 ~~2010; Twohy et al., 2010; Corbin et al., 2012) or biogenic aerosol (e.g. Trimborn, 2002; Pratt~~
34 ~~and Prather, 2010). Closer consideration of the three different carbon clusters (BC, BC/OC,~~

1 OC) shows that potassium is present in nearly every mass spectrum. In the background
2 aerosol 45282 mass spectra including black or organic carbon were measured: 92 % of all
3 these mass spectra show potassium. The BC type includes the mass spectra without potassium
4 (20 %; only 1 % in the OC/BC type and 6 % in the OC type). The same observation holds for
5 the IPR composition: The particle types including organic carbon measured by the use of the
6 Ice-CVI as well as the ISI show more spectra including potassium (94 % of all OC and
7 OC/BC spectra while using the Ice-CVI and 98 % while using the ISI). Because of this results
8 spectra with a potassium peak cannot clearly assigned to biomass burning or biological
9 particles.

11 3.4 Influence of the air mass trajectories on the aerosol composition

12 The chemical composition of the background (out-of-cloud) aerosol has been shown in Figure
13 8. The high variability of the measured IPR might be due to the different aerosol properties
14 when air masses arrive from different geographic origin and/or different altitudes at the
15 Jungfrauoch. Therefore, we investigate here how air masses origin influences the aerosol
16 properties. Because of the saddle position of the JFJ, there are only two possibilities of how
17 the air masses can approach the measurement platform (Fig. 6). Predominantly, the air masses
18 arrive from northwestern direction over the Swiss plateau (wind direction of approx. 315°).
19 Less frequently, the approach was from a southeastern direction from the inner Alps (approx.
20 135°, via the Aletsch Glacier). According to the direction from which air masses approach the
21 measurement platform, the chemical composition is influenced predominantly by
22 anthropogenic and organic emissions or by mineral dust sources. To assess the influence of
23 origin and the average altitude of the air masses during their transport to the Jungfrauoch, we
24 compare two time periods with aerosol measurements using the total inlet (11.02. and
25 19.02.2013). The chosen time periods exhibit nearly the same relative humidity, potential wet
26 bulb temperature and temperature (Fig. 6).

27 Fig. 9 shows the chemical composition of the aerosol particles for both time periods, along
28 with corresponding back-trajectories. The comparison shows that more particles containing
29 BC (internally mixed with ammonium or the Bio/Min/Sal-type) and the Bio/Min/Sal-type are
30 observed in the air masses arriving from a northwestern direction (11.02.2013), while the
31 measurements during the SE-event show more OC containing particles (internally mixed with

1 ammonium or the Bio/Min/Sal-type). The fraction of particles measured containing only
2 potassium and pure organic carbon is very similar for both events.

3 The air masses not only approached locally from different directions, but also had different
4 long-range origins (see back trajectories Fig. 9). The air masses measured on 19.02.2013
5 (NW-event) approached from the north over Germany and have remained at approximately
6 the same altitude as the Jungfrauoch during the last 72 hours. Thus, these air masses have
7 been in the free troposphere for at least three days prior to the measurement. The chemical
8 composition of the measured particles is dominated by black carbon internally mixed with
9 ammonium and by the Bio/Min/Sal-type. In contrast to the 19.02.2013, the air masses on
10 11.02.2013 (SE-event) approached over southern France and the western Po Valley, have
11 been lifted from low altitudes and clearly influenced by the boundary layer. These air masses
12 contain higher amounts of OC containing particles. This shows that the vertical uplifting
13 brings anthropogenic emissions (e.g., from the Po Valley) up to the altitude of the
14 measurement station, while the air masses measured during the NW-event contain a higher
15 amount of sea salt or mineral dust (both contained in the Bio/Min/Sal-type) and aged,
16 processed BC particles.

17

18 3.5 Size distribution of IPR and background aerosol

19 Ice-CVI and ISI both extract small ice particles in the size range from 5 μm to 20 μm from
20 mixed-phase clouds (Mertes et al., 2007; Kupiszewski et al., 2014) while the upper cut-off of
21 the total inlet was 40 μm for wind speeds up to 20 m/s (Weingartner et al., 1999). In Figure 10
22 is shown the size distributions of IPR measured with the ALABAMA (a, c, e) and the Sky-
23 OPC (b, d, f) compared with ESEM measurements (a and b). Figure 10a shows the size
24 distributions of IPR measured by ALABAMA and ESEM applying the Ice-CVI. Figure 10e
25 the size distributions measured by ALABAMA and ESEM using the ISI. In Figure 10b and d,
26 the corresponding size distributions measured with the Sky-OPC are shown. Figure 10c
27 shows the size distributions measured by ALABAMA and Fig. 10d measured by the Sky-
28 OPC using the ISI. Fig. 10e and f show the size distribution measured by ALABAMA and the
29 Sky-OPC using the total inlet. The measurement times for Ice-CVI and ISI are given in Table
30 1; the measurements using the total inlet were done during all cloud-free periods. For all three
31 inlets (total, Ice-CVI, ISI) most of the detected IPR measured with the ALABAMA and also
32 with the Sky-OPC is in the size range of 300–650 nm. The IPR size distributions measured
33 by ALABAMA and SEM behind the Ice-CVI are in very good agreement (Fig. 10a). In

1 contrast, the IPR size distribution measured behind the ISI are somewhat different. (Fig. 10c):
2 Both distributions show two maxima, but the positions of the maxima are not the same. The
3 ALABAMA IPR distribution has a primary maximum in the size bin 0.4–0.5 μm and a
4 secondary maximum in the size bin 1.3–1.6 μm . The SEM IPR distribution both maxima are
5 shifted to larger sizes. The first maximum is in the 1–1.5 μm interval and the second
6 maximum is in the 2–2.5 μm interval. However, total count rates are very low, so this
7 difference should not be overemphasized. Furthermore, SEM measured geometric diameters,
8 while the sizes determined by ALABAMA refer to the vacuum aerodynamic diameter. SEM
9 and ALABAMA measure the size distribution in different ways: ALABAMA measures
10 vacuum aerodynamic diameter and SEM geometric diameter. To compare both data sets the
11 SEM data were converted to the aerodynamic diameter. The vacuum aerodynamic diameter
12 was calculated according to DeCarlo et al. (2004) with the assumption that the projected area
13 diameter from the electron microscopy analysis equals the volume-equivalent diameter.
14 Furthermore, an average dynamic shape factor of 1.2 was used for the calculations. This
15 seems to be justified, as most non-extremely shaped particles show low variation in shape
16 factor (Schneider et al., 2006; Zelenyuk et al., 2006), except for soot with high fractal
17 dimension (Slowik et al., 2004) which was not commonly encountered in the present work.
18 The density ratios required for the calculation were estimated from the major composition of
19 the particle according to the values from Weinbruch et al. (2014) (Table S2). The IPR size
20 distributions measured by ALABAMA and SEM behind the Ice-CVI show the same behavior
21 (Fig. 10a) with shifting the SEM graph to larger sizes. Both distributions show a slow
22 increase at small size ranges and a higher number of larger particles. The ALABAMA IPR
23 distribution has a primary maximum in the size bin 300–400 μm and a secondary maximum
24 in the size bin 500–600 μm . The SEM size distribution shows a single maximum at about
25 900 μm . However, total count rates are very low, so this difference should not be
26 overemphasized. For all three inlets (total, Ice-CVI, ISI) most of the detected particles
27 measured with the ALABAMA are in the size range of 300–800 nm. In contrast to the size
28 distribution measured with the ALABAMA (and also ESEM for the Ice-CVI), the size
29 distributions measured with Sky-OPC (b, d, f) do not show a maximum but only a decreasing
30 number concentration of particles with increasing particle diameter for all three inlet types.
31 The difference to the ALABAMA size distributions is a result of the detection and ionization
32 efficiency of the ALABAMA which is the highest around 400 nm. The IPR size distributions
33 measured with the ESEM and Sky-OPC (10b) show both a decreasing number of particles at
34 larger size ranges. In contrast to the size distribution measured with the Sky-OPC the size

1 distribution measured with ESEM shows a lower number of particles at smaller size ranges.
2 The Sky-OPC size distribution measured behind the ISI (10d) shows an unexplained sudden
3 decrease above 3 μm . Figure 10f shows that the background aerosol particles (Sky-OPC) have
4 a size range of up to approximately 20 μm but with highest number concentration in the
5 smaller range ($< 1 \mu\text{m}$). The relative amount of larger particles is ($d > 1 \mu\text{m}$) clearly elevated
6 for the IPR, both behind the ISI and Ice-CVI (10b and d) in comparison to the background
7 particles (10f). Note that the measurements of background particles (out of cloud) and IPR
8 were conducted by definition at different times, such that the absolute amount of particles
9 cannot be compared.

10 As mentioned above, relatively more IPR larger than 1 μm were observed compared to the
11 background aerosol particles. The percentage of the background aerosol particles larger than
12 1 μm (vacuum aerodynamic diameter) measured by ALABAMA was only 3 %, while 12 -
13 13 % of the IPR behind the Ice-CVI and ISI were larger than 1 μm . Therefore, the chemical
14 composition of these particles has been analyzed separately:

15 Figure 11 shows the chemical composition of the IPR and background aerosol particles larger
16 than 1 μm . The most frequent particle types found in the IPR larger than 1 μm are OC, lead
17 containing particles, Bio/Min/Sal, and minerals for the Ice-CVI, and Bio/Min/Sal and
18 minerals for the ISI. Lead containing particles are found in the IPR sampled by the Ice-CVI to
19 a similar percentage (14 %) as in all IPR (7 %, see Figs. 2 and 8). Interestingly, the
20 background aerosol supermicron particles are dominated by the Bio/Min/Sal-type and OC.
21 The finding strengthens the assumption that the metal ions detected in these mass spectra are
22 likely metal cations of primary aerosol like sea salt, minerals or biological particles, which are
23 mainly found in the coarse mode (e.g., Seinfeld and Pandis, 2006). Such large primary
24 particles are also expected to act efficiently as INP, and it is therefore not surprising that they
25 are found in the supermicrom IPR. More surprising is the large fraction of OC and BC/OC
26 particles detected in the supermicron IPR. These large particles containing organic material
27 appear to be even better INP than the supermicron particles assigned to the Bio/Min/Sal
28 category. It has recently been suggested that porous and glassy organic particles under certain
29 conditions play an important role as INP (Murray et al., 2010; Adler et al., 2013), and this
30 may explain the results presented here. But also the origin of these supermicron organic
31 particles remains unclear. Primary biological material as a source for these particles is
32 regarded to be unlikely, because the marker peaks observed in cations of biological particles
33 (like K^+ , Na^+ , Ca^{2+}) were not observed in these particle spectra assigned to the OC and BC/OC

1 types. However, particle classification of single particle mass spectra is never absolutely
2 certain, and future work may reveal more insight into the nature and origin of these particles.

3 The particle composition of the particle smaller than 1000 nm closely resembled the
4 composition of the whole data set, because the particle smaller than 1000 nm dominate the
5 analyzed particles by number. Only the BC/OC-type is increased in the particles smaller than
6 1000 nm measured while using the Ice-CVI.

7 The size distribution allow also for an estimation of the ice active site (e.g., Vali et al., 2014)
8 density of particles larger than 1 μm compared to those smaller than 1 μm : Assuming that
9 each IPR corresponds to at least one ice active site on the original aerosol particle (otherwise
10 it would not have acted as an INP), we can estimate the ice active site density for the particles
11 analyzed by ALABAMA, separated for particles smaller than 1 μm and larger than 1 μm . The
12 number of ice active sites per IPR surface (ice active site density) is $2.0 \cdot 10^{-7} \text{ nm}^{-2}$ for
13 $d > 1 \mu\text{m}$ and $1.6 \cdot 10^{-6} \text{ nm}^{-2}$ for particles with $d < 1 \mu\text{m}$. Relating the number of ice active sites
14 to the total aerosol surface yields $7.1 \cdot 10^{-10} \text{ nm}^{-2}$ for $d > 1 \mu\text{m}$ and $4.3 \cdot 10^{-9} \text{ nm}^{-2}$ for $d < 1 \mu\text{m}$.
15 In both cases the ice active site density is larger for particles smaller than 1 μm . This is an
16 important finding and explains the high number of IPR found in the size range below 1 μm .
17 However, it should be noted that the assumption that each IPR corresponds to one ice active
18 site may underestimate the number of ice active sites. In cases where more than one ice active
19 site is found on the particles, also only one ice crystal will form and one IPR will remain.
20 Thus the estimated number yields a lower limit for the ice active sites.

21 22 4 Summary and Conclusions

23 This paper presents results of the single particle measurements during the INUIT-JFJ/CLACE
24 2013 campaign conducted at the Jungfraujoch in January/February 2013. In agreement with
25 previous measurements at the Jungfraujoch (Chou et al., 2011; Kamphus et al., 2010; Mertes
26 et al., 2007), it was found that larger particles are more efficient ice nuclei. Specific analysis
27 of only those particles $> 1 \mu\text{m}$ showed that the chemical composition of these larger particles
28 is dominated by organic material and the "Bio/Min/Sal" type, both in the IPR as well as in the
29 background aerosol. Besides, the "minerals" group was found to be one of the main fractions
30 of the IPR measured behind the Ice-CVI. From the finding that IPR have a higher relative
31 number of larger particles than the background aerosol particles we conclude and confirm a
32 better ice nucleation ability for the larger, primary aerosol particles such as minerals, salt and
33 biological particles.

1 In general, IPR are enriched in organic material, partly also internally mixed with BC.
2 Additionally, minerals and lead were found in IPR as has already been observed in previous
3 measurements conducted at the JFJ (Mertes et al., 2007; Cozic et al., 2008b; Cziczo et al.,
4 2009; Kamphus et al., 2010; Ebert et al., 2011). In comparison to the composition of the IPR
5 measured using the Ice-CVI, the measured composition using the ISI is dominated by
6 minerals, and no lead containing particles were found, while 7 % of the IPR sampled using
7 the Ice-CVI included lead. In contrast to Cozic et al. (2008) we found no enrichment of pure
8 black carbon in the IPR composition. Only the chemical composition of the background
9 aerosol particles shows a high fraction of black carbon. These results agree with previous
10 investigations (DeMott et al., 1999; Dymarska et al., 2006; Hoose and Möhler, 2012)
11 describing black carbon as a good ice nucleus but only at lower temperatures and its ice
12 nucleating ability appears to be reduced if coatings by organic material or sulfuric acid are
13 present. During the INUIT-JFJ/CLACE 2013 campaign the temperatures were never lower
14 than -30 °C; see Fig. 6. In the background aerosol, the main particle fraction is also organic
15 carbon. The high amount of organic material in the background aerosol as well as in the IPR
16 motivates further investigation of different organic material by single particle mass
17 spectrometry to better characterize the organic fraction. While there have been previous
18 observations that organic matter is of general importance for ice nucleation ability (DeMott et
19 al., 2003a; Cziczo et al., 2004b), recent laboratory studies have shown the importance of
20 porous and glassy organic matter for ice nucleation (Murray et al., 2010; Adler et al., 2013).
21 The investigation of the influence of the temperature and the origin and altitude of the air
22 masses on the chemical composition of IPR and aerosol particles indicate that organic
23 material dominates the IPR composition at higher temperatures and metal components from
24 mineral or salt at lower temperatures which agrees with previous findings (e.g. Möhler et al.,
25 2008; Hoose and Möhler, 2012). It was illustrated that the origin (geographic and altitude) of
26 the air masses influenced the chemical composition of the aerosol particles. For the non-cloud
27 aerosol, the particles sampled in air masses characterized by free tropospheric air and long
28 distance transport were found to be dominated by BC and single metal ions from salt, mineral
29 or biological sources (Bio/Min/Sal-type). These particle types were probably partly mixed
30 with secondary inorganic components, because NH_4^+ was detected in some spectra. In contrast
31 to that, the particles in air masses which are influenced by surface emissions are dominated by
32 organic carbon and potassium.

33

34 **Appendix A: Parameters underlying the clustering algorithm**

1 This section describes the cluster parameters of the software package CRISP. The chosen
2 parameters are listed in Table A.

3 *Normalization type and time*

4 To compensate for differences in the ionization efficiency, each mass spectrum is normalized
5 to the sum of the signal intensities with preservation of the relative relationship of the signals.
6 By this, the influence of absolute signal intensity is decreased. Absolute signal intensity is not
7 needed because the laser ablation method does not measure quantitatively. The point at which
8 the normalization is applied in the analysis sequence can be chosen. In case of measuring both
9 polarities the spectra of both polarities are first merged, and normalization can be applied
10 before, after or before and after concatenation.

11

12 *Preprocessing type*

13 Preprocessing (before normalization) can be applied to increase mass signals with lower
14 intensity with respect to signals with a higher intensity, such that the presence of a certain m/z
15 has more significance than the signal intensity in the calculation of the distance to the
16 reference spectrum. Typically the square root of the signal intensities is used.

17

18 *Initialisation type*

19 This parameter defines the way the reference mass spectra are selected. Two options are
20 available:

- 21 - *find different startcluster*: different spectra are randomly selected according to certain
22 criteria
- 23 - *random*: reference spectra are chosen randomly

24 Reference spectra can also be determined manually, however, this last option is not very
25 useful for field data because the number of particle types is unknown.

26

27 *Number of cluster*

28 The result of the clustering is highly dependent on the pre-selected number of clusters. In the
29 case that the number of clusters is too small, some cluster types cannot be found, while in the
30 case that the number is too large, too many similar spectra are assigned to different clusters.
31 In the fuzzy c-means algorithm all non-matched spectra are collected in a rest cluster.

32

33 *Cluster difference*

1 This parameter determines the distance between the spectra which are chosen as start
 2 references at 'find different startcluster'. The *cluster difference* is between 1 and 0, where a
 3 *cluster difference* of 1 means that the chosen startclusters are identically. This distance results
 4 from the Pearson correlation and affects the number of the resulting clusters. The number of
 5 clusters increases with increasing similarity of the references and is constant at a value of 0.7
 6 (Roth, 2014). If the *cluster difference* is too small, the distinctions between the clusters are too
 7 large, resulting in too few cluster types. Thus, it is recommended to use more similar
 8 reference mass spectra and to summarize those clusters that show similar mass spectra at the
 9 end of the clustering.

10

11 *Fuzzifier and fuzzy abort*

12 The *fuzzifier* (also called *fuzzy weighting* exponent) is a dimension of fuzziness of the
 13 classification of the cluster ($1 \leq \textit{fuzzifier} \leq \infty$; e.g. Huang et al., 2012). The bigger the
 14 *fuzzifier*, the more inaccurate is the assignment to the references, because the spectra cannot
 15 exactly be assigned to one cluster. The distance d_{ij} between spectra i and reference j is
 16 weighted with:

$$17 \quad d_{ij}^{\frac{1}{z-1}} \quad (1)$$

18 where z is the *fuzzifier*. When the preprocessing option of CRISP is used, it has been found
 19 that the result of the clustering is independent of the *fuzzifier* value (Roth, 2014).

20 During the clustering, each mass spectrum is compared to the reference spectra in terms of
 21 distance, membership and correlation. If these parameters fulfill the pre-selected criteria, the
 22 mass spectrum is sorted into the cluster represented by the reference and the average spectrum
 23 is calculated again. Subsequently all mass spectra are compared again with the reference
 24 spectra. This procedure is repeated until the criterion of abort (*fuzzy abort*) is reached, such
 25 that the clustering stops when the value of the difference of all reference spectra between two
 26 iterations is smaller than the value defined by *fuzzy abort*.

27 For the data evaluation of the current dataset (both IPR and background aerosol particles) a
 28 mixture of manual and automatic clustering was used. First, an automatic clustering was done
 29 with the following parameters:

30

31 Table A: Chosen clustering parameter.

Preprocessing type	Power each m/z
Preprocessing power	0.5
Normalization type	Sum
Cluster difference	0.7 (0.6)
Distance	Correlation
Fuzzifier	1.2
Fuzzy abort	0.0001

1
2 As already mentioned the result of the clustering is highly dependent on the chosen initial
3 number of clusters. If this initial number of clusters is too small, some cluster types may not
4 be found. Therefore we chose a high number of clusters. In the case of the background aerosol
5 (71064 spectra) we started the first clustering with 200 clusters. Each of the resulting 200
6 clusters was manually inspected, and based on its ion signatures it was assigned to one
7 particle type. Those spectra that cannot be sorted by the algorithm into one of the 200 clusters
8 (membership coefficient below a pre-defined threshold) are assigned to a “rest cluster”
9 (12407 spectra in the case of the background aerosol). This rest cluster was clustered again
10 with a reduced condition for the cluster difference and with an initial number of clusters of 25.
11 The number of cluster was still too large after the clustering of the “rest cluster”, so it was
12 further analyzed. First, the remaining spectra were sorted by the use of specific marker peaks
13 and the resulting clusters were then clustered again with changing the fuzzyfier from 1.2 to
14 1.3 and a cluster difference of 0.7. After that, the resulting clusters were manually inspected
15 and sorted (with the criterion $r^2 \geq 0.7$). By this, we could reduce the number of spectra in the
16 rest cluster from 12407 to 3243. Due to this sorting procedure based on both automatic
17 clustering and manual cluster inspection one particle type typically contains different clusters
18 with different fragmentations. For example, the particle type “organic carbon” includes
19 clusters showing aliphatic hydrocarbon, aromatic carbon, nitrogen and oxidized carbon
20 fragmentation patterns. In order to restrict the result to a reasonable number of particle types,
21 we summarized these clusters to one particle type.

22

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6

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13

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1 Table 1: Cloud events during which measurements were taken behind Ice-CVI or ISI, along with the ALABAMA sampling time, the number of the
 2 measured spectra, the evaluation of the Ice-CVI-sampling-periods and the weather conditions and cloud formation during these events. The times of
 3 each cloud event based ^{a)} on the particle counter operated behind the Ice-CVI or ^{b)} on the liquid water content measured by two PVM instruments
 4 and a CDP outside the laboratory.

Event	Sampling time (local time)	Inlet	Number of spectra	Classification of the Ice CVI- sampling- periods	Weather conditions & clouds
1	^{a)} 22.01.2013 01:48 – 12:02	CVI	174	++	Warm front occlusive low pressure system; $\bar{T} = -19.2\text{ °C}$; wind direction $wd = 325^\circ$; wind speed $\bar{v} = 8.1\text{ ms}^{-1}$
2	^{a)} 27.01.2013 16:27 – 28.01.2013 09:44	CVI	78	++	Occlusive frontal system, Ns; $\bar{T} = -12.7\text{ °C}$; $wd = 318^\circ$; $\bar{v} = 8.4\text{ ms}^{-1}$
3	^{a)} 1. 29.01.2013 04:30 – 13:57 2. 29.01.2013 19:27 – 19:52	CVI	20 3	++ ++	Unstable warm front; first Ns than Cb; $\bar{T} = -7.8\text{ °C}$; $wd = 320^\circ$; $\bar{v} = 12.6\text{ ms}^{-1}$
4	^{a)} 30.01.2013 16:14 – 31.01.2013 01:03	CVI	39	++	Squall line at cold front; Cb; $\bar{T} = -8.6\text{ °C}$; $wd = 323^\circ$; $\bar{v} = 16.9\text{ ms}^{-1}$
5	^{a)} 1. 01.02.2013 17:22 – 02.02.2013 01:30 2. 02.02.2013 01:30 – 13:07 3. 02.02.2013 17:58 – 03.02.2013 01:00 4. 03.02.2013 01:00 – 10:45	CVI	134 701 209 73	++ + + ++	31.01.: cellular convection; Cu; $\bar{T} = -12.5\text{ °C}$; $wd = 324^\circ$; $\bar{v} = 17.7\text{ ms}^{-1}$ 01.02. – 02.02.: frontal wave; Ns and Cb; $\bar{T} = -13.7\text{ °C}$; $wd = 319^\circ$; $\bar{v} = 13.4\text{ ms}^{-1}$ Until 03.02. cellular convection; Cb; $\bar{T} = -23.1\text{ °C}$; $wd = 308^\circ$; $\bar{v} = 9.7\text{ ms}^{-1}$

	b) 1. 31.01.2013 18:55 – 21:42 2. 01.02.2013 01:53 – 11:05	ISI	9 18		
6	a) 1. 05.02.2013 19:06 – 23:00 2. 05.02.2013 23:00 – 06.02.2013 04:20 3. 06.02.2013 04:20 – 05:00	CVI	24 42 3	++ + ++	Squall line at postfrontal convergence line; Cb; $\bar{T} = -19.8^{\circ}\text{C}$; wd = 331°; $\bar{v} = 10.5 \text{ ms}^{-1}$
7	a) 1. 06.02.2013 08:33 – 11:00 2. 06.02.2013 11:00 – 12:30 3. 06.02.2013 12:30 – 14:56 4. 06.02.2013 15:44 – 15:53 5. 06.02.2013 23:32 – 07.02.2013 04:30 6. 07.02.2013 04:30 – 08:45 7. 07.02.2013 08:45 – 09:49 8. 07.02.2013 20:29 – 08.02.2013 05:50 9. 08.02.2013 05:50 – 09:20	CVI	26 4 15 3 8 6 2 31 2	+ ++ + + ++ + ++ + ++	06.02: Convective dominating low-pressure vortex; Cb; $\bar{T} = -24.3^{\circ}\text{C}$; wd = 310°; $\bar{v} = 8.0 \text{ ms}^{-1}$ From 07.02. on: cellular convection; Cu; $\bar{T} = -20.8^{\circ}\text{C}$; wd = 324°; $\bar{v} = 7.6 \text{ ms}^{-1}$
8	a) 1. 09.02.2013 01:09 – 02:30 2. 09.02.2013 02:30 – 09:00 3. 09.02.2013 09:00 – 09:41	CVI	4 32 3	++ + ++	Diamond dust and cellular convection at convergence line; Ci, Cu (Cb); $\bar{T} = -26.7^{\circ}\text{C}$; wd = 316°; $\bar{v} = 7.2 \text{ ms}^{-1}$
9	a) 10.02.2013 18:10 – 18:24	CVI	2	++	Approaching warm front; Ci, Cs, As; $\bar{T} = -15.7^{\circ}\text{C}$; wd = 324°; $\bar{v} = 9.5 \text{ ms}^{-1}$
10	a) 1. 11.02.2013 08:03 – 10:31 2. 11.02.2013 15:08 – 12.02.2013 06:11	CVI	1 11	++ ++	Warm front; Ns; $\bar{T} = -18.7^{\circ}\text{C}$; wd = 227°; $\bar{v} = 6.6 \text{ ms}^{-1}$

11	^{a)} 12.02.2013 16:07 – 13.02.2013 01:33	CVI	8	++	Back of a low with northeast stream; Ns, Ac, As; $\bar{T} = -20.1^{\circ}\text{C}$; wd = 319°; $\bar{v} = 7.9 \text{ ms}^{-1}$
12	^{b)} 15.02.2013 01:17 – 09:10	ISI	114		Low pressure system; As, Cu, Cb, Ac; $\bar{T} = -16.9^{\circ}\text{C}$; wd = 322°; $\bar{v} = 7.7 \text{ ms}^{-1}$
13	^{a)} 19.02.2013 16:46 – 20.02.2013 16:47	CVI	1	++	Cold front from North; Ac, Ns, Sc, Cu; $\bar{T} = -14.3^{\circ}\text{C}$; wd = 321°; $\bar{v} = 8.2 \text{ ms}^{-1}$
14	^{b)} 24.02.2013 06:57 – 24.02.2013 09:31	ISI	3		Approaching warm front with precipitation; Cs, As, Ns; $\bar{T} = -20.4^{\circ}\text{C}$, wd = 150°; $\bar{v} = 8.5 \text{ ms}^{-1}$

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2 Ac: altocumulus

3 As: altostratus

4 Cb: cumulonimbus

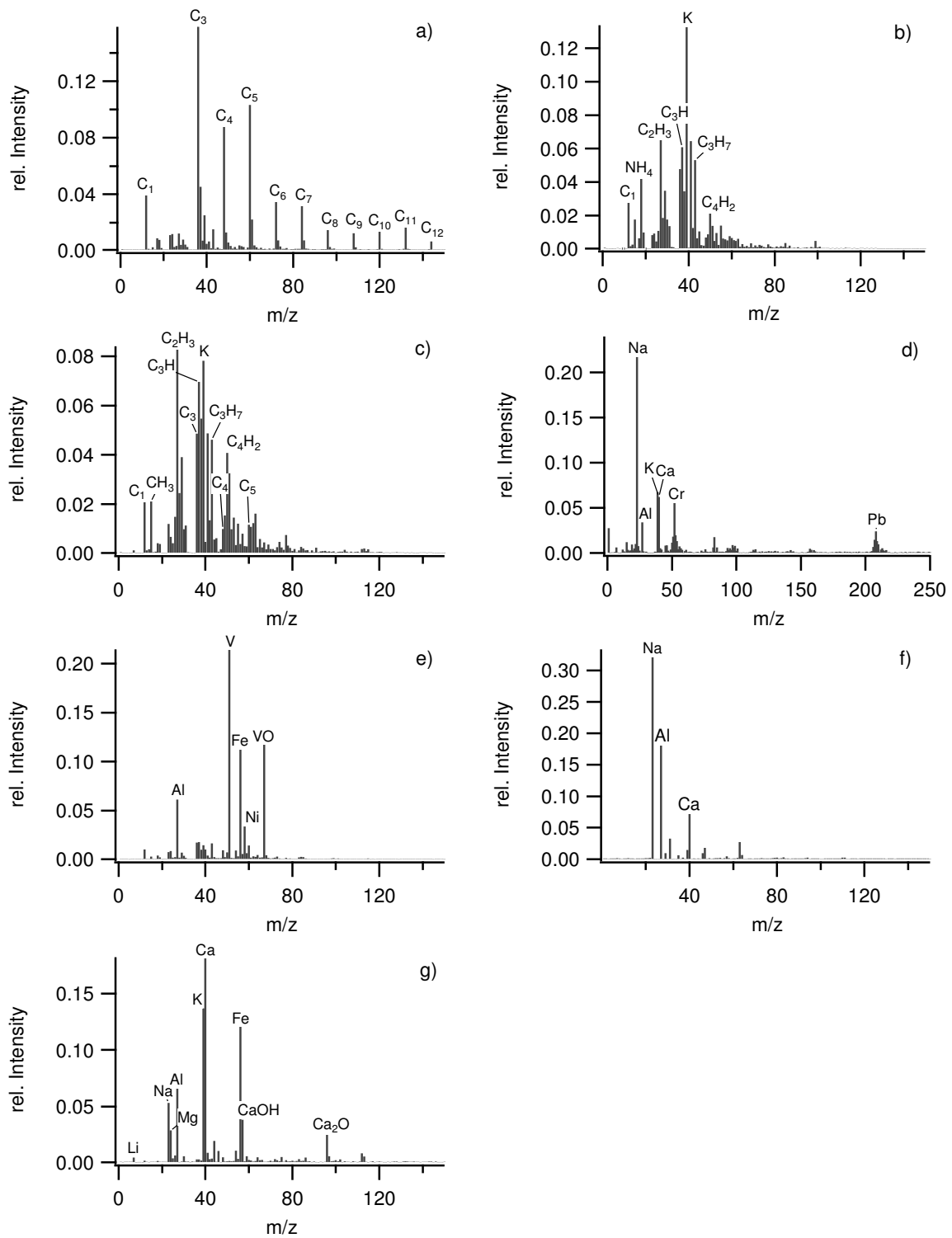
5 Ci: cirrus

6 Cs: cirrostratus

7 Cu: cumulus

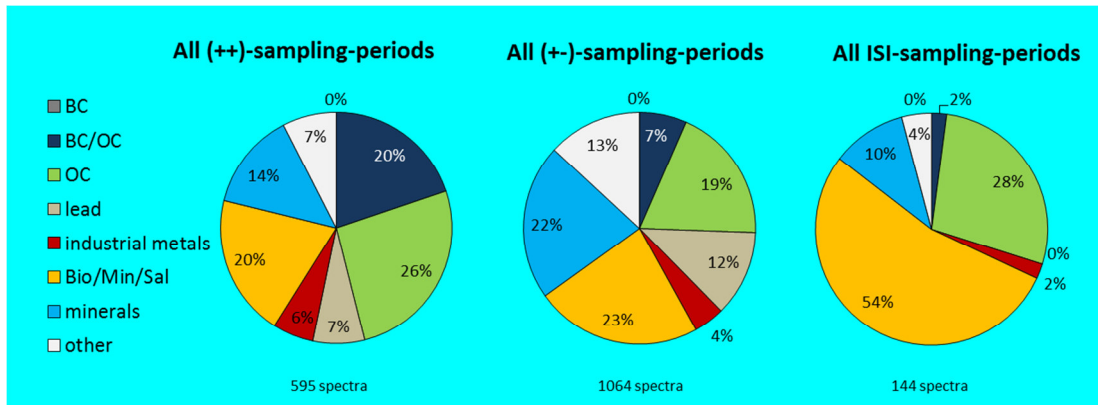
8 Ns: nimbostratus

9 Sc: stratocumulus



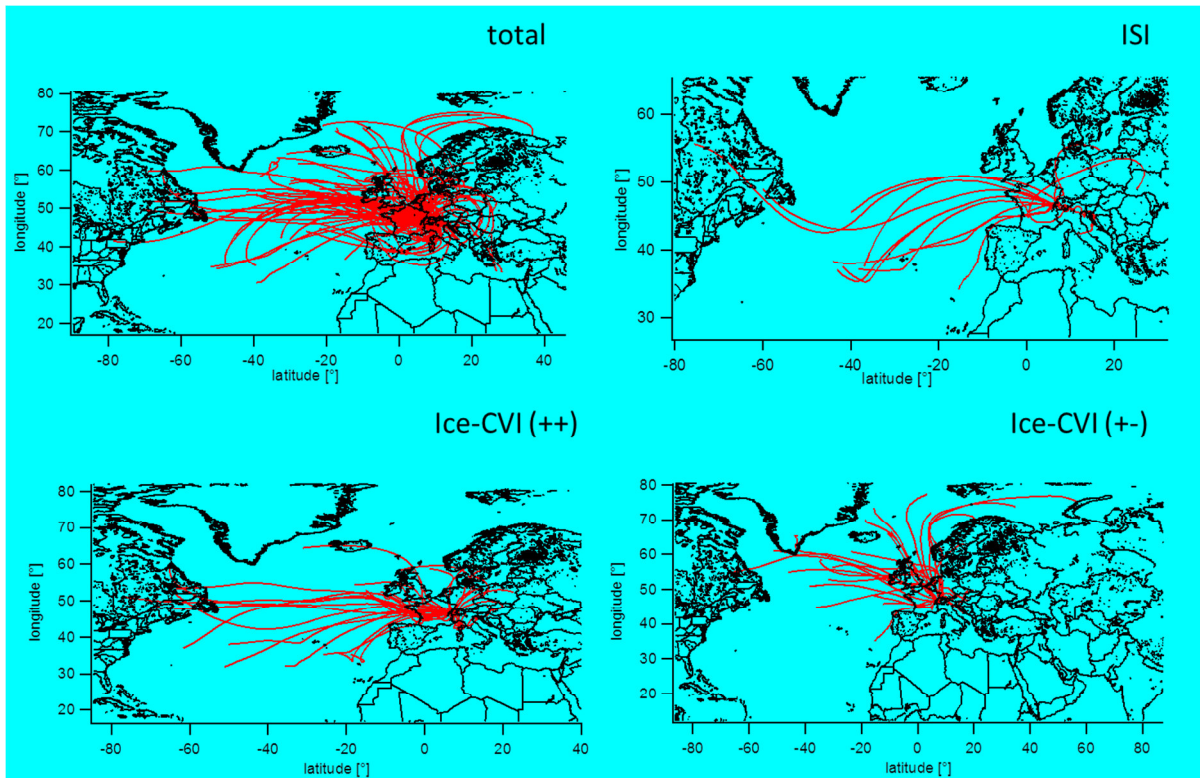
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Figure 1: Average mass spectra of each particle type. a) black carbon; b) organic carbon; c) black carbon internally mixed with organic carbon; d) lead containing particles; e) industrial metals; f) **Bio/Min/Sal**; g) minerals



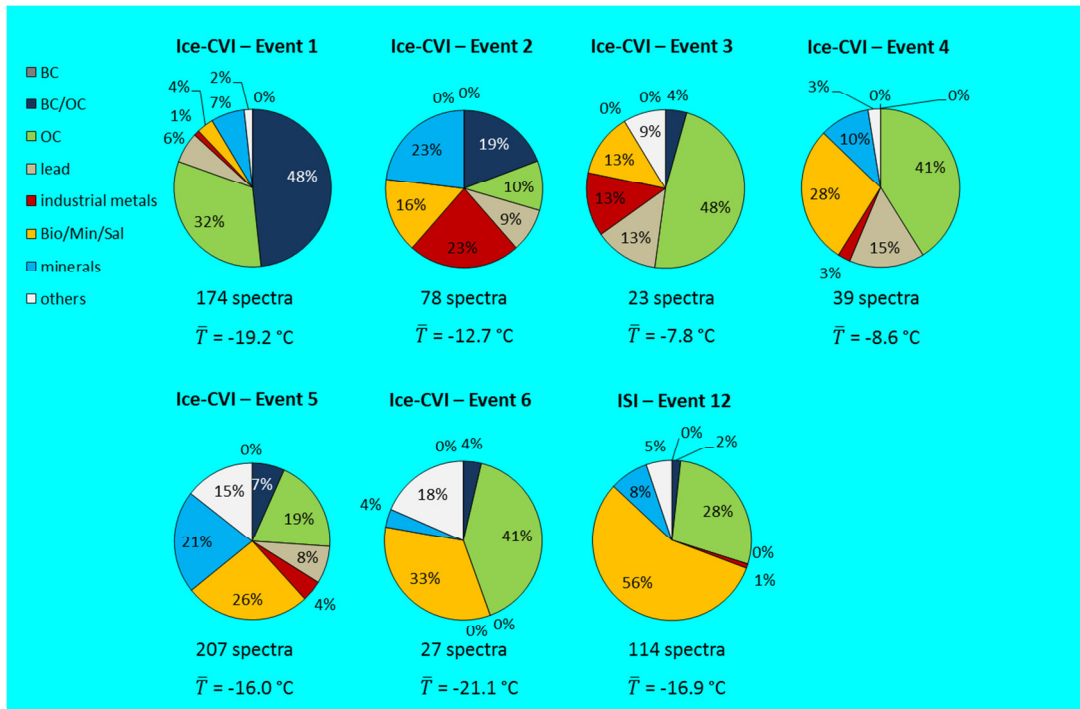
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Figure 2: Results of the IPR composition analysis. Left and middle: measurements behind the Ice-CVI (left: all (++)-sampling-periods; middle: all (+-)-sampling-periods). Right: IPR composition measured behind the ISI.



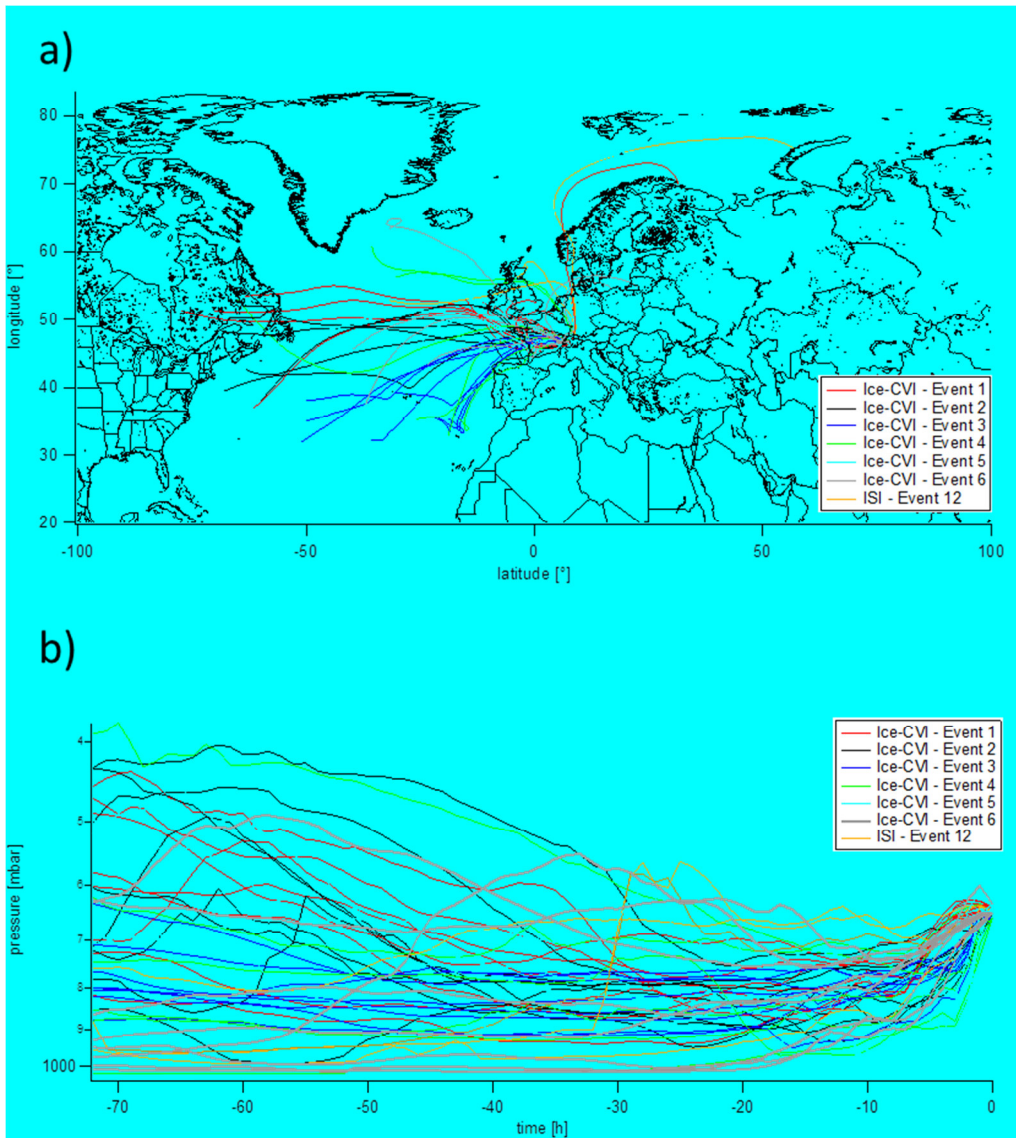
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Figure 3: 72 h backward trajectories calculated with CRISP/HYSPLIT (one trajectory every 6 h)



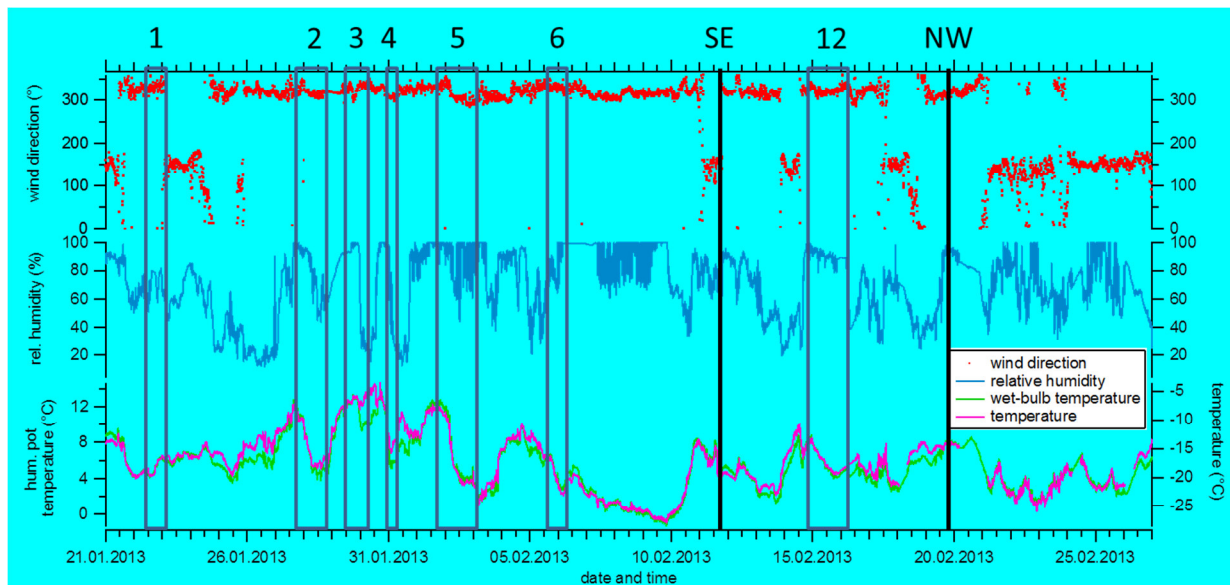
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Figure 4: Comparison of the composition analysis of seven events measuring behind the Ice-CVI (all (++)-sampling-periods, Event 1: 22.01.2013 01:48 – 12:02; Event 2: 27.01.2013 16:27 – 28.01.2013 09:44; Event 3: 3.1 29.01.2013 04:30 – 13:57; 3.2 29.01.2013 19:27 – 19:52; Event 4: 30.01.2013 16:14 – 31.01.2013 01:03; Event 5: 5.1 01.02.2013 17:22 – 02.02.2013 01:30; 5.4 03.02.2013 01:00 – 10:45 and Event 6: 6.1 05.02.2013 19:06 – 23:00; 6.3 06.02.2013 04:20 – 05:00) and the ISI (Event 12: 15.02.2013 01:17 – 09:10) together with the corresponding average temperature during each event.



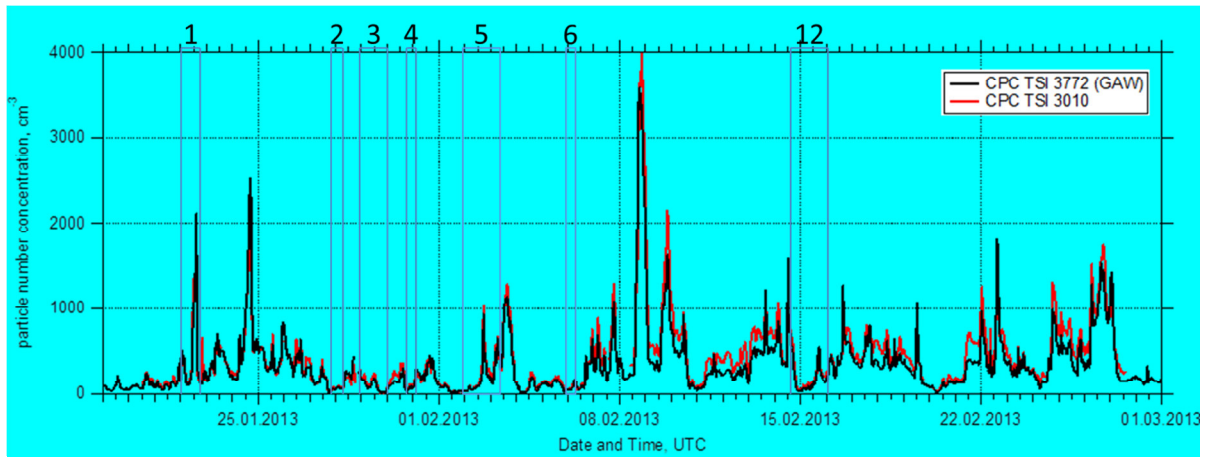
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Figure 5: a) 72 h backward trajectories (one trajectory every three hours) calculated with CRISP for each event. b) The altitudes of air masses reaching the Jungfraujoeh as a function of time, converted to pressure units.



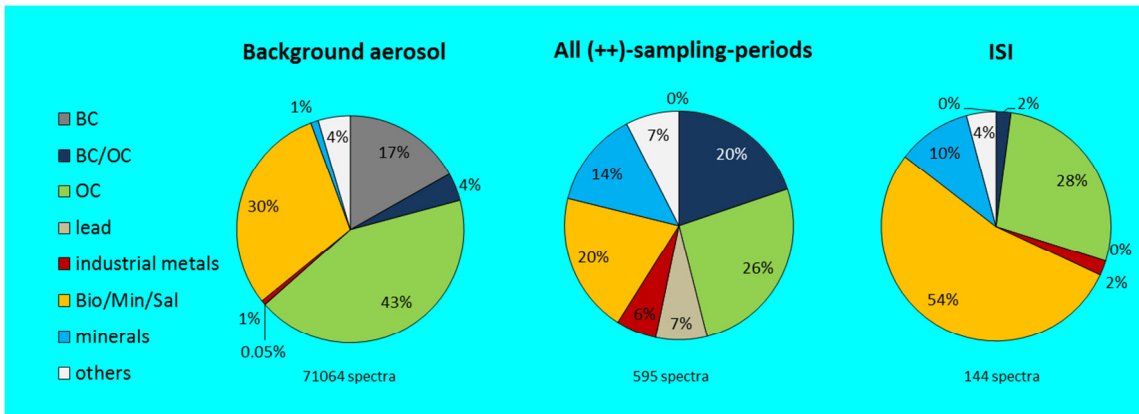
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3 Figure 6: Wind direction, relative humidity, potential wet-bulb temperature and temperature
 4 over the whole measurement period (data from MeteoSwiss at the JFJ station). Black lines
 5 denote the events with different air mass origin (discussed in section 3.4). Events highlighted
 6 with blue bars denote the 7 different events from Section 2.1.1.



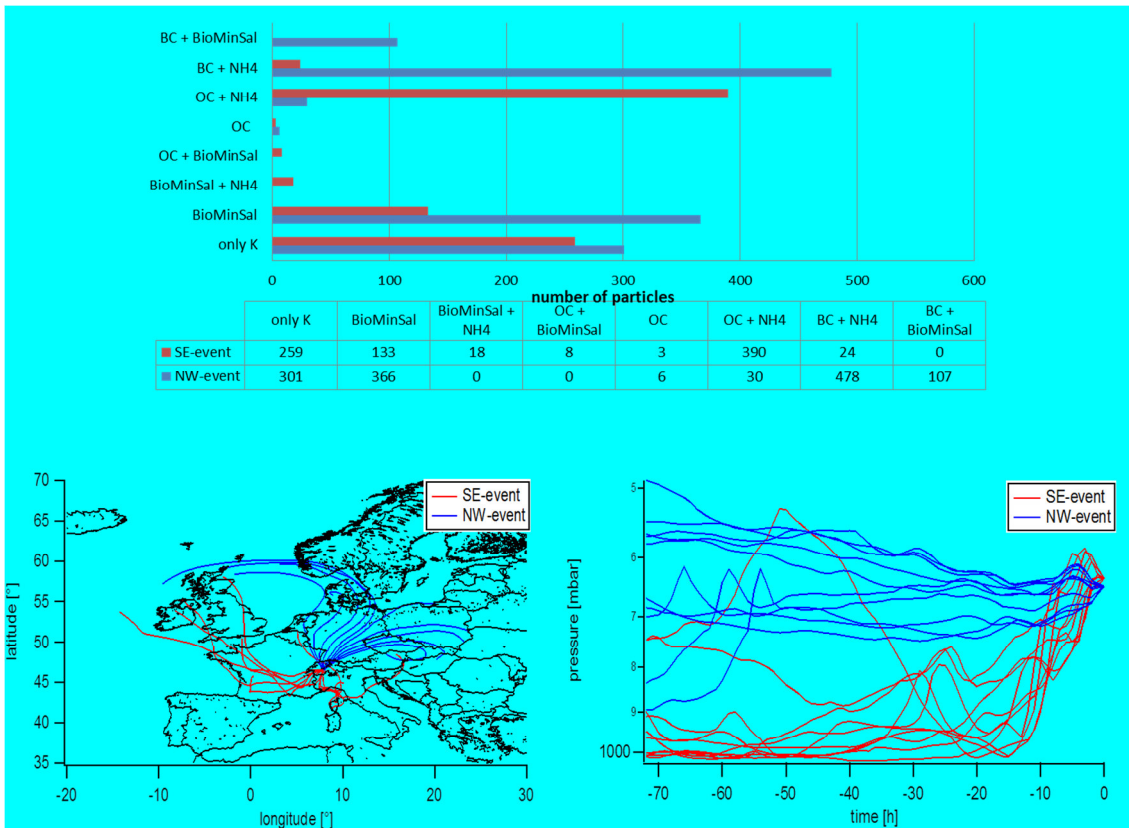
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Figure 7: Particle number concentrations measured during the INUIT-JFJ/CLACE 2013 campaign by two different condensation particle counters (CPC): The GAW-CPC which is located directly behind the total inlet, and a TSI 3010 that was operated with a much longer sampling line (approx. 7 m) next to one of the aerosol mass spectrometers. Short elevated concentrations indicate local emissions. Events highlighted with blue bars denote the 7 different events from Section 2.1.1



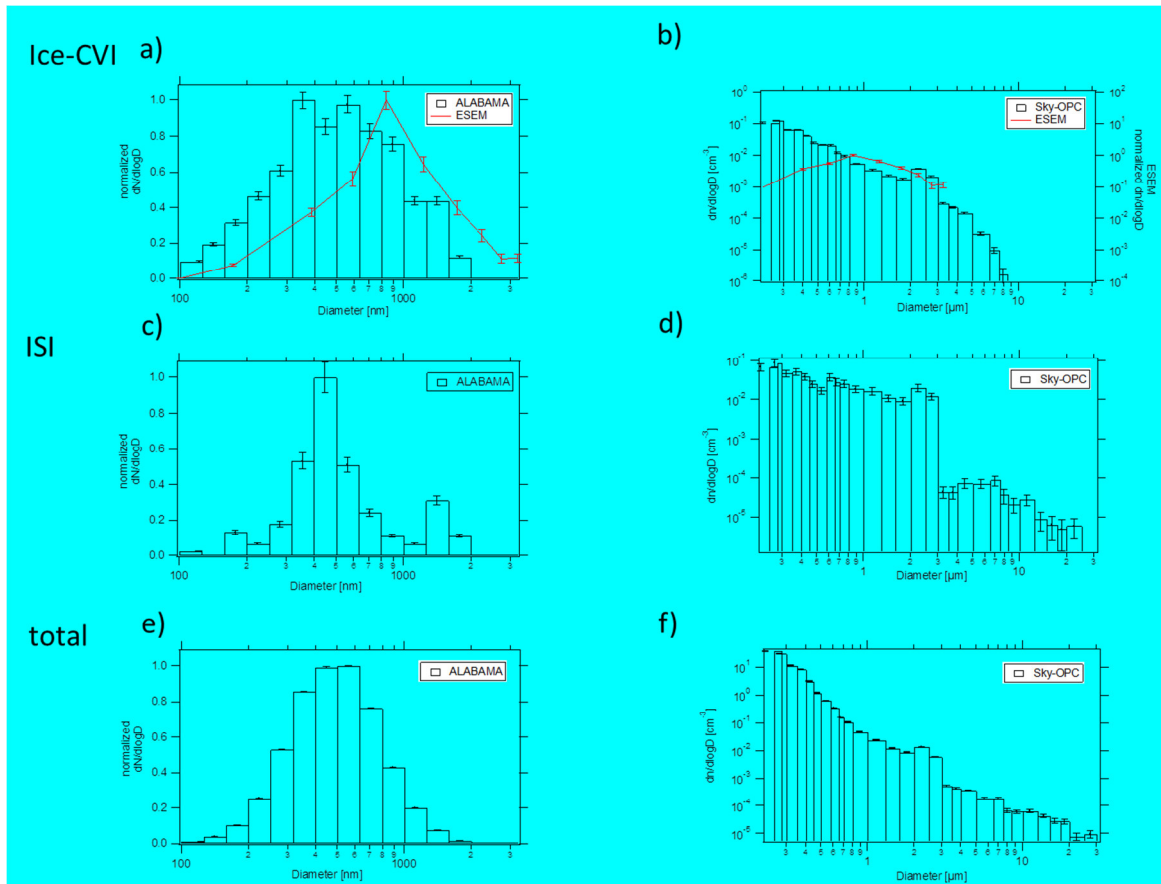
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Figure 8: Comparison between the chemical composition of background aerosol particles (left) and IPR measured behind Ice-CVI (middle) and ISI (right).



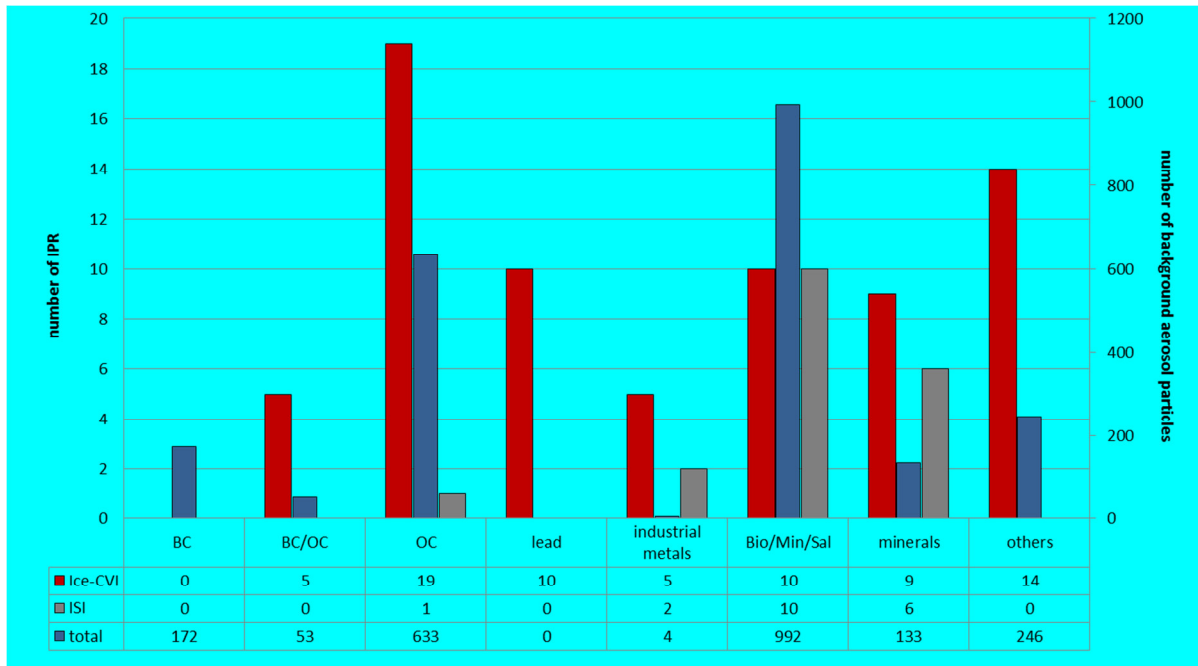
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Figure 9: Comparison of two events measured during non-cloud episodes. The northwestern event (NW; blue) was on 19.02.2013 14:00 – 16:14 and the southeastern event (SE; red) was on 11.02.2013 10:32 – 14:27. 72 h back trajectories were calculated with one trajectory every 2 hours.



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Figure 10: Measured size distribution of the IPR and background aerosol particles with the ALABAMA (bars; a, c, e) and Sky-OPC (bars; b, d, f) compared with the off-line SEM analysis of IPR samples (line; a and b). The error bars for the ALABAMA data result from counting statistics (averaged errors; $\Delta_{\text{Ice-CVI}} = 5.5 \%$; $\Delta_{\text{ISI}} = 8.3 \%$; $\Delta_{\text{total}} = 4 \%$). The error of the OPC data results from Gaussian propagation of uncertainty, including counting statistics, the manufacturer-given error of the OPC of 3 %, and the error of the enrichment factor (4 % for the Ice-CVI and 20 % for the ISI). The error of the ESEM dataset was determined by counting statistics. Note the different axis scaling. The y-axis is linear in a), c), e) and logarithmic in b), d), f). The x-axis range is 100 nm – 3250 nm in a), c), e) and 200 nm – 30 μm in b), d), f).



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Figure 11: Chemical composition of IPR and background aerosol particles larger than 1000 nm measured behind the Ice-CVI (red), ISI (grey) and total inlet (blue). The error bars results from counting statistics.