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Interactive comment on "In-situ single submicron particle composition analysis of ice residuals from mountain-top mixed-phase clouds in Central Europe" *by* S. Schmidt et al.

Anonymous Referee #2

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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 not 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 the methodology.

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 by ALABAMA are used to draw major conclusions, it is important to explicitly state the transmission efficiency of particles as a function if diameter through the mass spectrometer inlet.

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,

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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 difference to the detection efficiency of ALABAMA and ESEM (pg 4697 lines 21-22) but once again do not explicitly state what this efficiency is. But, they do not acknowledge that differences might also be influenced by the different diameters measured.

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 than 1 μm.

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.

It would be better if the authors did not readily presume that the ice formation was

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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 the 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.

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.

Compositional Analysis

In the 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.

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 no 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.

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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.

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 that 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.

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.

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.
- pg. 4681, line 1 - "replace have good ice nucleating capabilities" with "are ice nuclei".
- pg. 4682, line 25 - "critical nozzle" should be "critical orifice" to maintain consistency with references within the manuscript as well as the literature.
- pg 4685, line 7 - typo, line should read "in order to prevent"
- 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".
- pg 4685, lines 23-24 - Provide references for the PPD and WELAS.
- pg 4688, line 23 - typo; should read "unambiguously".
- pg 4690, lines 13-14 - Mentions "sampling efficiency and properties of the Ice-CVI", but this not discussed in detail anywhere in the manuscript.
- pg 4691, lines 26-29 - The manuscript states that back trajectories "were calculated with CRISP", but section 2.6 states that 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 a particular meteorological data set.

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- pg 4691, line 24 - typo; "such that also..." should read "such that ..."
- pg. 4692, line 17 - typo; "is one of the ..." should be "are two of the..."
- 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.
- pg. 4697, line 3 - typo; sentence should start "In Figure 10c..."
- pg. 4699 line 25 - typo; The meaning of this sentence if unclear. What does it mean to have results that "comply with previous investigations"?

References

Tobo, Y., P.J. DeMott, Hill, T. C. J., Prenni, A. J., Swoboda-Colberg, N. G., Franc, G. D. and Kriedenweis, S. M.: Organic matter matters of ice nuclei of agricultural soil origin, Atmos. Chem. Phys., 14, 8521-8531, 2014.

Murphy, D. M.: The Design of Single Particle Laser Mass Spectrometers, Mass Spec. Rev., 26, 150-165, 2007.

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