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Discussions

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 #3

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The study describes the measurement of ice particle residual composition using the ALABAMA single particle mass spectrometer behind two specialized ice-selective inlets at the JFJ mountaintop station. Results are presented for several mixed phase cloud events and analyzed in the context of air mass history and previous JFJ IPR studies. This study adds what is still a fairly small list of ambient IPR studies and can potentially provide important information on glaciation for mixed-phase clouds over continental regions. However, the manuscript has numerous problems with data analysis and interpretation. This study might be saved by major revisions and what essentially amounts to a reanalysis of the dataset.

The results are very difficult to interpret and therefore have limited scientific impact. The difficulties result from a combination of factors: 1) The compositional categories are muddled. 2) There are several artifact sources that omit important compositional markers, including Al and Si, unless further analysis can better differentiate the artifacts from real IPR. 3) The dataset is inherently small. Although this is to similar to other mountaintop IPR studies, it leads to a variety of inconsistencies in the dataset, particularly when comparing results from the two ice-selective IPR inlets and EM in Worringen. 4) The study lacks other field measurements, even simple gas-phase tracers such as CO, to help decipher air mass histories and interpret the aerosol data and instead relies completely on back-trajectory analysis.

Removing all suspect and speculative results would render this study too inconclusive to afford publication. This study hints at some interesting results, but often the authors present them without context or adequate description.

Major comments

1) Inlet contamination

What is essentially a companion paper, (Worringen) describes EM analysis of IPR, some of which were sampled at similar conditions, and is currently under review in ACPD. One principal finding from that study is that artifacts were generated from the ice crystal inlets used in the current study, with contamination rates sometimes being very large. Possible artifacts are addressed by the authors here and primarily include particles with Al, Si, and Pb. However, the artifact analysis is based more on possibilities and suspicions than a demonstrated ability of ALABAMA to differentiate artifacts. In particular, the lack of ability to remove inlet impaction artifacts that are presumably pure Al alloys or pure SiOx (glass?) hampers the identification of crustal material as IPR and complicates the interpretation of the Biominsal category. The study would benefit from a more refined analysis of artifacts that considers internal versus external mixtures, particle size, and a presentation of example spectra, and a lab study that

generates artifacts from the inlet materials.

The observation of Pb-rich particles from only one of the IPR inlets is very suspect. While Pb would be a surprising artifact from inlet materials, internal mixtures with Fe with Cr (and Mo??) may also indicate stainless steel artifacts. The authors mention the Worringen paper that describes Pb artifacts from EM analysis (p.4692). However, they do not adequately explain the source of the Pb-rich particles in their analysis or that they are different than in Worringen. Weren't the EM sampler and ALABAMA sampling from the same inlet(s) and thus subject to the same artifacts? It is not adequate to state that the P-rich particles detected by ALABAMA were not the same as those in Worringen because they also contain organics (which can accumulate on surfaces) or metals (possibly indicative of inlet materials, particularly brazing or soldering). Also, I do not understand the origin of the Pb-rich particles (l. 22) that "might be artifacts from mechanical resuspension". Are the authors suggesting that these Pb-rich particles were previously impacted on the Ice-CVI?

The authors need to explain the inconsistent Pb signatures, perhaps by investigating subpopulations of category 1d further, and reconcile these results with that of the Worringen paper that presents Pb artifacts from the EM analysis. If this cannot be accomplished, then discussion of Pb-rich particles should be removed.

2) Compositional categories.

The analysis is constrained by the results of the clustering algorithm, which is not separating compositional classes well. Some classes (1b and 1c) are very similar, whereas other classes probably contain distinct subpopulations. In this way the single-particle nature of the data is not well used. The authors employ the clustering results without further refinement. While this is understandable as a semi-objective approach, the lack of further refinement or analysis based on chemical knowledge and compositional information from the literature fundamentally limits the interpretation of the results and overall impact of the study. The authors should consider further analysis, which may

include allowing additional clusters, refining clustering parameters, and investigating sub-classes.

Fig 1b (Organic Carbon) and 1c (BC with Organic Carbon) have nearly identical average spectra, the only difference being intensity of the K+ peak and an NH4+ peak in 1b. The Cn/CnHx ratios are not consistently higher in the 1c BC/OC category, so what suggests that these have higher BC content? This appears to be an example of how the clustering algorithm is separating spectra based on the dominant signature (K+), despite that 1b and some of 1c belong to the same broad compositional class. The K+ signal clearly identifies 1b as having a biomass burning origin (see also Hudson JGR 2004). 1b is labeled somewhat generally as Organic Carbon. This labeling is a little misleading and causes problems later where the authors state, "the data indicate that organic material dominates the IPR composition..." (4693, line 21), citing the 1b category but neglecting that these BB particles also contain BC and inorganic material (K, Na, associated anions), which may be important for ice nucleation. Also p.4699 l. 9. 1c (BC/OC) is probably a mixture of BB and other types and is therefore difficult to interpret. Can 1c be more clearly separated from 1b using different clustering parameters?

Later in the Results section the authors discuss BB particles and state that K+ was present in nearly every BC, BC/OC, OC mass spectrum (or can it be C3H3+?), with the K+ appearance being consistent across the different sampling inlets. It is therefore not clear why the authors state on p.4695 line 9 that these spectra cannot be clearly assigned to BB or biological particles. Certainly the authors can invoke knowledge from their previous field studies and/or use other BB tracers to confirm the particles' identities. Provided this assumption is true, would some of the BB text and identification be better placed in section 2, and the categories labeled appropriately? Several conclusions about the origin of particulate organic material at the sampling site can be made here but are not discussed (wintertime biofuels, power generation, comparison to previous JFJ studies, etc).

As the authors state, the BioMinSal is not a clearly defined category, and is therefore problematic to this study. There is too much speculation here, and this category requires further analysis to be presented at all. The last thing the literature needs is another SPMS paper reporting possible biological material based on weak analysis. In fact, the authors state in the conclusions (p. 4699 l. 15) "we conclude and confirm a better ice nucleation ability for ... biological particles". This statement is not supported by the SPMS data as presented, and much more careful validation in the laboratory and/or by other bio-specific measurement techniques is required. BioMinSal could possibly be split into multiple categories or at least the populated spectra should be analyzed further. For instance, aluminum is a dominant marker in the cluster and is clearly indicative of crustal material and not biological material, yet is not mentioned. The authors do concede that Al and Si are possible inlet contaminants, but it is unclear how widespread and in what form that contamination is observed (can Al contamination really be observed as an internal mixture in submicron particles?). What % of the spectra contain Al, from both inlets? Iron is not labeled and very hard to see in the figure – is it really Fe or CaO? The authors claim to observe the 54Fe isotope, yet they state that 56 could be due to ions other than Fe, thus some inconsistency. Fe may be an unusual/minor marker for biological material (no clear consensus in the literature). The authors' suggestion of hemoglobin as the Fe source would necessitate animal cellular material and is highly speculative without including a reference. Other strong unlabeled signals appear to be nitrogen oxides and phosphorus, which is inorganic phosphate from minerals or may possibly be a biological marker.

The BC category is only presented for the background aerosol in Fig 8, and is absent for all IPR data in Fig 2, 4, and 8. Was this category manually incorporated into the BC/OC category, or did this category simply have zero population? If the latter, then add the BC category to the legends of Fig 2 and 4. Also, this is an important scientific point. Please discuss the lack of BC in IPR. The authors state (p. 4692 l. 13) "an enrichment of BC is not observed in our measurements", but in the conclusions (p. 4699 l. 25) they also state that this study describes "BC as a good ice nuclei". Please

fully clarify the analysis and ensure the conclusions are consistent with the data.

Minor comments

Section 2.3. What fraction of droplets >5 microns are not impacted on the preimpactor and thus make it through the CVI and can then be observed as IPR? This has to do with the sharpness of the preimactor transmission curve, and Mertes 2007 can be referenced if those data can be applied to the cloud conditions under study here. This is important because in mixed phase clouds ~5 micron droplets can be much more abundant than ~5-20 micron crystals such that the IPR analysis would be dominated instead by droplet residues. Also, do >20 micron crystals bounce upon impact in the omni-directional inlet (and therefore remain in the sample flow), similar to the designed bounce that happens in the preimpactor?

1e is a very distinct compositional category but labeling it as "industrial metals" is too general and possibly erroneous. See Jang AE 2006, Ault EST 2010, Sodeman EST 2005, Lake AE 2004, many others.

The compositional categories in Fig 9 are not consistent with the rest of the paper.

Sulfate and nitrate are likely to account for a significant mass fraction of submicron aerosol. Are these compounds detected by ALABAMA, and in which categories?

Consider presenting spectra intensities on a log scale so that important minor contributions are not hidden. Many of the signatures described in 2.6 cannot be seen in the mass spectra. Isotope signatures such as 54Fe are not clear.

p.4690 l. 15. How were periods of contamination by secondary ice and snowflake fragments identified?

Fig 6 – what do the black lines denote?

In the discussion of lead-containing particles (p. 4694 l.20), the authors cite disagreement between their ambient results and literature studies. However, the comparison is

critically dependent on how the various groups identified lead-containing particles. In the current manuscript, it appears only particles where lead is a major ion are included in this category, whereas other groups may use very different criteria.

In the comparison of size distributions (p. 4697), the authors mention that ALABAMA (and ESEM – really?) has a size-dependent detection efficiency. This should be considered when stating that agreement between measurements is "very good" or otherwise. Likewise, the particle density could play a significant role in comparing vacuum aerodynamic with geometric diameter, eg, in Fig 10a. The y-axes for Fig 10a,c,e are labeled dN/dlogD, but I suspect this is incorrect since no units are given and there is no mention of how to obtain quantitative size distributions from ALABAMA. Were the data normalized and if so how? Please be clear. What is the reason for the 2 order magnitude drop in OPC concentration over 1 bin in 10d? Typo in caption: 3 um.

Fig 11. The authors present statistical differences between background aerosol and IPR for the OC and Biominsal categories, but these principal results are presented with essentially no interpretation or context (p. 4698).

Reference formatting is not consistent. Sometimes "et al." is omitted. Differentiate between the two Cziczo et al. 2004 papers.

Wording and phrasing: p. 4685 l. 15 and 18. "released"

p. 4688 l. 23

p. 4692 l. 7

p. 4692 l. 17 verb tense

p. 4698 l. 13

p.4699, l. 11

p. 4702 l. 10 & 12

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Lake et al., Atmos Environ, 38 (2004) 5311–5320.

Jang et al., Atmos Environ, 41 (2007) 1053–1063.

Ault et al., Environ. Sci. Technol., 2005, 39 (12), pp 4569–4580, DOI: 10.1021/es0489947

Sodeman et al., Environ. Sci. Technol., 2005, 39 (12), pp 4569–4580, DOI: 10.1021/es0489947

Hudson et al., J. Geophys. Res., 2004, 109, D23S27, doi:10.1029/2003JD004398.