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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "On-line single particle analysis of ice particle residuals from mountain-top mixed-phase clouds using laboratory derived particle type assignment" *by* S. Schmidt et al.

Anonymous Referee #1

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Review of Schmidt et al., On-line single particle analysis of ice particle residuals from mountain-top mixed-phase clouds using laboratory derived particle type assignment

General comments:

The manuscript by Schmidt et al. presents valuable measurements of single-particle mass spectra from ice clouds, focusing on the composition of ice residual particles (IPR) in mixed-phase clouds. The manuscript is well formatted and presents a valuable experiment. Given the rarity of such measurements and the apparent success of the experiment, which was a difficult and complex one, the manuscript is appropriate for

publication in ACP. This manuscript is also important for having attempted a direct laboratory confirmation of each particle class.

However, I think there are several opportunities for the authors to improve the way in which the data are analyzed and reported, with respect to interpretation and statistical significance. In the following comments I will use the format p13,28 to refer to line 28 on page 13.

Major comments:

1-

The first question that comes to mind while reading this paper is the uncertainty of all reported values. Some effort was made for Fig. 3 but not for the clustering results. Roth et al. (2016, by the same group) describe a procedure to estimate uncertainties for these clustering results, why was this not applied here? If the authors have a good reason for not adapting the Roth 2016 method, and I realize some adaptation would be necessary, then they should use some other approach to numerically report their best estimated clustering uncertainties.

Clustering uncertainties should also be combined (eg in quadrature) with Poisson based sampling uncertainties to take sampling times into account. With these two sources of statistical uncertainty addressed, perhaps some of the rarer classes in Figs 2 and 6 may fall below the method limit of quantification.

Other uncertainties to be discussed include the % of laboratory particles that did not show the marker peaks and potential cross sensitivity of different marker peaks.

After uncertainties are estimated each stated percentage value % should include an uncertainty, for example those stated in Section 3.2.2.

2-

What makes this paper special compared to other single-particle mass spec papers is the laboratory study of different particle types. Section 2.3. This must have taken a significant effort, and is well motivated. Therefore, the laboratory results should be published in full detail!

Average mass spectra for each particle type, including error bars, could be added. These could be added in the supplement and also placed next to the identified particle types in Figure 1.

The authors suggest that marker ions may be instrument specific. However, the importance or unimportance of this variability is unknown until multiple labs publish such data. Moreover, I do not see why such markers should be instrument specific if all variables (eg laser wavelength, fluence, and pulse duration) are controlled. LDI mass spectrometry databases do exist outside of aerosol science.

3-

In Section 2.3 when discussing the lab spectra it is stated "only those mass spectra that represented the majority of the different fragmentation patterns were considered". What % defines majority? Moreover, this % should be used to define a correction factor (with corresponding uncertainty propagated into the result). If only 60% of particles were measured for salt but 90% for soot, then the reported IPR numbers should be scaled up by 1/0.6 and 1/0.9 respectively.

4-

Table 1 means nothing to the reader who has not read Roth (2014), since none of the parameters were defined or explained. Roth (2014) is a PhD thesis in German, and is therefore not accessible to the general community. I have quickly looked at the other publication by Roth et al. (2016) and it looks like a great deal of effort was put into the clustering algorithm, including uncertainty consideration. So it is a pity if the reader of the present manuscript does not know that.

Could the authors please include uncertainty analysis of the clustering results in this

manuscript. Also a brief description of the conceptual basis of the chosen clustering algorithm and corresponding uncertainty are missing from Section 2.2 (p4,3).

Finally, this manuscript used the name "rest cluster" whereas Roth et al. (2016) used the name "others cluster". I find the name "rest" confusing because this word has multiple meanings. "Others" has only one..

5-

I have several comments about the marker peaks and particle types:

5a- Although the general principle of finding unique marker ions is valid, I cannot see from the manuscript how the marker ion approach was possible. On p7,2 the text states that Table 3 contains "specific" marker peaks, but since these peaks overlap in almost all cases they are not specific.

A step by step explanation of how these markers were applied is necessary to understand what was done. A flow chart would be helpful.

5b- It would be a great improvement to split the marker peaks in Table 3 into two subtypes, one containing marker peaks that are truly specific and allowed unambiguous identification of a particle type, and the other containing marker peaks that provide supporting information.

Please also clarify the meaning of the colors in Table 3. The caption says that red colors are specific to each type, but this is not true, e.g. minerals and desert dust and volcano dust all share peak 27. Bacteria and pollen share 71. etc.

5c- Cn peaks are present in cigarette smoke, fuel exhaust, soot, desert dust, volcano dust. So which peaks were used as markers to distinguish these classes? Were the minor differences in the Cn range really enough to distinguish these types? This is connected to the previous point.

5d- Please add proposed/suggested elemental formulas to each ion in Table 3. Currently only Cn peaks are identified.

5e- p8,1-3 discusses that "biological particles" showed marker peaks related to amine-like or oxidized organic structures. How have these particles been identified as biological and not simply amine-like? If the particle type cannot be unambiguously identified as biological, it should be called "biological/amine" or similar, as was done for sea salt/cooking. I don't see how these particles were recognized as biological.

5f- The ambiguity between sea salt and cooking emissions is a significant issue. Were there no complementary measurements, eg AMS or molecular markers, performed during this field study which could help to udnerstand the nature of these particles? Moreover, I don't understand why there is any ambiguity since I can see more than one unique peak for sea salt in Table 3. e.g. 135 and 158. Or could peak heights be used?

5g- how has the PAH cluster been identified? I do not see any PAHs listed in the laboratory samples and I missed a discussion in the text. It looks like some aromatic related peaks are present but are they polyaromatic?

5h- Since reference spectra of pure composition were used, the manuscript should discuss the possibility of matrix effects when internally mixed atmospheric particles were measured.

6-

p6,20 What is the probability of a small particle passing through the CVI? I can imagine that the ratio N(ice) / N(total) is similar to the ratio prob(small) / prob(large), so that small particle leakage could be a significant source of error.

7-

p11,9-14 I am not convinced by the argument that Kdominated particles were biomass burning simply because they were smaller, although it is an interesting hypothesis. Perhaps the authors could use their laboratory data to investigate this hypothesis.

8-

The larger average size of IPR is interpreted as indicative that larger particles are better INP. Has the alternative hypothesis that larger particles pass more easily through the sampling apparatus and CVI been excluded?

9-

p12,15-21. Here the authors argue that relatively more PAH/soot particles were measured during one episode because the air mass rose higher and preferentially lost other better CCN particles to wet removal. Comparing absolute instead of relative numbers would better test this hypothesis. The speculation of picking up additional local emissions after rising higher is not justified since the air mass did not fall especially low after rising higher. Either a complete and detailed analysis is needed to test this hypothesis, or the speculation should be omitted.

10-

on p12,8, "these findings agree with the general statement that natural primary aerosol such as biological particles, soil dust or minerals serve as typical ice nucleators" does not come across as a scientific. Why is this general statement being proposed? If because of recent publications, then the citations are missing.

If I am not mistaken, what the current manuscript provides is a valuable demonstration of the presence of such IPR in the field (if the statistical analysis indicates that these conclusions are robust and if proper consideration to amine or other interpretations of "biological" are given).

A better phrasing of this statement would be something like, "This case study illustrates the potentially significant contribution of biological, soil dust, minerals, and sea salt/cooking emissions on INP concentrations in mixed phase clouds, as has been identified in the laboratory (citations)".

11-

The only category for organic aerosol in this study was "aged material" which contributed 30% of the total out of cloud particle number.

It is my opinion that the chemical composition measured by ALABAMA is highly skewed relative to the chemical composition measured by quantitative techniques (e.g. AMS OA, sulfate, nitrate, and ammonium, combined with dust and EC). Presumably the ALABAMA instrument therefore has significant biases towards or against certain species. A detailed and quantitative discussion of instrument sensitivity towards different species must be included in this manuscript, if the reported pie charts are to be interpreted quantitatively.

12-

As the authors note, the present data do not allow ice nucleation rates for different particle types to be determined. Therefore please change "particles have good ice nucleating ability" to "particles were observed within ice crystal residuals" on p12,26 and please change "The high ice nucleation ability of etc etc could be confirmed" to "The presence of INP from etc etc was observed". This avoids overstating the results, which are nonetheless valuable and interesting.

The authors may also improve their manuscript by comparing the relative fractions of each particle type they have observed to previous studies of IPR or IN composition. That is, by comparing to the Cziczo citation given later in this review and the various citations already present in the manuscript. Although ice nucleation rates cannot be determined, a quantitative comparison in another dimension can nevertheless be added.

Minor:

- Percentages of particle types are frequently reported, but it is not always clear what the reference is (% of all IPR vs % relative to all of that particle type?). Please give a universal definition in Section 2. Please also add uncertainties to each reported %.

Section 3.2.1. Some particle types are given no discussion at all (engine and PAH) while others are given extensive discussion (industrial and lead). If there is some reason why engine and PAH particles were not further discussed, please make a brief note for the reader.

- p3,21 This description of LDI (laser desorption/ionization) incorrectly implies two-step vaporization and ionization. The laser does not "vaporize a fraction of created gas molecules" since ionization can occur during desorption. Better would be "the pulsed laser fires and vaporizes/ionizes the particle partly or completely."

- p3,25 what refractive index was assumed for particle sizing?

- p4,33 cooking is not combustion, so change "directly produced by combustion" to "directly sampled from the source"

- p4,33 I believe "supernatant" is the scientific term for "washing water"

p5,3 when using the word majority, please give a number

p5,29 does the manual switching mean that there is some bias in the results? Was there always a cloud free period measured at the end of the in cloud periods? Please clarify.

p6,14, what is meant by "ambient temperatures below 0 C"? Either ambient, or below 0 C.

p7,18 please define "PAH fragmentation" including citations. Can "PAH" be recognized separately from "aromatic"?

p7,20 please give the physical reason why only sodium or potassium would be observed.

p9,30 please cite a paper for this point

p9,34 I don’t understand the motivation behind this sentence. The message seems to be that a similar number fraction of biomass burning particles in the aerosol and in the IPR is an unexpected result. Why would it be unexpected?

Fig 2 and 6. Please add uncertainties for all values. Please sort the table by either out-of-cloud or IPR values. Please add a column to the table "%IPR / %out-of-cloud" to estimate the relevance enhancement of each category, including uncertainties.

-The following articles should be cited in this manuscript: Jaenicke, Abundance of Cellular Material and Proteins in the Atmosphere, Science, 308, 5718, pp 73, 2005. Cziczo et al., Clarifying the Dominant Sources and Mechanisms of Cirrus Cloud Formation, Science, 340, 6138, pp 1320-1324.

Very minor comments:

p1,20, unclear wording. try, "the outcome of these laboratory studies was particle type specific marker peaks for each investigated particle type."

p2,5 starting from "therefore" is a repetition of the previous statement which takes some thinking to realize.

p2,22 please also discuss Cziczo et al., Science 2013.

p2,28 "first results" to me is synonymous with "preliminary results". Perhaps better is "Inspection of the data set showed"

p10,35-37. "does not represent the real distribution" is more clearly phrased as "is not corrected for sampling and detection efficiency"

p11,27 with temperature and relative humidity, the wet-bulb temperature is already given?

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