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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chemical composition of ambient aerosol, ice residues and cloud droplet residues in mixed-phase clouds: single particle analysis during the Cloud and Aerosol Characterization Experiment (CLACE 6)" *by* M. Kamphus et al.

Anonymous Referee #4

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The end message of this paper is simple and useful, but the path taken to get there is long and arduous. I think the structure of the presentation is good, but the paper is very long for ice results that are apparently not so unexpected and for droplet results that are more limited in scope. The results are important because they are unique and direct observations in an important environment.

The authors could improve the paper considerably with a little judicial editing. For

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example, keep the references in the introduction but leave out the many experimental details of others; only provide the salient facts pertaining to the results of IN or IFN measurements. Elsewhere there are many places where statements are repeated, in some cases more than one repeat. Many extra or redundant words are often used, and there are statements for which the meaning is unclear.

I have a concern about the authors' statement concerning lead: "Although lead was frequently detected in the BG and IR particles it was not a dominating compound in the particle spectra and therefore it did not form a separate particle class. A detailed discussion of the enhanced frequency of lead occurence in ice residues, its effects for ice nucleation and the consequences for cloud formation and climate is given by Cziczo et al. (2009)." Lead is present in clear and significant concentrations in classes 2 and 5 that make up 37% of the IR particles. It is suggested by Cziczo et al. that lead is a very efficient IN, and if their hypothesis is correct, then we would at least expect higher IR fractions for classes 2 and 5 compared with the BG fractions. In fact from the SPLAT results in Figure 4 the highest relative increases for classes observed in the IR compared to the BG particles are for classes 2 and 5. So why do you discount lead in the present study? Does lead have to be by itself in order for it to be more efficient as implied by your statement above?

I have a number of minor technical and editorial aspects that also need to be addressed before this work is suitable for publication in ACP.

1. The intake system and the efficiencies of the instrument with respect to particle size are complex, and there is no guarantee that the overall inlet performed as suggested. No apparent characterization of the inlet for the sampling period is provided. Were there at least measurements of cloud droplet number concentrations at JFJ available to compare with total particle counts from a CPC downstream of the CVI?

2. There is some discussion of processes that contribute to the chemicals measured in the aerosol and residues, but processes pertaining to in-cloud oxidation are not

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mentioned. Surely for a mixed-phase cloud study, this is important?

3. Abstract – only 57% of the SPLAT IR were dominated by minerals. This is misleading as mineral components were found in both other classes at not insignificant concentrations. “dominated” needs to be changed or defined.

4. 15378 – line 11 – “assumed”?

5. 15379 – lines 11-12 – what does “no activity in the decomposition mode” mean? – lines 15-16 – “Instead, it must be assumed that deposition and condensation are also good contact IN.” meaning? – Line 19 – “Here” refers to ?

6. 15380 – The activated fraction of dust particles forming ice varied from 5–10% at −20_C to 20–40% at temperatures colder than −40_C. How do you separate heterogeneous from homogeneous freezing when the temp is <-40oC? – define INSPECT. – What is the point of the statement: “sometimes located in the free atmosphere.”? Was it in the FT for these measurements? This appears to be answered later (see point 9), but why is it not succinctly addressed in one spot.

7. 15381 – It is stated that the “Operation of a CVI onboard a research aircraft has some major problems due to the high relative sampling velocity” after which you go on to discuss airborne CVI measurements of IN residuals. So are we to believe the studies of Targino et al and of Cziczo et al. or not? Please don’t misinterpret this comment as a criticism of those studies; it is a criticism of this discussion.

8. 15282 – “In contrast, it was not possible. . .” Is it now?

9. 15383 – Rather than the five pages of introduction describing in some detail a number of (mostly recent) ice nucleation experiments, I suggest a concise summary of the previous relevant work that can help put the present work in proper perspective. What are the main messages from the previous work? – “During the winter months it is mostly located in the free troposphere (Coen et al., 2007) and frequently surrounded by mixed-phase clouds.” Is it clear that the mixed-phase clouds you studied were not

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connected with the BL?

10. 15384 – “and it samples the entire aerosol population (interstitial aerosol particles, cloud droplet residues and ice residues) during cloud conditions.“ That is a difficult thing to do. There is a sense of confidence within this statement that is too high. At very least a reference is needed. – “The 90o sampling” is with respect to the horizontal wind? – In the first paragraph of section 2.2, it is stated that 20 um particles are sampled with an efficiency of 0.9. In the next paragraph, the collection efficiency is nearly 1. This needs to be clarified.

11. 15385 – What is the velocity of the aerosol at the pre-impactor (PI)? Could not the freezing droplets splatter and produce small ice crystals? How do you know that the ice crystals just bounce and do not fragment? If splintering mechanisms are possible in the atmosphere, as discussed later on this page with respect to secondary ice production, then why not for high velocity impaction? Was the PI tested with a CPC counter downstream to measure total particle concentrations? – Are the designed 10 and 4 um cut offs based on droplets? – “which is needed to reach a D50% cut size of about 5 μm (Schwarzenbock et al., 2000)”. In the controlled environment of a wind tunnel, a 5um cut for a CVI might be possible, but you need to explain why your situation should it be any different than airborne CVI measurements for which cut sizes are actually closer to 10-12 um. – What do you mean by “some condensable material”? Are you referring only to secondary production of particle mass? Or is this a reference to components of ice nuclei that result from condensation following high-temperature combustion (e.g. metals)?

12. 15386 – With apologies to Mertes et al (2007), this means that all ice crystal nuclei are larger than 100 nm? – A reference for the enrichment factor is necessary.

13. 15389 – Rather than “Because of this, no particles larger than 2000nm dva were detected during CLACE 6.”, say “Therefore, it was not possible to detect particles larger than 2000nm dva during CLACE 6.” – “Insufficient scattered light leads to reduced de-

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tection efficiency below about 300nm dva, although this limit is ultimately dependent on the specific light scattering property of the particle." What would be the compositions of dome of the particles <150 nm that the ATOFMS can measure? – "CCN were sampled by both mass spectrometers. . ." By CCN, do you mean cloud droplet residuals? If so, you need to use DR not CCN; the true CCN are modified by ambient in-cloud processes as well as by drying in the inlet.

14. 15393 and Figure 2 – "The size statistics for the background aerosol over the whole measurement period show a bimodal size distribution but this is largely attributed to the integral statistics for the long time period and the variation in the aerosol size distribution over the course of the campaign." The sentence is a little awkward. You have already noted that the efficiency of SPLAT is 300-400 nm, and thus the bimodal result may also a factor of sampling efficiency, especially when compared with the ATOFMS that maximizes at the minimum in the SPLAT distribution and shows only a weak suggestion of a bimodal feature. – You say "there was a larger average aerosol particle size during cloud-influenced periods whereas in periods without clouds the smaller mode at 300–400 nm dominated." And later, you say "Larger yet was the mode diameter of the CCN particles, peaking at about 600 nm." Again, these are residuals not necessarily the true CCN. Why are the DR larger relative to the other measurements? Is it due to sampling methodology, or perhaps they were modified by aqueous-phase chemistry. Aqueous-phase addition of sulphate would make them larger and reinforces the importance of not referring to the DR as CCN. – "The average total concentration of particles with sizes >300nm measured with the OPC during that time was 2.6 particles $cm-3$. This has been stated once before in the text and in the caption of Figure 1. Why is a third needed?

15. 15394 – Lines 4-8 – nitrate also seems to be increased in a relative sense. – "In class 4 (the corresponding class center from the ice residue classification is shown in Fig. 3). . ." What does this mean?

16. 15395 – "All classes, except class 1, show a fairly high degree of internal mixing for

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the background aerosol," is interesting because class 1 is also that with the lowest sulphate. – I don't understand the following statement: "There are some small differences to class 1 for the background aerosol where also a small signal for $NO-2$ and less carbon/organic content is found." – "Class 5, potassium with the largest variety of anions has gained increased importance in the ice residues compared to the background. . ." This sentence is unclear.

17. 15396 – "The OPC measured total particle concentrations for particle sizes >300nm between 0.05 particles $cm-3$ and 3.1 particles $cm-3$." Were there no measurements of cloud droplet number concentrations or by a CPC downstream of the CVI? It seems unusual to conduct this sort of detailed experiment without having the means to evaluate your CVI. – Line 25, spelling of completely. – It would be helpful to have the fractions of the totals placed beside BG, IR and DR in each panel of figure 3. – "Interestingly, class 5, potassium with a large variety of anions, and class 6, potassium with nitrates, were not found for the DR classification on this day." Why is this it interesting?

18. 15398 – "an enhancement of sulfate compared to the background aerosol and thus the importance of sulfate particles acting as CCN at the JFJ, at least for the one day of DR-measurements." Why could the enhancement of sulphate not been due to aqueous-phase oxidation? – It is clear from the SPLAT results in Figure 4 that classes 2 and 5 are significantly enhanced in the IR compared to BG. What stands out in these two classes is the lead. If potassium more important, then were Cziczo et al. (2009) wrong? – Line 14 – were, not was.

19. Figures 3 and 4 – In Figure 4, you classify SPLAT class 4 as "Sulfate carbon/organic", yet there are clear indications in your spectra (Figure 3) of Si, Fe and Ca, and a tiny bit of Pb. Why do you either ignore or discount these?

20. 15399 – Nowhere in any of the discussion on the sulphate residues is aqueous-phase oxidation mentioned; "gas-phase uptake" is mentioned with respect to particles

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and implies uptake of H2SO4, not SO2. A lot of the sulphate could be from that process and have nothing to do with the fine particles that nucleated the cloud particles. – Lines 14-15 – again, also aqueous-phase production. Considering that you were measuring mixed-phase clouds it is more likely that the ice particles resulted from freezing of droplets rather than deposition. – Lines 22-24 – is BC the only thing that may have nucleated the ice phase?

21. 15400 – Should be "(e.g. Pruppacher and Klett, 1997)". They helped a lot, but the concept you are discussing here came from many years before even P&K, 1978. – Lines 22-25 – this is a very interesting comparison because it could imply that the reason that supercooled droplets were present was due to the absence of mineral or metal components. I don't why people insist on discussing BC as something that can nucleate either the liquid or ice phase in clouds, but it is small here and perhaps that is enough for people to stop spending time and money on its activation aspects; although that doesn't mean that its not important as a substrate.

22. 15401 – Lines 9-10 - 2% of the IR are associated with class 5, which dominates the ATOFMS BG. Is 2% not within the uncertainty of the CVI measurement? – Lines 12-13 – has been stated at least twice before this. – "As for the IR there was a significant depletion of the potassium containing class 5 from 79% in the background aerosol particles to 3% in the DR." But, this could just mean that the apparent biomass burning air masses were relatively dry and not conducive to cloud formation at your site. – Lines 23-26 – Dust and BC were <2% of the BG particles. Does this mean that the dust particles were generally too big and that the BC particles were generally too small to be measured, or they just weren't that prominent? – Line 1 – perhaps, but 94% of the IR had mineral or metallic components, which may just reflect a good crystallographic match to ice. This statement depends on how you determine or specify classes.

23. 15402 – An important question is whether the minerals and metals are predominantly natural or anthropogenic? Why can we seemingly affect cloud droplet numbers but much less so ice crystal numbers, and what does this say for precipitation effects?

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24. 15404 – "...whereas it comprises about 25% of the SPLAT data (class 4). Since ice nucleation in mixed-phase clouds requires the presence of an IN, it is possible that this material is an agglomeration with an insoluble core that acts as the IN. This discrepancy warrants further field and laboratory investigation." Class 4 of SPLAT contains Ca, Fe and Si. What are you trying to say here? – "Also, iron was generally not found to be a dominating compound in the SPLAT IR data." In Figure 4, the SPLAT IR is comprised of classes 1, 2, 4 and 5. Each of those four classes has a peak labelled as Fe (also CaO) and the peaks are not insignificant. So what is the basis for this sentence? – Line 11-12 - Why do we consider the absence of droplet residues of biomass burning aerosol striking? And why must potassium come only from biomass burning?

25. 15405 – Lines 5-25 and Figure 5 – the long tail of the BG hits by SPLAT aside, both SPLAT and ATOFMS show modes of the IR particles at larger sizes than the modes of the BG particles. E.g. for SPLAT the mode is about 350 nm for the BG particles and just below 400 nm for the IR particles; for ATOFMS, the IR mode is about 600 nm compared with something closer to 500 nm for the BG particles. Is this instrumental or is this a real feature of the IR?

26. 15406 – Line 10 – why is it "highly interesting"?

27. 15408 – Line 15 – "young" might not always be correct.

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