

***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.**

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We thank referee #4 for providing a thorough review and many detailed and thoughtful comments.

Anonymous Referee #4

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Interactive Discussion

Discussion Paper



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 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.

Response: The introduction is significantly revised and shortened by about 30%.

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.

Response: Redundancies are omitted where possible in the revised version. We clarified and revised the statements from the list of minor comments.

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 occurrence 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?

Response: There seems to be a misunderstanding here. The authors fully agree about the important role of lead (as most of the authors are also authors of the Cziczo et al paper). The discussion of lead was omitted in the present paper as we thought that the discussion in Cziczo et al., 2009, is already fairly exhaustive and should not be repeated in the present paper. Furthermore, we tried to explain here that lead was found in many IN residue (and, yes, we think that it might play an important role for the ice formation), but it is not found as a compound that dominates the mass spectrum and therefore it is not responsible for the particle classification of the k-means algorithm. This is all that we wanted to say with our statement. In the revised version we now give a more comprehensive discussion of the lead results.

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?

Response: The Ice-CVI intake system and its sampling characteristics are evaluated in detail in Mertes et al. (AS&T, 41, 848-864, 2007). Using the identical setup and settings there is no reason to suspect that the inlet performance was different. This is also supported by the sampled residue number concentration and IWC that were quite similar to the values measured during the former inlet characterization. During the inlet characterization (Mertes et al., 2007) it was shown that the sampling efficiency for supercooled drops is significantly below 100%. Thus the comparison suggested by the reviewer is no suitable test of the sampling performance. Moreover the suggested approach would not provide any information about the ice particle sampling.

2. There is some discussion of processes that contribute to the chemicals measured

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in the aerosol and residues, but processes pertaining to in-cloud oxidation are not mentioned. Surely for a mixed-phase cloud study, this is important?

Response: We agree that potential in-cloud processing could have influenced the measured chemical composition of the residues. This fact is now mentioned in the text.

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.

Response: The statement is clarified in the abstract.

4. 15378 – line 11 – “assumed”?,
changed

5. 15379 – lines 11-12 – what does “no activity in the decomposition mode” mean? –

Response: "No significant activation in the deposition mode" is meant, but we shortened this paragraph to comply with the reviewer's main criticism.

lines 15-16 – “Instead, it must be assumed that deposition and condensation are also good contact IN.” meaning?

Response: We removed this sentence to comply with the reviewer's suggestion for a more concise introduction

– Line 19 – “Here” refers to ?

Response: "Here" refers to the paper of Ettner et al., referenced in the previous sentence. This sentence is also changed for the sake of a more concise introduction.

6. 15380 – The activated fraction of dust particles forming ice varied from 5–10% at $-20\text{ }^{\circ}\text{C}$ to 20–40% at temperatures colder than $-40\text{ }^{\circ}\text{C}$. How do you separate heterogeneous from homogeneous freezing when the temp is $<-40\text{ }^{\circ}\text{C}$?

Response: We removed the statement to comply with the reviewer's suggestion for a
C11936

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more concise introduction

– define INSPECT. –

Response: done; INSPECT = Ice Nuclei Spectroscopy campaign, Storm Peak Lab 2001 and 2004.

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.

Response: The introduction is shortened at this point. The issue of FT measurements is addressed later.

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.

Response: The high velocity of the airborne measurements might cause ice particle shattering, i.e. fragments are sampled as well. This has consequences on particle number concentration but hardly on the chemical composition of the large residues that is discussed in this section mentioning the results of Targino et al and Cziczo et al. Artifacts discussed by Murphy et al. like abrasion of metal particles can be detected and are considered by Targino et al and Cziczo et al. However, the criticism of Reviewer #4 on the chain of argumentation in this discussion is justified and the sentence mentioning the problems of airborne measurements is removed in order to avoid to confuse the reader.

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

Response: Yes, this is the basic concept of the Ice-CVI (cf. Mertes et al., 2007). Maybe the expression “in contrast” is misleading, so the sentence is changed to simply “But it

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



was not possible. . .”

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? –

Response: We revised the introduction considerably to be more concise and to summarize the main messages from 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 connected with the BL?

Response: Several observations (e.g. absence of diurnal cycles for CN-concentration and other aerosol parameters) give experimental evidence that the measurements at JFJ during the winter months are sampled from FT air masses and are not influenced by injections from the BL (e.g., Coen et al., JGR, 1997). We omitted the word "mostly".

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. –

Response: We revised the statement and included a reference: "The permanently installed total aerosol inlet, which is part of the Global Atmosphere Watch (GAW) project, is heated to 25°C and is designed to sample the total aerosol when no clouds are present (termed ambient or background aerosol) and to sample the entire aerosol population (interstitial aerosol particles, cloud droplet residues and ice residues of hydrometeors up to 40 μm) during cloud conditions (Weingartner et al., 1999)." Weingartner et al., (JGR, 104, 26809-26820, 1999)

“The 90° sampling” is with respect to the horizontal wind? – In the first paragraph of

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



section 2.2, it is stated that 20 μm particles are sampled with an efficiency of 0.9. In the next paragraph, the collection efficiency is nearly 1. This needs to be clarified.

Response: Yes, 90 degree sampling is related to the horizontal wind. The aspiration efficiency of cloud particles of a given diameter is a function of horizontal wind velocity (Noone et al., J. Aerosol Sci., 23, 153-164, 1992). - The first statement of a sampling efficiency of 0.9 for 20 μm particles is explicitly related to a wind velocity of 3 m/sec. The second statement of a collection efficiency of nearly 1 is related to the complete size range of ice particle sizes between 5 and 20 μm , since particles smaller than 20 μm have a higher aspiration efficiency. Thus, the two statements do not contradict with each other. In order to avoid confusion, the first expression that was intended to provide a particle size – wind speed – aspiration efficiency example is omitted in the revised version.

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 μm 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 5 μm 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 μm . – 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)?

Response: The particle velocity at the second stage of the PI is only (compared to aircraft measurements) 28 m/sec. As discussed extensively in Mertes et al. (2007) the

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design of the entire ICE-CVI is adjusted to avoid ice particle and drop break-up inside the system. These setup considerations are based on the work of Vidaurre and Hallett (12th conference of cloud physics, AMS, Madison, 2006), who defined a kinetic to surface energy ratio L for ice particles/drops and a limit L_{crit} below which ice particles/drops do not shatter. The parameters that can be controlled to be below L_{crit} are the particle velocity and its size, which is the reason that the upper accepted diameter determined by the settings of the VI is only $20 \mu\text{m}$. Splintering as a secondary ice production mechanism is related to much larger ice crystals (hundreds of μm) and not to the small ice particles ($\leq 20 \mu\text{m}$) that pass the VI and enter the PI. The authors do not understand exactly what Reviewer #4 wanted to find out concerning the PI with a measurement of the total particle concentration. Under cloud free conditions the particle concentration was equal to the total inlet, which is not surprising, since the ambient particles are smaller than $4 \mu\text{m}$. - Yes the PI cut-offs are determined for drops. But there is not much difference to ice particles, since they have a density of 0.9 g/cm^3 in this size range. - The newer designs of airborne CVIs using a shroud and operated onboard fast research aircrafts reach a lower cut-off around $5 \mu\text{m}$ as well. Thus there is no difference of our samplings to the airborne ice particle collections. But, a major difference is that the airborne CVI systems do not have a clearly defined upper cut-size. In general they sample ice particles up to $50 \mu\text{m}$ with a rather high efficiency. It is not possible to conclude the respective consequences on the results of the residue analysis. But this is not intended in this study, since the comparison with airborne measurements has to be derived from different cloud types. - "...some condensable material from the drop activating CCN...". Here the reference is to secondary ice particles only, where small residues can be produced when those particles are evaporated in the system. These residues may contain material such as sulfates from the original drop activating CCN which is part of the secondary ice particle mass after e.g. riming and splintering. The chemical composition of the ice nuclei is discussed in the result section. We removed "some condensable" to avoid confusion.

12. 15386 – With apologies to Mertes et al (2007), this means that all ice crystal nuclei
C11940

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are larger than 100 nm? – A reference for the enrichment factor is necessary.

Response: No, the text did not say that there are no IN smaller than 100 nm, but no statements can be made which of the small residues served as IN and which did not. There is a much higher probability that the analyzed larger residues acted as IN according to Mertes et al. (2007). - The enrichment is a consequence of the counterflow principle and is mostly not explicitly mentioned in the CVI literature. The basic reference of the CVI principle including the enrichment consequence is Ogren, J. A., Heintzenberg, J. and Charlson, R. J. 1985. In-situ sampling of clouds with a droplet to aerosol converter. Geophys. Res. Lett., 12, 121-124. Due to the request of Reviewer #4, this reference is added.

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.”

Response: ok

– “Insufficient scattered light leads to reduced de- tecton 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 some of the particles <150 nm that the ATOFMS can measure? –

Response: Examples of particle composition for the smallest detected particles (150-200 nm) are given in the revised version.

“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.

Response: Ok, changed to DR.

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

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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.

Response: clarified

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. –

Response: omitted here

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. –

Response: changed to DR and mentioned the possibility of aqueous phase processing.

“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?

Response: Ok, omitted.

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?

Response: Some class centers were very similar for ice residue and background

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aerosol. In these cases we only displayed one of the two class centers. This is noted here again. As we had stated this fact before, we omit it here in the revised version.

16. 15395 – “All classes, except class 1, show a fairly high degree of internal mixing for the background aerosol,” is interesting because class 1 is also that with the lowest sulphate.

Response: We mention the low sulphate now explicitly.

– 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 NO₂– and less carbon/organic content is found.”

Response: We removed the sentence to avoid confusing the reader. The statement is again just an additional information about the small differences in class centers between the IR and BG analysis and is not very important at this point.

– “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.

Response: rephrased

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.

Response: Please refer to the reply of the authors to comment 1 of Reviewer #4. A new evaluation of the intake characteristics is not needed, since the settings of the sampling system are identical to previous measurements. Moreover, the sampling of supercooled drops is not quantitative and would not provide any hint for the sampling efficiency of ice particles. The authors do not think that it would be necessary to repeat the evaluation of a sampler again and again after showing its characteristics in a first

dedicated experiment, which is presented in Mertes et al. (2007).

- Line 25, spelling of completely.

Ok

– It would be helpful to have the fractions of the totals placed beside BG, IR and DR in each panel of figure 3.

Ok

– “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?

Response: Removed "interestingly".

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?

Response: Certainly aqueous-phase oxidation of SO₂ may have led to the large amount of sulphate, on the other hand, the fact that other compounds are hardly found does show that the original CCN did also not contain other compounds, indicating sulphate as the main CCN. The more detailed analysis of the BG particles before and after the DR analysis additionally elucidates this issue.

– 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?

Response: We agree. Lead and its role is now discussed. We do not intend to dispute the findings of Cziczo et al., see discussion in the beginning (review 4, before point 1).

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



– Line 14 – were, not was.

ok

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?

Response: Indications of Si, Fe and Ca are now mentioned and discussed. See comment 24.

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 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.

Response: We mention the possibility of aqueous-phase production of sulphate again.

– Lines 22-24 – is BC the only thing that may have nucleated the ice phase?

Response: We do not understand this statement. P. 15399, l. 22-24 is about BC in the background particles. Nothing is stated here about nucleating the ice phase. Later on, it is stated that only 2 % of the IR were classified as BC particles.

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.

ok

– 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 [understand] why people insist on discussing BC as

Full Screen / Esc

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Interactive Discussion

Discussion Paper



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.

Response: We agree with this comment.

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?

Response: Yes, this could be within the uncertainty.

– 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. –

Response: As the new discussion about the DR event shows there were somewhat fewer potassium containing particles present in the air masses of 6 March in the BG particles, and much less in the DR particles.

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?

Response: The measurements indicate that BC and mineral dust were not that prominent. This is, for example, indicated by the fact that the OPC measured arldy any particles >2 μm , so we did not miss a lot of mineral dust particles that were too big for the mass spec analysis.

– 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.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Response: We do not understand to which statement this comment refers to, it does not fit to p. 15401, line 1 or 15402, line 1.

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?

Response: We agree, some discussion on the potential anthropogenic effects is added. Again, lead may be an important substance of anthropogenic origin. Potential effects for the radiation budget are discussed for cirrus clouds in Cziczo et al., Nature Geoscience, 2009. Potential effects on precipitation are beyond the scope of our paper.

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?

Response: We changed this statement to "Class 4 of SPLAT contains some signals from Ca, Fe and Si, therefore it is likely that this class represents particles with an insoluble core that can act as the IN that are coated by soluble compounds like sulphate, nitrate and organics."

– “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?

Response: We removed the 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?

Response: We rephrased the "striking" statement. Large potassium signal is typically

a good indicator for biomass burning aerosol but biomass burning aerosol is not the only source of potassium in the aerosol particles.

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?

Response: This could be an instrumental effect as the IR are expected to be more often non-spherical than the BG particles, and detection efficiency is different for non-spherical particles, as already discussed in the instrumental section.

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

changed

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

changed

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 15375, 2009.

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