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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.

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We thank referee #5 for providing a thorough review and many detailed and thoughtful comments.

Anonymous Referee #5 Received and published: 8 September 2009

The manuscript by Kamphus et al provides a valuable dataset detailing the composition

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Interactive Discussion

Discussion Paper

of ice nuclei and CCN within a mixed phase clouds sampled at a mountaintop site. However, the analysis of the data provides only general conclusions about nucleation processes that are not well established. The authors should address the major points listed below as well as comment on minor points prior to publication.

Major points:

1. The principal limitation of the study is that of comparing ice (IR) and droplet residue (DR) data to background (BG) data for a variety of meteorological conditions. This approach is understandable because the sampling method inherently gives low particle rates and poor statistics for individual cloud events. However, the useful information gained by using this approach is very limited. One example in the text (15397, line 1) describes a lack of spectra classes 5 & 6 in DR compared to mission-averaged BG abundance rather than BG abundance for that event. Considering the variability of aerosol properties within different air masses, what conclusion can be drawn from this comparison? Other examples are 15402 line 8 and 15404 line 11, where DR data could be compared to biomass aerosol in the BG. In these DR cases and wherever feasible, the authors should compare DR and IR to the BG data for that specific event, which unlike residue data, should be plentiful. Additionally, two possible general resolutions are 1) divide the analysis into 2-3 broad scenarios based on wind direction, cloud type, or an appropriate tracer such as CO, NOx, or black carbon; or 2) focus on the IR intensive March 1-2 cloud event as a case study. In some way, demonstrate that chemical and meteorological conditions are similar for any DR & IR comparisons with BG.

Response: As discussed already in the replies to reviewers 1, 3 and 4, we agree with this criticism and we therefore add a discussion for the comparison of BG and DR measurements around 6 March in ther revised manuscript.

2. The definition of aerosol types based on classes from a clustering algorithm does not appear to efficiently separate spectra based on chemical composition or IN capa-

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bility. Throughout the manuscript, some spectra cluster classes are labeled 'mineral dust', eg., SPLAT classes 1 & 2. However, all of the SPLAT classes in Fig 3 except class 3 have metallic components (other than K) characteristic of crustal material – Fe, Ca, Si. The authors then present fractional abundance of these classes in Fig 4, where it appears that the vast majority of BG aerosols contain crustal material. Is this expected? Or instead is this a product of a small fraction of spectra in each class that contained large metallic signatures that when averaged, produce minor peaks in the cluster centers? Furthermore, SPLAT classes with low/no metallic signatures (3 & 6) are the only classes that are underrepresented in IR, which also demonstrates the lack of selectivity of the clustering routine. Please elaborate on the homogeneity of populations within the clusters. Explain the ramifications on the analysis (for example, the small fraction of mineral dust aerosols present in multiple clusters), and explain the compositional labels for classes. Similarly, the separation of cluster classes is necessarily subjective. The authors should consider refining some classes based on spectra features. As an example, it appears that SPLAT classes 2 & 4 are essentially the same, ie, processed mineral dust, that differ only slightly in relative organic signal.

Response: We agree that there are some problems with the clustering algorithms when trying to identify, for example, IN capability of aerosol particles. The k-means algorithm, for example, does classify based on the most pronounced signals. Some small signals which can be very important for the ice nucleation ability of a particle, e.g., the lead signal or some smaller mineral or metallic compounds are not critical for the separation into classes by this classification scheme. Nevertheless, development of new classification schemes is beyond the scope of this paper. We ensured that the population within a cluster is fairly homogeneous. This means for example, that small peaks in Fig 3 are caused by small peaks that are present in almost all of the spectra that make up the class and they do not come from a few spectra with very high signals for these compounds. We explained these issues in more detail in the revised version and we give some additional analysis results (e.g. what fraction of BG and of IR particles contains lead, what fraction contains potassium, minor signatures of Si, Fe,

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etc.). The number of classes is somewhat subjective, and we agree that classes 2 and 4 are fairly similar, nevertheless, we prefer to keep SPLAT classes 2 and 4 separate, as some readers might be interested in the differences in the organic signals.

Minor points: Fig 3. The intensity of the negative ion peak at 55-56 m/z tracks the HSO4– intensity. It is probably a secondary electron peak created by a process (e.g., impaction) within the time-of-flight region. Could a similar process occurring during mass analysis also explain the high intensity signals at negative <10 m/z?

Response: We agree, we rephrased the discussion of this issue.

15383 line 25. List typical residence times and temperatures for the sampling inlets.

Response: The residence times and temperatures are now given in Section 2.1 and 2.2. In detail for the Ice-CVI temperatures are: From inlet via VI and PI to CVI tip: ice particles are guided at low velocities at ambient temperature. From CVI to sensors: ice particles are injected into a dry and particle-free carrier air at "lab" temperature, i.e. 25 to 30 °C. Ice-CVI residence times: From inlet via VI and PI to CVI tip: 6 sec CVI tip to evaporation tube: 0.01 sec inside evaporation tube: 6 sec evaporation tube to sensor: 1 – 2 sec

15385 lines 3-10. Specify that cut-off diameters are lower cut-off diameters.

Response: No, the PI cut-offs are upper cut-offs in order to pre-segregate the super-cooled drops with diameters larger than the cut-offs. Larger ice particles, but smaller than 20 μm due to the VI segregation, bounce off the plates, so that they overcome the PI (Tenberken-Poetzsch et al., 2000, Atmos. Environ., 34, 3629-3633).

15385 line 14. List temperature of this section.

Response: Ambient temperature. All CVI temperatures and residence times are now listed at the end of section 2.2.

15385 line 23. By sampling only the smallest ice crystals that have presumably nucle-

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ated ice most recently, is it likely that the Ice-CVI sampling will miss the most efficient ice nuclei (those that formed initially and have grown beyond the Ice-CVI size range)? Please comment here.

Response: Indeed, we have no information about the sampling location within the cloud, i.e. cloud base, cloud top, cloud edge or cloud core. Moreover, we don't know the heterogeneous nucleation processes that were active (deposition, immersion, contact freezing etc.). Thus we cannot rule out the scenario, which is described by reviewer #5, but it is just as well possible that conditions were encountered where only the most efficient ice nuclei produce ice particles, so that we miss the less efficient ones. With regard to the ice particle sampling we had to restrict the upper cut-off in order to avoid artefacts like particle shattering in the inlet system. Therefore we can only state that the sampled ice particles had to small and therefore most likely are quite young. Assuming measured ice particle growth rates between 0.4 and 0.9 μm/sec (Mertes et al., Atmos. Res., 58, 267-294, 2001) result in ice particle "life times" before sampling between 22 and 50 seconds.

15386 line 17. 'IN concentrations' measured by the OPC?

Response: Corrected to IR.

15387 line 4. Does the 300-400 nm maximum represent the overall 'detection' efficiency for the entire instrument (inlet transmission + light scattering detection + ionization hit rate) or just the transmission efficiency of the aerodynamic lens?

Response: Yes, the overall detection efficiency is meant (aerodynamic lens transmission + light scattering detection + ionization hit rate)

15393 line 11. Fig 2 shows a strong size dependence for CCN, particularly in the ATOFMS data, where only very large CCN (hundreds of nm) appear to be activating preferentially. Please comment on whether the large size of DR is an effect of the sampling method or is representative of a cloud microphysical processes, e.g., very

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small supersaturation of water.

Response: We are not aware of any influence of the sampling method nor the detectors on the DR size. Apparently the droplet residuals – which are not the original CCN – were indeed fairly large. Additional uptake of sulphate and nitrate as well as cloud processing of SO2 may have led to the large DR sizes. This is discussed later.

15397, l 25: DR are relatively enhanced in sulfate-containing spectra, or equivalently, spectra with metallic components are depleted in DR compared to BG (for this event?). Since largely, CCN activity follows aerosol size rather than composition, it would be interesting to mention whether the CCN-inactive mineral dust aerosols presumably in the background were larger than the sulfate-rich CCN-active aerosols. It also appears that mineral dust aerosols were coated with secondary material. This does not appear to enhance their CCN properties. Please provide a few comments.

Response: Again, please note that the DR probably have undergone further cloud processing. A more detailed discussion of the DR chemistry and the background aerosol sampled before and after the droplet sampling is now added.

15399 line 26. The authors state that the dominant BG class (ATOFMS class 5) is consistent with biomass burning aerosol. Is this 79% level typical of other tropospheric ATOFMS studies? Does this indicate a high biomass burning influence throughout the campaign? Do all of the class 5 particles contain potassium?

Response: Yes, all the class 5 particles contain potassium, and high potassium is typically a marker of biomass burning aerosol. Some amounts of potassium are very usual for aged free tropospheric aerosol and such high levels are not unusual for ATOFMS studies performed in the lower free troposphere. Note that also class 3 and 4 of the SPLAT classification contain substantial amounts of potassium, consistent with the ATOFMS. From the back trajectories, we were not able to connect the data with specific biomass burning events.

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15404 line 2. State whether any of the SPLAT IR class 4 spectra show indications of insoluble material.

Response: Yes, the SPLAT class 4 spectra (Fig 3) do contain also insoluble material. The text is changed 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."

15406 line 9. The authors should consider shortening the lengthy comparison to airborne IR data (although highlighting enhancement of metallic and dust components across various IR data is important), and instead compare to previous mountaintop measurements during the INSPECT campaign referenced in the text. State how the overall conclusions of IR composition and nucleation mechanisms for the CLACE study compare with those of INSPECT.

Response: We shorten the discussion of the airborne IR data and give a more detailed comparison to the INSPECT data (DeMott et al., PNAS, 2003, Richardson et al., JGR, 2007) in the revised manuscript. In general, the findings for the ice residual composition are similar, as mineral dust/fly ash and metallic compounds are found as the predominant classes of the IR in the JFJ data as well as the Storm Peak data. These groups are strongly enhanced in the ice residuals over the ambient background aerosol in all cases. Similar to the SPLAT findings, particles of mainly sulphate and organics are found for the ice residues with $\sim$15% (Richardson, Fig.5) to $\sim$25% (de Mott et al., Fig. 4), similar to the ice residues of classes 4 and 5 found by SPLAT in our measurements.

Technical corrections:

Fig 4a. Reds and greens are too similar. Change colors for clarity.

ok

15404 line 17. replace are with is.

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ok

15380 line 23, 15396 line 28, 15408 line 22: replace extend with extent.

ok

15395 line 26. Replace Different with Compared.

ok

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

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Interactive Comment