

***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 #1 for providing a very thorough review and many detailed and thoughtful comments.

Anonymous Referee #1 Received and published: 28 July 2009 General comments

This paper describes measurements from CLACE 6 from two single particle mass

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spectrometers at the Swiss High Alpine Research Station Jungfraujoch. Chemical composition data are compared for background aerosol, droplet residues and ice residues. Results are consistent with previous work, suggesting an enhancement of mineral dusts in ice residues and an enhancement of sulfates in the droplet residues. The data are a useful addition to the existing literature, and the manuscript should be published, but I believe that some additional analysis would make the dataset most useful to the reader.

Specific comments

1. p. 4, line 9. Given the appropriate ice nucleus, ice nucleation can occur in theory at any temperature below 0 °C, and ice nucleation has been observed very near this limit for some biological particles (see summary of [Szyrmer and Zawadzki, 1997]).

Response: We changed the text accordingly and included the reference.

2. A. p. 17, lines 1-3. Was the ATOFMS connected to the ice-CVI out of cloud for a long enough time to 'verify zero particle counts' with any confidence? From Figure 1, it appears that the ATOFMS was on the Ice-CVI inlet for ~6 days total. During this time, the ATOFMS characterized 152 ice particles, and, if similar to the SPLAT instrument, many of these were detected over an ~8 hour period on March 1-2. This corresponds to only about 1 particle per hour detected. One could calculate how many hours of sampling would be needed to verify 'zero particle counts' with 95% confidence, e.g. assuming a Poisson process. My initial guess is that the ATOFMS was not connected to the ice-CVI out of cloud for a long enough time period to verify zero particle counts with any real confidence.

Response: The ATOFMS itself was connected for several hours to the Ice-CVI before and after cloud events, when it did not detect any particles. To prove the proper functioning of the Ice-CVI, this is statistically not sufficient but the OPC and CPC data are used to verify that the Ice-CVI does not collect any spurious aerosol particles (see next comment). To be exact, 2-4 particles were typically detected per hour during cloud

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events.

B. p. 17, lines 1-3 and p. 17, lines 19-22. Along these same lines, were any particles detected from the ice-CVI inlet when sampling out of cloud, either by the ATOFMS or the OPC? Can the authors provide an estimate of the fraction of unactivated aerosol particles that are carried in the minor flow of the Ice-CVI? Even if the Ice-CVI is 99.9% effective at removing aerosol particles, 10% of the 'ice' signal would come from aerosol that has passed through the minor flow of the Ice-CVI. This might help explain some of the unexpected results described later in the paper (e.g. ice residues of 25% sulfate from the SPLAT measurement).

Response: During completely cloud-free periods when the Ice-CVI was tested, the CPC counted about 100-1000 times less particles than during cloud events (CPC concentrations $<0.005 \text{ cm}^{-3}$ vs. $1-10 \text{ cm}^{-3}$ during cloud events). Only the rare particles $>5 \mu\text{m}$ will pass the Ice-CVI and are counted during cloud-free periods. During cloud-events we assume that all particles $>5 \mu\text{m}$ have activated either as CCN or as IN. Therefore we are confident that the Ice-CVI is very efficient at removing all the ambient aerosol particles that are not activated. As statistics are much better for the CPC, testing for much shorter time periods (<1 hour) is sufficient in this case. This test was done in the beginning, several times during and at the end of the campaign.

3. p. 21, lines 16-20 and Figure 1. From figure 1, there is no clear change in the trend of the OPC signal when switching from the Ice-CVI to the total inlet on March 2, whereas most times the total inlet measurements are significantly greater than the Ice-CVI. This, combined with the relatively high ice concentrations (0.55 cm^{-3}) compared to the rest of the project, the statement that there were 'strong westerly flow conditions' for that time period, and the possibility for 'mechanical fracturing of falling or windblown ice crystals, especially during snow fall' [Mertes et al., 2007], suggest that the site was likely influenced by blowing snow at this time. How strong were local winds during this period? Given that nearly half of all of the ice residue data come from this period, it would be worthwhile to discuss differences in ice residue chemical composition from

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this period with the remainder of the project.

Response: It is correct that there was comparably little change in the OPC signal on 2 March when changing from the Ice-CVI to the total inlet. Wind speeds measured by Meteo Swiss during the cloud phase 1-2 March were generally 5-10 m/s reaching 10-15 m/s on the morning of 2 March (6 am-10am). Wind speeds measured directly at the Ice-CVI inlet were generally somewhat lower than the Meteo Swiss measurements as the Ice-CVI stands not as exposed as the Meteo Swiss measurement site. Therefore, wind speeds seem not to be too high in this case. Nevertheless, snow fell during this time and PVM measurements by PSI and Univ. of Manchester clogged up with snow. Also, CPC measurements behind the Ice-CVI were high (up to 20 cm⁻³). This indicates that a fraction of the IR after the Ice-CVI stem from secondary ice. Mertes et al. (2007) shows that the residuals from these secondary ice particles are smaller than 200 nm and are therefore not detected by the mass spectrometers. Nevertheless, some secondary ice residuals may have influenced the measurements during that time. A caveat about this situation is given in the revised text.

4. p. 21, line 27- p. 22, line 1. The fact that class 5, representative of biomass burning particles, is enhanced in the ice residues is consistent with recent remote sensing [Lin et al., 2006; Sassen and Khvorostyanov, 2008] and laboratory studies [Petters et al., 2009] which suggest that smoke particles can impact ice nucleation in the atmosphere. In fact, many of the components listed in class 5, including potassium, nitrite, chloride and sodium, were shown to be correlated with the production of ice nuclei from fires in the Petters et al. study.

Response: We are thankful for pointing out these references. We mention these consistent results and include the references in the revised ms.

5. p. 22, line 28 – p. 23, line 1. The fact that classes 5 and 6 are not observed in the droplet residues may simply reflect the fact that the air mass that was not affected by biomass burning. The authors might compare the back trajectories to fire observations

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from MODIS during this time period (<http://rapidfire.sci.gsfc.nasa.gov/>).

Response: This possibility is mentioned in the text already: p 28, lines 8-10. Nevertheless, a comprehensive discussion of the DR event and the background aerosol sampled before and after the event is now given in the text (see next comment). The MODIS data for this time does not indicate recent contact with larger biomass burning events.

6. Section 3.2.4. Although I understand the reasoning behind averaging the results for the ice residues to the background aerosol averaged over the entire project, the droplet residues were only collected during one day, and it would be useful to know how the DR compare to the background aerosol on this day (there should be sufficient particle counts for each category). As noted in the previous comment, it may simply be that the airmass did not contain any biomass burning particles. On the other hand, if there is a major contribution from class 5 in the background aerosol, but it is absent from the droplet residues, this would say something about the ability of smoke particles to act as CCN. In any case, it is a more useful comparison.

Response: This comment is similar to comments by several other reviewers. We do agree that it is more useful to compare only the background aerosol for a specific situation/air mass with the corresponding ice and droplet residuals. For the droplet residuals this is possible and the discussion is included in the revised version of the paper. Due to the low counting statistics this is not possible for the IR. Nevertheless, the IR proved to be fairly homogeneous over time, e.g., mineral particles as well as lead containing particles were observed throughout the campaign with a fairly constant rate of occurrence.

7. p. 23, lines 13-19 and Figure 4. The relative increases for coated versus uncoated mineral dust particles in the IR data compared to the BG data are surprising. Namely, class 1, thought to represent unprocessed mineral dusts, increase by a factor of <3 in the ice residues, whereas class 2, the processed mineral dust particles, increase

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by a factor of >6 . This is somewhat unexpected, given that laboratory studies (e.g. [Eastwood et al., 2009]) suggest that unprocessed mineral dusts are more IN active than processed particles.

Response: The comparison between IR and BG is limited anyhow as we are not comparing identical air masses, as noted in comment 6. It could be that cloud processing, e.g. uptake of sulfates and organics, explains why some of the uncoated mineral dust particles change into coated ones. Referee #2 notes in the first comment that he/she would actually expect mineral dust coated with some soluble compounds would be favored as ice nuclei over pure mineral dust as at the mixed phase cloud conditions at Jungfraujoch the freezing mechanism should be immersion or condensation freezing.

8. p. 23, line 28-p. 24, line 3. From the data presented, the results do not support the claim of the ‘importance of sulfate particles acting as CCN at the JFJ.’ First, as noted in the previous comment, the DR data need to be compared to the BG data from this day only. Second, significant cloud processing could be occurring in the droplets, adding sulfate mass to the particles after the particles have activated as droplets and causing a shift in their classification. In fact, the large size of the droplet residues (Fig 2) supports the notion that some cloud processing has occurred.

Response: Yes, cloud processing may have contributed significantly to the sulphate mass after activation. Also, in the revised manuscript, the discussion is now confined to a comparison with the BG data from this day. Nevertheless, a fraction of the class 3 particles of the DR data show really just sulphate and nitrate, so for these particles there were no cores that were not sulphate/nitrate.

9. p. 27, lines 7-9 and Figure 4. Although the authors note later in the text that the SPLAT and ATOFMS categories cannot be compared directly, it is surprising the dramatic differences in the biomass burning categories for BG (11% vs 79%) and IR (enhancement of biomass burning particles in the SPLAT instrument and depletion in the ATOFMS) compositions from Figure 4 for SPLAT and the ATOFMS. How do the data

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compare when considering identical sampling periods?

Response: A specific discussion of the potassium signals for BG, IR and DR for time periods when both mass spectrometers measured simultaneously is now added to the revised ms which resolves some of the apparent inconsistencies. Nevertheless, due to the instrumental differences between the two instruments some of the differences remain.

10. p. 31, lines 2-4. Just looking at Figure 4, I come to very different conclusions about the chemical composition of the BG and IR based on the ATOFMS dataset compared to the SPLAT dataset. The authors clearly recognize the difficulty in interpreting the results from the two measurements, so much so that they deem it necessary to tell me (p. 29, lines 21-22) that the two datasets 'do not represent a contradiction.' With that said, although it was not the intent of the authors to do a comprehensive comparison of the 2 mass specs, it seems like a relatively straightforward exercise for Section 3.4 to compare data from the two instruments for the same sampling periods. Such a comparison would be much more useful than simply explaining why the two datasets (which should yield similar data) cannot be directly compared (do we need multiple single particle mass specs at every field campaign?). If after comparing measurements from identical time periods, the two instruments still yield different results, this would at least help the reader better appreciate the biases that each instrument has, so that (s)he can better judge data from these instruments in future field campaigns. I would go so far as to say that it would be most useful (although I'm not sure if it's possible) to analyze the data using the same classification schemes for the two instruments.

Response: A comparison for identical sampling periods for DR and BG particles on 6 March is added. Differences still exist but can be explained by the different ablation/ionization wavelength and the different classification schemes. Using the same classification schemes in the future is clearly desirable but beyond the scope of the present paper. Altogether it should be seen as an advantage that we had two single particle mass spectrometers present. Interpretation of the data is not as straight for-

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ward as in cases when only one MS is present but eventually more is learnt about the data each of the mass spectrometers produces.

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

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