

***Interactive comment on* “Observation of chemical modification of Asian Dust particles during long-range transport by the combined use of quantitative ED-EPMA and ATR-FT-IR imaging” by Young-Chul Song et al.**

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Response to comments of Anonymous Referee #3

We thank Anonymous Referees #3 for his/her valuable comments. We realized how carefully his/her review was done on our manuscript. I would like respond to the reviewer's comments in the raised order, comment-by-comment.

\* Reviewer's General comments: This article is focused on the chemical modification of Asian dust particles which could occur during long range transport by using

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combined SEM-EDX and ATR-FTIR imaging. Authors have previously collected and characterized particles during Asian dust storm events from 2000 to 2006; the results are reported in previous publications. One of the samples (from one day in 2002) was unique because it mainly contained calcium rich particles. This work focuses on the elemental and molecular characterisation of these calcium containing particles. The main results of this work concerns the detailed mineralogical characterization of 109 particles by complementary used of single particle analysis techniques. This original methodology was successfully applied by authors in previous papers published by the group. In addition to the detailed characterization of particles, authors highlighted in this manuscript, amorphous calcium carbonate and CaCl<sub>2</sub> particles in the unique sample. Undoubtedly, this work well demonstrates that using complementary single particle analyses are valuable to properly describe the chemical transformation of particles occurring in the atmosphere. However, the main drawback of the paper concerns the number of particles which were analysed. In my opinion, results and discussion are based on a too restricted number of particles. For example the number of amorphous carbonate was found for 4 particles and CaCl<sub>2</sub> for 3 particles and described as “a significant portion of Ca-containing particles”. The “chemical modification of Asian Dust Particles during long range transport” (as announced in the paper’s title) cannot be described with solely 109 particles collected during one day and for the only one size fraction of particles (> 4 μm). Authors should strongly demonstrate that such little number of particles is adequate to draw a general conclusion about chemical modification of Asian Dust particles. Finally, there are several over interpretations of the results (see specific comments) that should be revised. The manuscript should be reconsidered before publication in ACP Journal.

Response: We appreciate the reviewer’s very helpful comments on our work. As all the general comments are raised again in the following specific comments, we would like to respond to the specific comments, rather than to the general comments.

\* Reviewer’s specific comments:

(1) P 27299 line 21-22: some more recent references should be cited.

Response: As suggested, more recent references will be included in the revision.

(2) P27300 line 16: 178 particles or 109 were analyzed?

Response: “178” is the number of particles analyzed in our previous work (Hwang and Ro, 2006). To make the statement clear, the phrase will be modified (Among overall 178 particles analyzed in that work, ...).

(3) P27302 lines 2-3: why only particles from the stage 3 were characterized?

Response: This Asian Dust event was one of the most famous ones in Korea, which occurred in the autumn as a record-breaking episode. As stated in the manuscript, Chung et al. (2003) described the details of this event such as the source, pathway, and mass concentrations. One of our previous articles (Hwang and Ro, 2005), where the backward trajectories were given, reported chemical compositions of particles of the wide size range (particles collected on stages 1-5 of May cascade impactor) collected at this Asian Dust event. In that work, particles of all the stage samples of this Asian Dust were observed to have experienced extensive chemical modification during long-range transport. As the stage 3 sample among all the stage samples showed extensive chemical modification, this stage sample was again investigated more in detail using low-Z particle EPMA to understand the characteristics of chemical modification which these Asian Dust particles experienced. This work was published in our cited article (Hwang and Ro, 2006). Also, in the manuscript (p.27301, lines 23-24), we stated that “The single particle analytical results for the samples using low-Z particle EPMA and more details on the samples can be found elsewhere (Ro et al., 2005; Hwang and Ro, 2005, 2006). (Ro et al., 2005; Hwang and Ro, 2005, 2006)”. Recently, we have developed a new analytical methodology which combines low-Z particle EPMA and ATR-FTIR imaging. We were curious how different information we could get from the Asian Dust sample, which we thought to have known very well. By the application of the new analytical methodology, it turned out that we observed some of new findings

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about these Asian Dust particles, for example, the first observation of ACC in Asian Dust particle sample. I think this historical introduction about this sample, which is also given briefly in the introduction part of the manuscript, can be the answer to the comment.

(4) P27302 line 10: High vacuum measurements should be specified.

Response: It is quite well known that SEM measurement is done in high vacuum so that we have never stated about the vacuum in our papers, except Environmental SEM measurement where the chamber pressure condition is important.

(5) P27304 lines 10-12: PCA analysis was performed on ATR-FTIR data. Is there any correlation between the different PC? That should be indicative for determining the mixing state within particles isn't it?

Response: PCA was used for the display of the ATR-FTIR image. PCA is not sufficient to specify the chemical compositions of particles, so that we worked with ATR-FTIR spectrum itself for each particle.

(6) P27304 line 15: by “equivalent diameter” Authors mean “geometric diameters”?

Response: In the manuscript, the “equivalent diameter” is explained as “the equivalent diameter was calculated by assuming that a particle with the same area for a particle on SEI is circular.” and it is “geometric diameter”.

(7) P27306 lines 27-28: cristobalite should be replaced by SiO<sub>2</sub>. Note that cristobalite is the high temperature crystallization form of silice. If cristobalite identification is confirmed (quartz is expected), what is the source?

Response: Indeed, ATR-FTIR can clearly distinguish cristobalite from quartz (two split IR peaks at  $\sim 795$  and  $\sim 775$  cm<sup>-1</sup> for cristobalite and one peak at  $\sim 795$  cm<sup>-1</sup> for quartz). Cristobalite is one of common minerals in the crust. Regarding the analytical details on cristobalite and quartz, please see our cited, previous papers (Jung et al., 2010; Malek et al., 2011).

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(8) P27309 line 2: I am not convinced that 4 particles can be considered as “significant fraction”

Response: In our single particle analysis, 4 particles among 41 is “a significant fraction”. However, the phrase will be deleted without deteriorating the context.

(9) P27309 and 27310 lines 27-28 and 1-2: ACC can be collected within a water droplet without to be hygroscopic. In addition, the spectrum from the particle # 62 (Figure 3) does not clearly show an IR bands from H<sub>2</sub>O. The broad band in this spectrum region can also be obtained from a false background correction.

Response: If ACC is not hygroscopic, but was collected within a water droplet, then ACC should be observed as somewhat segregated moiety in the dark, circular water droplet. However, the water droplets containing ACC are homogeneous, which is the same to water-soluble organics and inorganics such as Ca(NO<sub>3</sub>)<sub>2</sub>. Figure 3 shows three ATR-FTIR spectra (which were not background corrected) together with X-ray spectra and SEIs, so that peaks in the ATR-FTIR spectra look smaller than original ones. In the full-scale spectra, the presence of the IR bands for H<sub>2</sub>O is very clear, although the H<sub>2</sub>O bands in Figure 3 are also clear for us.

(10) P27310 lines 3-5: 3 particles of CaCl<sub>2</sub> is not significant and cannot be considered as “a significant portion”

Response: This is the same argument as above. In our single particle analysis, 3 particles among 41 is “a significant portion”. However, the phrase will be deleted without deteriorating the context.

(11) P27310 line 4: CaCl<sub>2</sub>-containing instead of “CaCl<sub>2</sub>-conatining”.

Response: Thank the reviewer for the correction. It will be changed.

(12) P27310 lines 12-14: this is an over interpretation of the results. There is no proof for an atmospheric CaCO<sub>3</sub> to CaCl<sub>2</sub> conversion. Only 3 particles over 109 were found as CaCl<sub>2</sub>.

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Response: We agree that there is no proof for an atmospheric  $\text{CaCO}_3$  to  $\text{CaCl}_2$  conversion, although it is very probable. In the revised version, we will use the phrase, “ $\text{CaCl}_2$  particles probably converted from  $\text{CaCO}_3$ ”.

(13) P27311 lines 7-10. Results undoubtedly shown chemical modification but stating about an “... extensive heterogeneous reactions during long-range transport” is again an over interpretation. This should be true if the results were supported by related backward trajectories.

Response: As stated in our response for comment #3, we used the argument based on our previous and current works, and the related backward trajectories were already published in our previous paper which is cited in this manuscript.

(14) P27312 line 10: “...are real or due to...” should be replaced by “are of atmospheric origin or due to...”

Response: Thank the reviewer for the correction. It will be changed.

(15) P27313 lines 11-12: “humic substances” should be replaced by “organic substances. FTIR spectrum does not provide any evidence of humic substances.

Response: Thank the reviewer for the valid suggestion. It will be changed.

(16) P27313 lines 17 and 24: There are some differences between elemental and molecular composition of particles. Sulphate and silicate (montmorillonite) were identified without detection of sulphur, Al and Si. Is there an explanation?

Response: The very similar thing also happened for  $\text{NaNO}_3$ -containing particle #33, for which there are some differences between elemental and molecular composition. In the manuscript (p. 27312, line 19 – p. 27313, line 12 - just before p.27313, lines 17-24), we explained why in details.

(17) P27314 lines 8-9: Calcite is not a silicate.

Response: Thank the reviewer for the correction. It will be changed.

(18) P27315 line 1-2: The sentence “The non-swelling silicate particles also contain water as well as nitrate and organic” should be removed. This is probably a mixing of compounds, isn't it?

Response: Thank the reviewer for the correction. The word, “contain”, will be changed as “be mixed with”.

(19) P27315 line 27: (see also figure 5 – particle # 45) Peak attribution at 1623 cm<sup>-1</sup> is doubtful, I can only see a broad peak centred around 1635 cm<sup>-1</sup> on the figure.

Response: As stated above, peak recognition is clear when dealing with the full-scale ATR-FTIR spectra.

(20) P27316 line 2: “Of these, the major focus has been on the ability of...” (on is missing)

Response: Thank the reviewer for the correction. It will be changed.

(21) P27316 line 4: “..to enhance their reactivity”

Response: Thank the reviewer for the correction. It will be changed.

(22) P27318 lines 18-19: The sentence “In addition, a significant number of ACC particles were encountered in the samples” is an over statement. Only 4 ACC particles were encountered in the unique sample.

Response: The “a significant number” will be deleted.

(23) P27319 lines 1-4: This study provided detailed information on the physicochemical characteristics of 109 particles collected during a specific dust event containing a huge amount of Ca-rich particles. But there is no proof from the presented results of an extensive chemical modification of Asian dust particles during long range transport in general. The conclusion should be modified as regard to the few number of particles analysed. Finally, it should be valuable for the discussion to add backward trajectories in this paper.

Response: In our previous responses, we responded to this comment.

(24) A table containing FTIR bands with respective assignments should be added (in the manuscript or in SI) for a better reading of the paper and figures.

Response: The table will be added in SI.

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 27297, 2012.

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