

## ***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 #2

We thank Anonymous Referees #2 for his/her comments, and for his/her valuable time and effort spent for the review. I would like respond to the reviewer's comments in the raised order, comment-by-comment.

\* Reviewer's comments:

(1) Song et al. present the single-particle analysis of just 109 individual particles col-C11725

lected in Korea during one day of an Asian dust storm event. The particles were analyzed using two complimentary methods: quantitative energy-dispersive electron probe X-ray microanalysis, and attenuated total reflectance FT-IR. The combined analysis by these two complementary methods appears to be the only novel aspect of this work. The single-particle analysis is presented largely as a few case studies in with the chemical composition derived by the two techniques is described in great detail. Little effort is made to really summarize the measurements from the rather small number of particles analyzed. The fact that so few particles were analyzed from a sample collected on just one day makes it difficult to draw conclusions about the typical composition and behavior of atmospheric dust particles. The analysis of this same one-day sample has in fact already been presented by these authors in three other publications. Overall, I am not sure what has been learned from this analysis. The combined methods certainly provide unique and valuable information, but I do not feel that any new significant findings have been reported here. The atmospheric aging of Asian dust particles has been extensively reported on in numerous reports. While these new single-particle methods could certainly provide valuable new information regarding the composition and aging mechanisms of mineral dust, no such new knowledge appears to be presented in the manuscript in its current form. Therefore, I must conclude that this paper does not satisfy the requirements for ACP, and recommend that it be rejected with the possibility for re-review after extensive revisions and expansion.

Response: This Asian Dust event, during which the sample was collected, 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; cited in the manuscript) described the details of this event such as the source, pathway, and mass concentrations. One of our previous articles (Hwang and Ro, 2005; cited in the manuscript), 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 the most extensive chemical modification, this stage sample was again investigated more in detail using only 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).”. After the development of the combined use of EPMA and ATR-FTIR imaging for the characterization of the same single particles, we applied this combined technique to the same stage sample for getting better speciation and characteristics of the chemically modified particles, which is the work presented in this manuscript. By the application of the new analytical methodology, it turned out that we observed some of new findings about these Asian Dust particles, for example, the first observation of ACC in Asian Dust particle sample. I think this historical introduction about this work, which is also given briefly in the introduction part of the manuscript, can be needed to answer to this general comment. The reviewer is quite critical about our work, mainly based on the rather small number of the analyzed particles for the single sample, and thus the reviewer think that it is difficult to draw conclusions about the “typical” composition and behavior of atmospheric dust particles. As stated above, in this work we never tried to draw conclusions about the “typical” composition and behavior of atmospheric dust particles. We already did that kind of works which were published in our previous papers (Geng et al., *JAWMA*, vol. 61, pp. 1183-1191, 2011; Geng et al., *Atmos. Chem. Phys.*, vol. 9, pp. 6933-6947, 2009; Hwang et al., *Atmos. Environ.*, vol. 42, pp. 8738-8746, 2008; Hwang and Ro, *J. Geophys. Res.*, vol. 110, D23201, 2005; Ro et al., *Environ. Sci. Technol.*, vol. 39, pp. 1409-1419, 2005). This work is to obtain new and more detailed information on the aged Asian dust particles, which we are already somewhat familiar with, by using a new analytical approach. Another point is how many particles are judged as too small or enough for the characterization of a sample in single particle analysis. Generally speaking, the representativeness in the

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single particle analysis can be valid for particles of major chemical species if the number of analyzed particles for a sample is  $\sim 150$  or more as shown in our previous work (*Anal. Chim. Acta*, vol. 389, pp. 151-160, 1999). The number of particle analyzed is not that big here, but we have focused on the new findings from the sample. I think that the new findings we observed in this sample are not denied by the number of particles analyzed.

(2) My main criticism is that it is not clear that questions or hypothesis are being probed by this study. The atmospheric aging of dust particles is too broad a topic to properly define these questions, and has already been explored by a very large number of publications – including many by these authors. What specific questions or processes are being explored here?

Response: As the title of this manuscript indicates, this work is about the new observation for the aged Asian dust particles by a new analytical methodology, i.e., the combined use of EPMA and ATR-FT-IR imaging. Maybe the title gives somewhat broad impression to the reviewer. The new title, “Investigation of aged Asian dust particles by the combined use of quantitative ED-EPMA and ATR-FT-IR imaging” will be better.

(3) The unique chemical information the authors are able to derive using their combined methods can provide valuable new insights into the aging of dust particles, but I did not think that this was explored very deeply in this paper. Several findings that have been reported in other recent dust aging papers could be explored using these methods. Some questions to explore include: Is sulfuric acid present with nitric or hydrochloric acids in the same dust particle, or is sulfuric acid not found mixed in high concentrations with other acids as has been reported by Sullivan et al. (2007a)? When is ammonium found in dust particles, if at all? What other secondary compounds are present with ammonium? What other compounds are found when organic compounds are found in dust? Is there any evidence for photochemical versus cloud processing as a formation pathway for carboxylic acids and other secondary organic compounds in dust? Refer to [Mochida et al., 2003; Sorooshian et al., 2007; Sullivan and Prather,

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2007]. How does the dust mineralogy influence the aging of the dust particles? Some insight into this is briefly given for silicate-containing particles that “did not experience chemical modification”. This is an important question and should be explored more deeply. An important issue is that the small number of particles examined here, all collected from the same sample, makes it difficult to reliably draw conclusions from this limited analysis to the real atmosphere. It can't be determined if the results obtained from this one sample represent typical atmospheric dust particles, or were unique.

Response: This is the first report on the characteristics of an Asian dust sample by the combined use of low-Z particle EPMA and ATR-FT-IR imaging on a single particle basis. We believe that our new technique provided quite interesting findings which could be obtainable only by this analytical approach. We did our best to extract scientific information about the aging of the Asian dust particles from our EDX and ATR-FT-IR spectral and SEI morphological data as much as possible by this much detailed interpretation of the spectral and morphological data for all the analyzed individual particles. There are many, many topics to be investigated about the aging of Asian dust particles, for example, as the reviewer listed just some of them in the comment, which should be answered in the future and by many different researchers and analytical methodologies.

(4) No discussion of the results is presented, just the results, and the conclusions are rather uninspired.

Response: When we present our results in our manuscript, we tried to discuss what we observed as much as possible. However, we will try to add some more discussion and modify some of conclusions.

(5) The number of self-citations is excessive here. I counted 18 different papers by Ro, C.-U. cited in this not very long manuscript. Most of these papers appear to describe highly similar topics. The number of self-citations should be reduced to a more appropriate level, while the related work from other researchers needs to be more properly

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and thoroughly cited here.

Response: I would try to respect the impression of the reviewer that made the reviewer to say that “most of the self-cited papers appear to describe highly similar topics”. When we revise the manuscript, we will minimize the self-citation as much as possible.

(6) [Jeong and Chun, 2006; Jeong, 2008] have presented some interesting single-particle analysis of Asian dust mineralogy that is closely related to this work and should be cited here. Do you find any evidence for or against his report of “microfibers” of calcite in Asian dust particles?

Response: As we have been well aware of his works, their works will be cited as recommended by the reviewer. To our best knowledge, his report of “microfiber” calcite has been the only one until now. We have worked with many Asian dust, urban, and Chinese soil particles, and yet we have not encountered the “microfiber” calcite yet.

(7) The presence of amorphous calcite was implied by [Sullivan et al., 2010] and the authors might find that report, and the references within, useful.

Response: It is very interesting to notice that in the mentioned paper the authors suggested the speculated existence of ACC as one of the possible explanations for their CCN activation observation of wet-generated standard calcite particles. Our approach clearly proves the existence of ACC in Asian dust particles, so that their speculation would be at least indirectly supported. In the revised version, we will make a reference of the work where the description of ACC in our manuscript is given.

(8) Analyzing different collection stage sizes would have produced more meaningful results. Apart from the particle size limitation of the ATR analysis, why was only one sample from one stage examined?

Response: I think that my response to comment #1 given above would be the answer to this comment.

(9) The ability to determine the specific minerals present in dust particles is a big ad-

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vantage and should be exploited more. For example, on page 27316 the authors state: "On the other hand, in this Asian Dust sample, the CaCO<sub>3</sub> moiety originally present in silicate mineral particles appears to be more important for their aging than their silicate mineral type." This is the type of interesting finding that should be explored in much more detail.

Response: This is the first work on Asian dust characterization by the combined use of low-Z particle EPMA and ATR-FT-IR imaging on a single-particle basis. We are pretty sure that we would find new additional things about the characteristics of Asian dust if we would apply this analytical approach further in the future.

(10) The individual particle mixing state naming scheme used here is clear and efficient.

Response: Thank the review for this comment.

(11) Tables are badly needed to properly summarize the findings. The single-particle analysis must be summarized and digested much more thoroughly.

Response: In our revised version, a table summarizing the number of the encountered particles based on the different chemical compositions will be provided, together with a table about FT-IR peak information on chemical species encountered in our analysis as also recommended by Referees #1 and 3.

(12) There are other reports of HCl reacting with dust particles [Ooki and Uematsu, 2005].

Response: In the mentioned paper, an in situ experiment to react ambient acid gases in the urban air of Tokyo with "standard" mineral dust particles loaded on a filter was performed. What they did was to analyze dissolved Cl<sup>-</sup> concentration before and after its reaction with the mineral particles, which didn't provide any clue on what chemicals in the mineral particles reacted with HCl. On the contrary, the cited papers in our manuscript clearly claimed the possible conversion of CaCO<sub>3</sub> into CaCl<sub>2</sub>.

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(13) Page 27310: "This is the first report of the field observation of CaCl<sub>2</sub> particles converted from CaCO<sub>3</sub> in a sample collected in the planetary boundary layer." I don't think this is accurate. See [Sullivan et al., 2007; Tobo et al., 2009] for example.

Response: This comment was also raised by Referee #1. Our response to that comment is repeated here. - Until now, there are just two report about CaCl<sub>2</sub> formation from CaCO<sub>3</sub> (Sullivan et al. 2007b and Tobo et al. 2010; cited in the manuscript), which were observed in marine boundary layer. In the text, we want to say this is the first inland observation on CaCl<sub>2</sub> formation from CaCO<sub>3</sub>. As the reviewer pointed out, "in the planetary boundary layer" has a different meaning from "inland". In the revised version, the words, "the first inland field observation", will be used.

(14) Should also reference the closely related work of [Shi et al., 2008].

Response: The mentioned paper reported the hygroscopic behavior of nitrate- or sulfate-containing dust particles. The paper will be cited when Ca-containing particles are described in our manuscript.

(15) Fig. 1C: Does the different color of the particles correspond to anything?

Response: Different PCs from PCA analysis are shown in different colors in Fig. 1C, which are used for the display of the ATR-FTIR image. PCA result is not sufficient to specify the chemical compositions of particles, so that we worked with ATR-FTIR spectrum itself for each particle.

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

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