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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Investigation of aged aerosols in size-resolved Asian dust storm particles transported from Beijing, China to Incheon, Korea using low-*Z* particle EPMA" *by* H. Geng et al.

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We greatly thank Anonymous Referees #1 for his/her valuable comments. Following the comments and suggestions, we modified our manuscript as much as possible. Our replies to the reviewer's comments are provided as follows.

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* COMMENT 1: Overall the paper presents a very detailed analysis of individual Asian

dust particle composition as measured by EPMA. The topic of this paper does not bring any new major ideas to the current knowledge of atmospheric chemistry. It has been known for years that Asian dust undergoes heterogeneous processing. The authors seem to want to use Mg/Si or Mg/Al ratios as "indices of the ageing process", but offer no insight as to why this may be of use. This result is highlighted in the abstract, results, and conclusions but offer no mechanism why the Mg/Si or Mg/Al ratio should change. In order for this manuscript to be published in ACP, I think the authors should thoroughly re-think the focus of the paper if they cannot provide solid reasons why the Mg/Si or Mg/Al ratios change in the manner that they do. The only way that one of the ratios would change is if 1) one element was preferentially deposited 2) the Mg, Al or Si volatilized (doubtful) 3) there were different source contributions or, 4) there is coagulation with sea salt. What kind of chemical reaction is expected? The authors should address these scenarios and indicate which is more likely. The authors should highlight the implications of their findings. How robust do they believe this metric will be? Can the results of this isolated study be applied to other studies to advance our understanding of heterogeneous processing?

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* RESPONSEïijŽ Thanks for the good comments. As pointed out, it has been known for years that Asian dust undergoes heterogeneous processing during their long-range transport. But few researches paid attention to the modifications of Mg levels in the aluminosilicates (a main fraction of mineral dust) when the Asian dust storm (ADS) particles passed over the sea. By using low-Z particle EPMA technique, we examined several thousands of ADS particles collected in Beijing, China and in Incheon, Korea when a strong ADS event occurred in April, 2005. We found that there was a significant increase in atomic concentration ratio of both Mg/Si and Mg/Al in Mg-containing aluminosilicates and suggested that the [Mg]/[Si] or [Mg]/[Al] ratios could be considered as "indices of the aging process" for the ADS particles. Indeed, we should explain why we used [Mg]/[Si] or [Mg]/[Al] ratios as "indices of the ageing process" and elucidate why

the [Mg]/[Si] or [Mg]/[Al] ratio should change in the marine atmosphere. Among the probable reasons for the ratio change provided in the comment (i.e., (1) one element was preferentially deposited; (2) the Mg, Al or Si volatilized (doubtful); (3) there were different source contributions; or (4) there is coagulation with sea salt), we think that coagulation on mineral dust with sea salt played the most important role. Many studies have demonstrated that an accumulation of the sea-salt component on individual dust particles would have occurred during transport over the marine atmosphere, leading to formation of dust particles internally mixed with sea salt. And mixtures of dust and sea-salt particles were previously observed in several locations of Korea and Japan (such as Nagasaki and Kumamoto in Japan and Incheon and Chunchuan in Korea), as well as over the ocean (such as the Yellow Sea), as shown in the following articles.

1. Ryan C. Sullivan, Sergio A. Guazzotti, David A. Sodeman, Youhua Tang, Gregory R. Carmichael, Kimberly A. Prather: Mineral dust is a sink for chlorine in the marine boundary layer, Atmospheric Environment, 41, 7166–7179, 2007.

2. Chang-Jin Ma, Susumu Tohno, Mikio Kasahara, Shinjiro Hayakawa: Properties of individual Asian dust storm particles collected at Kosan, Korea during ACE-Asia, Atmospheric Environment, 38, 1133–1143, 2004.

3. Tomoko Kojima, Peter R. Buseck, Yasunobu Iwasaka, Atsushi Matsuki, Dmitri Trochkine, Sulfate-coated dust particles in the free troposphere over Japan, Atmospheric Research, 82, 698–708, 2006.

4. M. Mikami, G.Y. Shi, I. Uno, et al., Aeolian dust experiment on climate impact: An overview of Japan–China joint project ADEC, Global and Planetary Change, 52, 142–172, 2006.

5. HeeJin Hwang, HyeKyeong Kim, Chul-Un Ro: Single-particle characterization of aerosol samples collected before and during an Asian dust storm in Chuncheon, Korea, Atmospheric Environment, 42, 8738–8746, 2008.

6. Geng, H., Park, Y., Hwang, H., Kang, S., and Ro, C.-U.: Elevated nitrogen-containing particles observed in Asian dust aerosol samples collected at the marine boundary layer of the Bohai Sea and the Yellow Sea, Atmos. Chem. Phys., 9, 6933–6947, doi:10.5194/acp-9-6933-2009, 2009.

7. Fan, X.B., Okada, K., Niimura, N., Kai, K., Arao, K., Shi, G.Y., Qin, Y., Mitsuta, Y.: Mineral particles collected in China and Japan during the same Asian dust-storm event, Atmospheric Environment, 1996, 30, 347–351.

8. Niimura, N., Okada, K., Fan, X.B., Kai, K., Arao, K., Shi, G.Y., Takahashi, S.: Formation of Asian dust-storm particles mixed internally with sea-salt in the atmosphere, Journal of the Meteorological Society of Japan, 76, 275–288. 1998.

9. Zhang, D.Z., Iwasaka, Y., Shi, G.Y., Zang, J.Y., Matsuki, A., Trochkine, D.: Mixture state and size of Asian dust particles collected at southwestern Japan in spring 2000. Journal of Geophysical ResearchâĂŤAtmospheres 108, doi:10.1029/2003JD003869. 2003.

10. Okada, K., Naruse, H., Tanaka, T., Nemoto, O., Iwasaka, Y., Wu, P.M., Ono, A., Duce, R.A., Uematsu, M., Merrill, J.T., Arao, K.: X-ray spectrometry of individual Asian dust storm particles over the Japanese islands and the north Pacific - Ocean, Atmospheric Environment, 24, 1369–1378, 1990.

11. Andreae, M.O., Charlson, R.J., Bruynseels, F., Storms, H., Van Grieken, R., Maenhaut, W.: Internal mixture of sea salt, silicates, and excess sulfate in marine aerosols, Science, 232, 1620–1623. 1986.

* Though the interaction of dust aerosols and sea salt is regarded as a likely and important process in composition changes of dust aerosols during long-range transport, Mg-containing aluminosilicate particles (accounting for more than 50% on average in aluminosilicates) have hardly been investigated carefully before our current work. We think the modification of Mg/Si and Mg/Al in atomic concentration ratios is mainly due

to the mixture or coagulation of Mg-containing aluminosilicate particles with fresh sea spray aerosol (SSA) which consists of NaCl, MgCl2, organic carbon species, and etc. or with reacted SSA which consists of NaNO3, Mg(NO3)2, Na2SO4, MgSO4, and etc. In the Mg-containing aluminosilicate particles of samples S2 and S3, Na signal is often observed. To illustrate the aging process of Mg-containing aluminosilicate particles, a possible mechanism was added in the last paragraph of the section "3.4 Mixing and aging processes of ADS particles during long-range transport" and in Figure 13 (newly added) of the revised manuscript. The implication of this finding is also added in the paragraph. It is important and interesting to know the detailed mixing or reaction process of Mg-containing aluminosilicates with SSA, which will be probed in the lab and field studies in the future. In addition, in order to clarify how robust we believe this metric is, we performed student t-test on the atomic concentration ratios of Mg/Al and Mg/Si for the Mg-containing aluminosilicate particles among samples S1, S2, and S3. The results showed that there is statistically significant increase in the atomic concentration ratios of Mg/Al and Mg/Si for the reacted (or aged) aluminosilicate particles between samples S2 and S1 and between samples S3 and S1 ($P < 0.05$). Correspondingly, the significance mark (*) was added on the column charts in Figure 9. As the Mg-containing aluminosilicates are an important part of ADS particles, the modification of their atomic concentration ratios of Mg/Al and Mg/Si can reflect the aging of mineral dust when ADS particles pass over the marine atmosphere. After finishing the above supplement and revisions, we thoroughly re-thought the focus of the paper and made some change on the abstract and conclusion. Please see the revised manuscript.

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* The paper is technically well put together and is most likely within the scope of ACP. I have a few other minor comments below:

* * COMMENT 2: Abstract, line 33: The authors should state why fine mode K-containing particles are important. An indication of the abundance of these particles should be added to the abstract.

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* RESPONSE: K-containing particles are commonly regarded as from biomass burning. Considering the comment 14 from the Anonymous Referees #2, we agree on the suggestion that "this part should be deleted because the whole paper focus on mineral dust not biomass burning". Thus, we removed the statement about K-containing particles in the section "Abstract" to make it concise and focus on mineral dust.

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* COMMENT 3: Abstract, line 44: By how much did the Mg ratios change? Standard error should be given with these ratios.

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* RESPONSE: We showed the ratio values of [Mg]/[Al] and [Mg]/[Si] in the revised Abstract and Text and also their standard errors are given. The modified sentence in the revised Abstract is: "In addition to partially- or totally-reacted CaCO3, reacted or aged Mg-containing aluminosilicates were observed frequently in samples S2 and S3; and furthermore, the student's t-test showed that both their atomic concentration ratios of [Mg]/[Al] and [Mg]/[Si] were significantly elevated ($P < 0.05$) compared to that in sample S1 (for [Mg]/[Al], 0.34 ± 0.09 and 0.40 ± 0.03 in sample S2 and S3, respectively, vs. 0.24 ± 0.01 in sample S1; for [Mg]/[Si], 0.21 ± 0.05 and 0.22 ± 0.01 in sample S2 and S3, respectively, vs. 0.12 ± 0.02 in sample S1).

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* COMMENT 4: Line 264: Instead of preceding the list with "they are" simply place a colon after the sentence followed by a numbered list.

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* RESPONSE: Done as suggested.

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* COMMENT 5: Line 312 and throughout the manuscript: Use “unreacted” or “fresh” opposed to “genuine”. *

* RESPONSE: Done as suggested.

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* COMMENT 6: Line 352-353: What kind of percentage is this? By number or by mass? Atomic % may be a more interpretable number opposed to the mass of Mg-containing species.

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* RESPONSE: This percentage was calculated by dividing the number of Mg-containing species by the number of unreacted or reacted aluminosilicate particles. For clarity, we added “By number” in the sentence.

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* COMMENT 7: Line 441: Remove “the” from the section heading.

* * RESPONSE: Done as suggested.

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* COMMENT 8: Line 472: is there any way to use elemental composition to bolster the claim that the fine mode NaCl was from dry lakebeds? Why would these particles be smaller (they are on stage 6) than sea salt? Another possibility is an industrial source.

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* RESPONSE: Thanks for the suggestion. By using low-Z particle EPMA, we found that NaCl-containing particles collected in Beijing are different from those collected in Incheon both in size and morphology, indicating they are not sea salt particles. They look dry and smaller than ordinary SSA particles in size, implying that they might be halite particles from the desert (Okada K and Kai K, Atmospheric Mineral Particles Collected

at Qira in the Taklamakan Desert, China. Atmos. Environ. 38: 6927–6935, 2004). The backward air-mass trajectory analysis suggests that they came from dried salt lakes or saline soils near Hunshandake Sandy Land or Hulunbeier Sandy Land in the Southeast and Northeast, respectively, of the Inner Mongolia plateau. We think the likelihood is very small that the dry and fine-mode NaCl particles come from the industrial source. With respect to the comment, we changed some statements in the first paragraph of 3.3.2 into “They look dry and smaller than ordinary SSA particles in size, implying they are halite from desert (Okada and Kai, 2004). They might come from dried salt lakes or saline soils near Hunshandake Sandy Land or Hulunbeier Sandy Land in the Southeast and Northeast, respectively, of the Inner Mongolia plateau (Zhang et al., 2010; Sun et al., 2010). The halite particles might be modified by NOx/HNO3 during transport and then transformed to NaNO3. Industrial source could not be excluded for the dry and fine-mode NaCl-containing particles although the likelihood is very small. ”

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* COMMENT 9: Line 495: change “they have much less abundance” to “they are less abundant” * COMMENT 10: Line 557: Change “This” to “These”. * COMMENT 11: Figure 2: Indicate which city/country the different samples were taken. This should be done on this figure or in the legend.

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* RESPONSE: Done as suggested.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 27971, 2013.