

Response to reviewers' comments to ACP-2012-539 by Nie et al.

Dear Editor,

We have revised the manuscript in response to the comments/suggestions of referee #1. The itemized replies are listed below. The revised texts are highlighted in blue in the manuscript.

Anonymous Referee #1

Received and published: 27 August 2012

This paper reports on the chemical processing of mineral dust as observed during an Asian dust storm at a rural mountain site in southern China. It specifically focuses on the heterogeneous processes modifying the dust particle composition with a potential link with changes in hygroscopicity.

It is shown, among other, that dust particles arriving at the observation site were strongly influenced by chemistry, and potentially by photochemistry, with a large enrichment in secondary species (or ions).

This manuscript is well written and documented. The topic fits perfectly in the scope of ACP. I therefore recommend this manuscript for publication once the authors have commented following points. Some aspects of the manuscript are totally new potentially highlighting processes so far only observed at the laboratory scale i.e., photochemistry of dust. In addition maybe the figures could be made more explicit.

Response: we have tried to make the figures more explicit in the revised manuscript.

The experimental section would gain in strength with more details about the used instrumentation and their associated uncertainties. In fact, some observed changes are small. Before discussing these changes in terms of chemical processing, a discussion on error and uncertainties would strengthen the overall paper and content. For example, the sulphate increase during ageing was from 1.7% to 2.4%. Is this change real when taking into account experimental uncertainties?

Response: We have added the information on the measurements uncertainties in

section 2.2 of the revised manuscript.

The uncertainties of the water soluble ions are about $\pm 10\%$. During the dust storm of 24-26 April, the sulfate concentrations in $PM_{>1}$ were about $12 \mu\text{g}/\text{m}^3$. That means the measurements uncertainties for supermicron sulfate are about $\pm 1.2 \mu\text{g}/\text{m}^3$. While the 0.7% (1.7% to 2.4%) changes of sulfate abundance in supermicron particles are about $3.15 \mu\text{g}/\text{m}^3$ ($0.7\% \times 450 \mu\text{g}/\text{m}^3$), much higher than its measurements uncertainties. So we think the observed increase of sulfate abundance was significant. Other ions are also under the same situation.

One of the key points of this study is to associate the dust processing with the photochemical age of the sampled air masses. I did find the discussion on that topic not strong enough and would encourage the authors to elaborate a bit more their ideas to get the message more convincing. For instance, why not merging figures 5 and 6 to illustrate the coupling between ion production and photochemical age?

Response: we have added some information, and changed some description and modified Figure 5 and 6 in the revised manuscript. We adopted the suggestion and merged Figure 5 and 6 to better link the photochemical age and the changes in the ratios of the secondary ions. We note that the first three samples had good relationship with the age indicator and changes in the ion enhancements from sample III to IV (with the same age) suggest other factor(s) also playing an important role. This point has been added in the revised manuscript.

The ammonium enrichment on dust and the corresponding ageing of carbonate-rich Asian dust is interesting. The authors conclude that their observations fit a conceptual model involving four stages (as shown in Figure 7). However, I'm not able from Figure 6 (which corresponds to the data supporting this conclusion) to identify these four stages. I would here recommend more information to make sure that the reader can analyze how strongly this four-stage process is supported by the data.

Response: The referee's points are well taken. In the revised manuscript, we have added a figure (the new Fig. 6 on the ratio of ammonium to PM) and re-arranged

other figures in order to better facilitate the discussion on photochemical age and the proposed concept model. Our evidence to support the 4-stage evolution is shown in the following figures (Fig. 4c and Fig. 6). For the dust sample of Mt. Hua near the dust source region, no accumulated ammonium was detected in the supermicron range (Fig. 4c). For the first three samples of Mt. Heng in southern China, ammonium appeared in the coarse mode, but at moderate level (Fig. 5c and Fig. 6). For the fourth sample at Mt. Heng (see the second figure), the abundance of ammonium increased significantly. We have added this information in the revised manuscript.

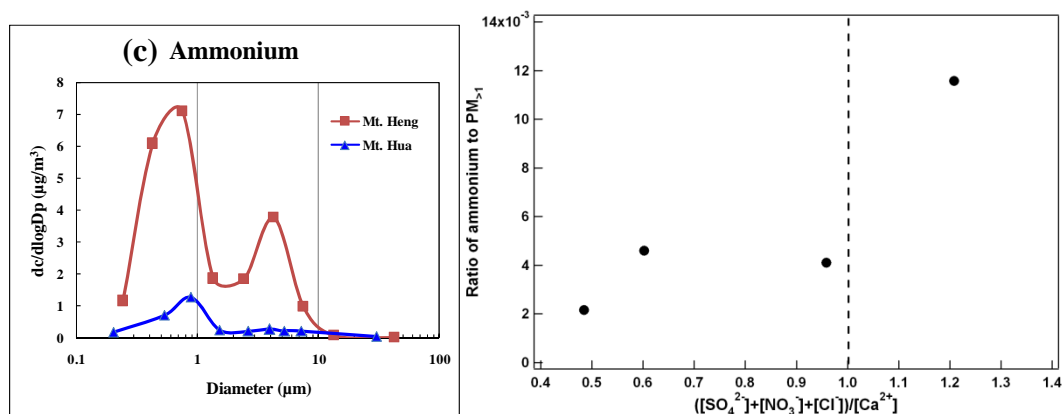


Fig. 4c and Fig. 6.

In the second paragraph of Section 3.2.3, we try to explain why the ammonium abundance increased sharply in the fourth sample comparing to the first three samples at Mt. Heng. As shown in Fig. 6, the difference between the first three samples and the fourth sample is the aerosol acidity (or the neutralization of carbonate). In the first three samples, the calcium carbonate was not fully neutralized, accumulated ammonium on dust particles was observed at moderate level; in the fourth sample, the calcium carbonate was fully neutralized, and the ammonium abundance increased sharply. These results indicate that the dust particles can have some accumulated ammonium after it has been coated with acidic species (sulfate or nitrate), but the abundance should not be much until all the alkaline mineral substance is fully neutralized. These observational results provide some supports to the subsequent conceptual model.

We have also added some information on the limitation of the 4-stage evolution process: (1) the conceptual model can only apply to the carbonate-containing dust

particles; (2) ambient ammonia concentrations will influence the development of the 4 stages.

The photo-enhanced nitrite formation during ageing is very interesting and warrants publication by itself. The TiO₂ content calculations were calculated from a formula given on page 11. However, is this supported by any publication? TiO₂ may be enriched in smaller particles enhancing the photochemical processing.

Response: we have added a reference to support this point in the revised manuscript.

“Zhang, X. Y., Gong, S. L., Arimoto, R., Shen, Z. X., Mei, F. M., Wang, D., and Cheng, Y.: Characterization and Temporal Variation of Asian Dust Aerosol from a Site in the Northern Chinese Deserts, Journal of Atmospheric Chemistry, 44, 241-257, 10.1023/a:1022900220357, 2003.”

The production of gaseous HONO is important as this gas acts as an atmospheric OH source. However its formation from nitrite depends on pH. The authors elaborated a complex four stage processes to highlight the pH change upon ageing. I'm surprised that they did not apply it to HONO formation and this kind of conceptual approach may be important. In fact, HONO release from dust is definitively associated with acidity and may not take place all the time as specific conditions are required. Maybe the authors elaborated a bit on this and use their four-stage model to highlight when and where HONO is produced? In fact the HONO levels provided in this manuscript are certainly upper limits and real release of HONO being limited by dust particle acidity.

Response: Thanks for the good suggestion. In the revised manuscript, we have added some discussions in Section 3.3 on the relationship between the particle acidity and HONO release. We removed the rough calculation of gas-phase HONO in the revised manuscript as more information on aerosol chemical property is needed to make a reliable calculation.