

Interactive comment on “Direct observations of the atmospheric processing of Asian mineral dust” by R. C. Sullivan et al.

R. C. Sullivan et al.

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Reply to Referee 1 (Referee comments in quotes)

"1. Figure 1: Showing an average mass spectrum of all dust particles does not make much sense in the context of this article, where you focus and work out different types of dust particles that underwent different reactions in the atmosphere. Replace this figure with one or two (average) mass spectra of different types of dust, or leave it out completely."

The purpose of Figure 1 is to illustrate the general mass spectral features that are measured from the Asian dust sampled and give some indication as to the wide variety of dust mineralogy and also the high degree of aging that the dust had experienced, indicated by the frequent presence of secondary acids. This figure is also used to help

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explain the selection of ions used to search for various species in the dust. From this figure we then go into much more detail regarding each of these topics. Figure 1 is designed to be the starting point for our results and demonstrate the broad topics that are then discussed extensively. While we could show the average mass spectrum from different types of dust particles sampled, high Al-dust vs. high-Ca dust for example, we feel this would not add any significant information to the paper that is not already displayed in the other figures.

"2. p. 4110 Discussion NO_y,g and volcanic SO₂ . Why so much attention in abstract and relatively little in manuscript?"

The role that NO_y and SO₂ play in the aging of dust is discussed extensively in the text, particularly in the context of the aging timeline of dust as it is transported out of the Chinese interior (Section 4.2).

"4. p. 4123 A table summarizing all the statistics would help."

We have added a table summarizing the mixing statistics (dust mixed with nitrate, with sulphate, with chloride, with nitrate and sulphate, etc.).

"5. p. 4132 I think we should not exclude the possibility that a certain amount of SO₄ was already present in the source region as gypsum."

There is likely some gypsum (CaSO₄) in the dust at its source. However, based on our source characterization studies of Asian dust, the signal from sulphate in the source dust is much smaller than the 5000 peak area threshold used, i.e. < 500 peak area. Sulphate already present in the dust as gypsum would also not give rise to the temporal pattern shown in Figure 2.

"6. p. 4133 I.6 Diffusion limited? This seems hard to believe. What is the reference for this? It would imply a very high gamma value, is that measured?"

The explanation of enriched sulphate in submicron particles being due to its diffusion limited uptake dates back to Bassett and Seinfeld (1984) and is also discussed in Song

and Carmichael (1999); both of these papers are cited in the following sentence in the original manuscript (pp. 4133, line 7). A diffusion limitation does not necessarily imply a large uptake coefficient as it is not necessary for the SO₂ to immediately react with the particle surface it encounters. Physisorption is also important (as Referee 2 pointed out) for the accumulation of SO₂ on particles, and the SO₂ can be oxidized to sulphate once it has adsorbed to the particle.

"7. P. 4114, line 1: Why is this reference made in a footnote and not in the reference list? Look also at the footnote indication on successive references to this planned paper, e.g. P. 4135, l. 15."

The citation style of ACP requires that papers submitted or in prep be cited as a footnote and not in the actual reference list.

"8. P. 4115, l. 23 ff.: Reference is made to ATOFMS experiments producing reference mass spectra from dust directly taken from Asian desert regions, but no such mass spectrum is shown in a figure. To make the story with atmospherically changed dust particles more convincing, it would be better to include at least one (average) dust mass spectrum from one source to this article. And if an article describing those mass spectra exists, it should be cited here."

The Asian source dust mass spectra were not included primarily for length considerations. As stated in the text, the source dust spectra are very similar to those of the ambient dust displayed in Figure 1. The major differences are the increased signals from secondary species such as ammonium, chloride, nitrate, and sulphate. We have included additional details in the Appendix that describe typical peak areas for these secondary species that were measured in the source dust.

"9. P. 4118, paragraph 3.2.: The description and explanation of 'filtering the mass spectra' to only evaluate dust particles belongs to paragraph 2, 'methods and instrumentation'. Then the reader also understands what is meant with 'filtered mineral dust particles' on p. 4116, l.3."

We have moved most of the details in the “Filtering Criteria” section (3.2) to the newly added Appendix, and made reference to these details in Methods and Instrumentation so that this terminology is clear.

"10. P. 4116, l. 10 ff: This statement can certainly not be drawn just from looking at the average over all mass spectra taken as shown in figure 1. Restate this."

The digital colour stack, used to plot the average mass spectrum, displays the fraction of particles that contain a particular ion with an area falling within a specified range. In this way, some insight into the heterogeneity of a particular set of single-particles can be obtained. We have much more information about the varying mineralogy of the Asian dust measured that stems from our detailed single-particle analysis of the data but which cannot be easily presented in this paper. One type of such information is the division of the mineral dust particles into over 30 different clusters by the ART-2a classification algorithm. Much of this division was caused by differences in the individual dust particle's mineralogy, producing dust particle clusters dominated by either Al, Ca, Na, K, Fe, etc. We have reworded this section about the complexity of the mineralogy of the Asian dust to reflect this.

"11. P. 4116, l. 27: CO₃-2 would show up at $m/z = -30$ and thus not interfere with SiO₂-, etc. Make your statement clearer."

Doubly-charged ions are not typically formed in laser desorption/ionization MS. The carbonate ion, CO₃-2, if ionized, would be expected to have a major peak at $m/z -60$ as [CO₃]-. The [CO₃]-2 ion is not expected and has not been observed by us or other groups using similar instrumentation.

"12. P. 4118, l. 2; p. 4125, l. 8; p. 4126, l. 2; p. 4129 l. 9: On several occasions, references to results are made that are 'not shown'. It is not elusive to include such 'results' to an article. Either present or make a reference to these results or leave them out!"

As explained in our answer to Question 8, we are not including the source dust spectra for length considerations, but have provided additional details about them in the Appendix. The results that are mentioned and “not shown” (p 4125, l. 8; p. 4126, l. 2) are merely extensions of the results that are already discussed at length in the manuscript. It would be a misuse of space to show them again. We mention them without showing them to reinforce the fact that these particular results were observed during more than one time period and are thus a common and robust observation. For the case of p. 4129, l. 9, these results are shown in Figure 9.

"13. P. 4118, l. 23: Explain this >5000 criterion a bit more precisely. Such criteria are used later as well and it would be illuminative for the reader to understand this criterion. Suggestion: As it is a peak area, maybe state the minimum value needed to be considered as a peak and the maximum value for a (highly) saturated peak."

Peaks with areas < 25 are generally considered to be in the noise. For the secondary inorganic species, an area < 500 is not considered large and is of the magnitude that can be measured in source dust spectra. This does not apply to ammonium, however, which is not commonly measured in the source dust with a peak area > 50. A peak area > 20,000 is a very large value that is never observed in the source dust and is not commonly seen in the ambient dust spectra. Thus, it reflects a very large amount of a secondary inorganic species, likely due to extensive aging. Peak areas up to and exceeding 40,000 have been observed (see Figure 4 for example). The peak area of 5000, though not yet quantified, represents a significant amount of secondary inorganic material beyond that detected in any source sample. A list of typical peak areas used to search for various particulate species is given in Liu et al. (2003) (see Table 1). These details have been added to the revised manuscript in the Appendix.

"14. P. 4123, l. 4 ff: Make it clearer why you didn't use the method presented in this paper in the Arimoto 2006 paper. Otherwise it is quite confusing why your team presents different findings on the same topic, especially within such a short time."

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Our analysis presented in the Arimoto et al. summary paper was designed to present a broad overview of some of our key findings regarding dust aging during ACE-Asia. We have included a similar statement in the revised manuscript. While that paper was published just a few weeks after this one was in ACPD, the Arimoto et al. paper was in fact submitted to GPC on March 24, 2005, almost one year before this one was submitted to ACPD. In the interim time period, we have performed more extensive analysis of the dust in ACE-Asia in an effort to better understand the reasons for the observed changes; those details are the focus of this much more detailed paper. The two papers were only published close to each other due to long publication delays. The only major difference between the two analysis methods used is that for the Arimoto et al. paper we did not exclude internal mixtures of dust and sea salt when searching for dust particles mixed with nitrate, sulphate, and chloride.

"15. P. 4126, l. 12: How can you draw that conclusion from an average mass spectrum? A mass spectrum with NH₄ and dust only will definitely be disguised in the average mass spectrum this is actually the feature of averaging. Restate this!"

The conclusions regarding the nature of the ammonium-dust particles were made by generating digital colour stacks of the average mass spectra of the particles and also through a combination of peak area searches within this subset of particles. This has been clarified in the revised text.

"16. P. 4130, l. 25ff: It's misleading to talk about "first report " and in the very next sentence "these results were presented". State clearly what makes them first as compared to the previously published results!"

We have corrected this sentence so that our ACE-Asia findings in general are referred to as the "first report" of these observations, including both the preliminary results presented in Arimoto et al., and the more detailed analysis given here.

"18. P. 4144, l.27: Update the citation with reference to the article!"

The citation has been updated now that the article has been published.

"19. P. 4158, table 1: Explain >5000 in the table or leave it out. What this means must be clear without reading the whole article."

We have omitted the > 5000 area notation in the table and left this issue to be explained in the text as it already is.

"20. P. 4160, F. 1: What's a "digital mass spectrum"? Rephrase and explain what you want to say!"

The digital mass spectrum displays the fraction of particles that contain a particular ion with a peak area falling within a specified range. It thus reflects the range of peak areas for a particular ion that an ensemble of particles produced and provides insight into the relative amount of various chemical species that this ensemble contained.

"21. P. 4160, F. 1: What are the other mass peaks in this spectrum; especially $m/z = 8$, 9, .. Instrument noise?"

These peaks between $m/z +8$ and $+11$ cannot be identified and are likely noise, possibly caused by ringing from the large Li peak at $m/z +7$, or from cross-talk from negative ions. The peaks in this range are not assigned to any important dust or secondary compounds and thus do not affect the analysis presented here.

"22. P. 4163, F. 4a: the 3 scatter plots are too small to be read on a printout. Furthermore, they don't give additional insight to the ternary plot, so leave them out."

We have increased the size of the scatter plots in the revised version. They do provide valuable information that the ternary plots do not show. The ternary plot displays relative peak areas while the scatter plots demonstrate the large range of absolute peak areas measured for these secondary species on the dust.

"23. P. 4166, F. 6: The insets are not recognisable on a printout! Enlarge them or leave them out."

The insets have been enlarged and the font size increased in particular to make these figures more legible.

"24. I would also propose to have a section (4.6 or in 5): How do our measurements challenge current parameterisations in models? Do your measurements indicate that models should use thermodynamic partitioning with dust just as a carrier material?"

We have added a brief review of the treatment of dust chemistry in various regional and global chemical models, which parameterize dust with varying degrees of detail. We then discuss how our results provide insights into improvements that can be made to improve these models' parameterizations of mineral dust chemistry. One particularly important aspect, which other researchers have pointed out and that we stress in the paper, is the role that dust mineralogy plays. Dust cannot be treated as a single entity with a single reaction rate with each species. The chemical composition of the dust, in particular the role of carbonates and catalysts such as iron must be included when accurately modeling the chemistry that dust experiences in the atmosphere. Also the role that water plays, both in changing the rates of reaction of gases with dust, and also in phase transitions of highly reacted dust (e.g. when mostly converted to $\text{Ca}(\text{NO}_3)_2$) must be included. Further lab study investigations are required to understand these effects and to be able to include them in models.

Reply to Referee 2 (Referee comments in quotes)

"1. The authors show that mineral dust is chemically aged during transport from the source region to the RHB. They hypothesize that acidic trace gases such as HNO_3 are the cause of this. A simple calculation using an approximated transport time and a rate expression (uptake coefficient etc.) for the uptake process would be useful to test this."

While a simple calculation of the degree of aging experienced by the dust using an average uptake coefficient and transport time might be useful, this very simplistic approach would not provide the same level of detail regarding the temporal evolution of dust that sophisticated chemical transport models currently do. Greg Carmichael's

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group employed the STEM-2K3 model for the ACE-Asia aerosol to help interpret the observations made and we have already collaborated with his group in the past to compare our field data with his model predictions. The results showing a comparison of the STEM-2K3 model and ATOFMS measurements for ACE-Asia are referenced several times in our paper: (Tang et al., 2004a; Tang et al., 2004b). We will add some additional details from these models in reference to ACE-Asia to reinforce our field observations and compare our results with the STEM-2K3 model's results.

"2. P4111, L19 Other laboratory data for uptake of NO_y to mineral dust exist: e.g. Vlasenko et al., (2006, Atmos. Chem. Phys. Disc), Hanisch and Crowley (2001, Phys. Chem. Chem. Phys)."

We have included the following additional references that report the reaction of NO_y (HNO₃, N₂O₅, NO₃) with dust: (Al-Hosney and Grassian, 2005; Karagulian and Rossi, 2005; Santschi and Rossi, 2006; Seisel et al., 2005; Vlasenko et al., 2005). This list focuses on those studies that explored the effect of water vapour in particular and thus simulated atmospherically relevant conditions. Most papers on this subject prior to 2002 are covered by citing the comprehensive review of Usher et al. so as to not inflate the already extensive reference list.

"3. P4115, L23 I've read this manuscript assuming that the analysis is conducted online. This statement appears to suggest that reference spectra were obtained from dust samples collected from source regions. Is this correct ?"

All of the field measurements were performed on-line. Several dust samples were collected in different source regions across Asia during 2001. These samples, along with the Certified Asian Mineral Dust sample (CJ-13), were then analyzed in the lab after the campaign. We have added additional wording to make this clearer.

"4. P4116, L5 The word *that* appears twice"

This typo was removed.

"5. P4116, L23-24 State what the acronyms LAMMA, SIMS and LDI stand for."

The acronyms have been spelled out in the revised manuscript: LAMMA (LAsER Microprobe Mass Spectrometry), SIMS (Secondary Ion Mass Spectrometry), and LDI (Laser Desorption/Ionization).

"6. P4121, L4 The rate of oxidation of NO₂ on a dust surface is probably low. Can NO₂ be considered a reactive gas when compared to e.g. HNO₃ or HCl? Are uptake coefficients for these species known?"

NO₂ is certainly less reactive than HNO₃ is with a dust particle; this has been shown in lab studies (the reactive uptake coefficient of NO₂ is generally 1-2 orders of magnitude slower compared to HNO₃; see Question 9 below). To our knowledge, the only lab report of HCl reacting with mineral dust is from Oooki et al. and no uptake coefficient is reported. Santschi and Rossi (2006) reacted calcite with HCl and reported an uptake coefficient of 0.1. HCl is most likely more reactive than NO₂ since it is an acid. However, the concentrations of NO₂ are typically higher (by several orders of magnitude) than HNO₃ or HCl and this factor must be considered as well. Overall, we agree that HNO₃ and HCl are likely more important for the aging of mineral dust; however, without further lab studies, we cannot distinguish a contribution to NO₂ (m/z = -46) measured on dust that is caused by the direct uptake of NO₂, or from fragmentation of HNO₃ by the LDI laser in the ATOFMS. NO₂ as a source of nitrate was included as a possibility for completeness. We have added additional details about the kinetics of these gases reacting with mineral dust in lab studies to make this clearer in the revised paper.

"7. P4125, L20 There is no need to abbreviate ammonium nitrate to AN. Avoid the mixed use of chemical name, abbreviated chemical name and chemical formula."

We have revised this section so that only the chemical name is used throughout this section to avoid confusion.

"8. P4126, L17 The implication of this sentence is that a single dust particle can support

uptake of both acidic and basic species, prerequisite for the uptake of basic species being that acidic sites are available. The authors may note that uptake of acidic gases may not only be restricted to reactive (alkaline) sites and that physisorption can also be important. Physisorbed acid gases will react with ammonium without consumption of alkalinity."

We agree that physisorption processes of reactive gases such as NO₂ and SO₂ to dust are important in addition to direct reaction with alkaline surface sites. We do not mean to imply that alkaline sites are required for the uptake of acidic gases, only that they likely accelerate the process. Note that lab and field studies have also demonstrated that carbonate in the bulk of dust can also be consumed by nitric acid (Krueger et al., 2004; Laskin et al., 2005). We have clarified this section to emphasise the role of both processes in the aging of dust. However, modeling studies compared with observations, such as those of Greg Carmichael's group, indicate that until the natural alkalinity in dust particles is consumed by acids, ammonium does not significantly partition to the dust particles. The presence of alkaline species such as carbonate make the dust "anion-rich" and prevent the uptake of ammonia until this carbonate is consumed and the dust becomes "cation-rich" (Tang et al., 2004b). Our results showing that the amount of ammonium tracks the amount of acids in the dust, as well as the lack of ammonium in dust without acids, agrees with this model. It is true that some of this could stem from physisorbed acids reacting with ammonia and thus not involve the carbonate in the dust. As the dust becomes acidified and more hygroscopic, the contribution from aqueous phase chemistry occurring in the wet dust particle should also be considered. We have added further details in the revised text to distinguish these potentially important processes.

"9. P4132, L3 Apart from Ooki and Uematsu, there are several laboratory measurements that compare the reactivities of SO₂, NO₂, and HNO₃ with mineral dust. These studies also show that HNO₃ is significantly more reactive than SO₂ or NO₂."

Several lab studies have reported the kinetics of SO₂, NO₂, and HNO₃ reacting with

mineral dust surfaces, though to our knowledge only Ooki and Uematsu reacted the same type of dust with these gases in one study, which is why we focused on it. It is a good idea to make reference to other previous studies which back up the findings that HNO_3 is much more reactive than NO_2 or SO_2 with dust and we have added the following references and additional discussion: (Hanisch and Crowley, 2001; Ullerstam et al., 2003; Underwood et al., 2001; Vlasenko et al., 2005).

"10. P4139, L10 It is suggested that the presence of e.g. Fe enhances the oxidation rate of SO_2 to sulphate on dust surfaces, and that uptake to calcite particles is less efficient. Is this consistent with the observation of Usher et al (2002, J. Geophys. Res.) that SO_2 is (slightly) more efficiently taken up to CaCO_3 than Fe_2O_3 ?"

In Knudsen cell studies, Usher et al. found the reactive uptake coefficient for SO_2 to be smaller on Fe_2O_3 ($7.0 \pm 2 \times 10^{-5}$) than on CaCO_3 ($1.4 \pm 0.7 \times 10^{-4}$). However, they also found $\gamma = 1.6 \pm 0.5 \times 10^{-4}$ on Al_2O_3 , which is almost identical to that found for CaCO_3 even though calcite is alkaline and alumina is not. Note that in our results we found sulphate to be more enriched in dust with elevated Fe and Al and attributed these to the Fe-rich aluminosilicate minerals. Seisel et al. (2006) measured initial uptake coefficients for SO_2 to be $8.8 \pm 0.4 \times 10^{-2}$ on Fe_2O_3 , and $7.4 \pm 0.9 \times 10^{-4}$ on Al_2O_3 , the opposite trend found by Usher et al. The Knudsen cell experiments of Usher et al. and Seisel et al. were performed dry and under high vacuum, while other studies have shown the importance that adsorbed water plays in the uptake kinetics of SO_2 to minerals such as calcite (Al-Hosney and Grassian, 2005; Santschi and Rossi, 2006). There was also no additional oxidant, such as O_3 or H_2O_2 , present to assist in the oxidation of adsorbed SO_2 . Given that there is disagreement as to which mineral SO_2 reacts with more efficiently, and that no water vapour was present, it is difficult to extrapolate these lab results to our field data reliably. To truly assess the question of which mineral type reacts most efficiently with different acidic gases, experiments would have to be conducted under atmospherically relevant conditions with multiple reactants present simultaneously.

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