

Interactive comment on “Observations of heterogeneous reactions between Asian pollution and mineral dust over the Eastern North Pacific during INTEX-B” by C. S. McNaughton et al.

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This paper presents a complete set of gas and particle-phase chemical measurements made of Asian dust-enriched aerosol sampled at altitude in the eastern Pacific. While a large number of reports exist concerning the uptake of nitrogen and sulphur oxides by Asian mineral dust, the simultaneous gas and particle-phase measurements provide important insight into the partitioning of these important trace gases. I present the following questions and suggestions in the hopes that they can help improve the revised manuscript.

In general I found it very difficult to follow what measurements from which instrument

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and aircraft were being presented. It seems that most of the data presented is from the filter measurements taken by UNH aboard the DC-8 and that very little AMS data from the C-130 is shown. I suggest that the measurement method be stated briefly in all the figure captions, and it made clear that the filter measurements are always being discussed unless otherwise stated.

Similarly it was not clear what size range of aerosol chemistry was being presented. The DC-8 filters measured all aerosol sizes? But there are also discussions of fine and coarse chemical composition. This has important implications for the interpretation of the aerosol chemistry observed, and it would help if this was also briefly stated in the relevant figure captions.

The uptake of nitrate and sulphur compounds by Asian mineral dust has been extensively studied. However, there exist just a few reports of the uptake of chlorine gases (Murphy et al., 2006; Sullivan et al., 2007a; Sullivan et al., 2007b; Tobo et al., 2009; Zhang and Iwasaka, 2001) and also dicarboxylic acids (Mochida et al., 2007; Sullivan and Prather, 2007) by (Asian) mineral dust. Do the filter or AMS measurements provide any insight into these processes? I note that filter measurements of chloride and oxalate were made.

Many of the observations reported here are strikingly similar to those obtained from the ACE-Asia campaign, which is the most extensive study of the chemistry of Asian mineral dust chemistry and the resulting optical properties to date. While several related papers from ACE-Asia are cited and briefly discussed here, I think the paper would benefit from a clearer comparison to the ACE-Asia observations. Specific similarities include the uptake of nitrate and sulphate by Asian dust (also observed during TRACE-P), and the resulting shifts in secondary mass from the submicron to supermicron modes with resulting changes in aerosol optical properties. Also, several closely related papers from ACE-Asia are missing here, including (Arimoto et al., 2006; Bates et al., 2004; Maxwell-Meier et al., 2004; Mochida et al., 2007; Quinn et al., 2004; Seinfeld et al., 2004; Sullivan et al., 2007a; Sullivan et al., 2007b; Sullivan and Prather,

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2007).

The uptake of ammonium by (acidified) dust is an important finding, though I feel the presentation and explanation could be made clearer. Previous model studies have predicted that mineral dust would displace ammonium to the gas-phase due to the cation-rich alkaline nature of Asian dust (Tang et al., 2004b). However, ammonium was observed to have mixed/reacted with acidified Asian dust during ACE-Asia (Sullivan et al., 2007a). Ammonium was enriched in the submicrom sulphate-rich dust, and the relative amount of ammonium correlated very well with the sum of nitrate, sulphate, and chloride ($R^2 = 0.88$). Evidence for both ammonium nitrate and ammonium bi/sulphate in individual dust particles was observed (Sullivan et al., 2007a). Therefore insights from your observations of ammonium in aged Asian dust can be quite valuable.

However, as you never observed the alkaline ($\text{CaCO}_3/\text{MgCa}(\text{CO}_3)_2$) content of the dust to be anywhere near completely neutralized by acid uptake, how is the presence of ammonium explained if the dust had not become acidified? Coagulation with ammonium nitrate/sulphate containing particles? Formation of ammonium salts on the surface of the dust via heterogeneous nucleation (Korhonen et al., 2003)? Or could it be that because total aerosol mass was measured, there exist some fraction of (smaller) dust particles whose alkalinity has been mostly consumed, are therefore acidic, and are then neutralized by ammonia?

P. 4849, line 21: "this could also indicate that the Jordan et al. assumption that all ammonium is associated with submicrometer sulfate or nitrate is inaccurate." Single-particle analysis of dust from ACE-Asia found most of the ammonium (in dust) was associated with sulphate-rich submicron dust (Sullivan et al., 2007a), thus largely supporting this assumption.

p. 8494, line 7. CaSO_4 is NOT soluble. It is almost as insoluble as calcite (CaCO_3), and does not deliquesce below 100% RH (Kelly et al., 2007; Sullivan et al., 2009). Therefore, it is incorrect to assign the same hygroscopic growth to $\text{Ca}(\text{NO}_3)_2$ and

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CaSO_4 ; CaSO_4 has effectively zero apparent hygroscopicity. In fact the formation of CaSO_4 versus $\text{Ca}(\text{NO}_3)_2$ or CaCl_2 has interesting ramifications for the hygroscopicity of mineral dust. It represents a reaction pathway that consumes alkaline carbonates yet does not increase the dust particle's hygroscopicity (Sullivan et al., 2007a; Sullivan et al., 2009). A similar effect can occur by the production of calcium oxalate (Sullivan and Prather, 2007; Sullivan et al., 2009). The effect of this chemical conversion on the dust's hygroscopic growth and thus optical properties should be revised in light of this.

p. 8495, line 23: Is an assumed ammonium sulphate composition justified by the actual measurements? If a large fraction of sulphate exists as CaSO_4 , this will be non-hygroscopic.

The partitioning measurements clearly show that there were always excess nitrogen and sulphur oxide gases present, yet a large fraction of calcite/dolomite mass remained unreacted. Do you have any indications as to what may have caused this, as it has also been observed (Jordan et al., 2003) and predicted (Tang et al., 2004a) by others. Some possibilities that come to mind: 1) not all of the calcite is accessible to reaction with gases, 2) there is insufficient contact/reaction time between the dust and reactive gases (though the rate constants are generally large), 3) the reaction rate and calcite accessibility is limited by water vapour (Maxwell-Meier et al., 2004), 4) the form of the nitrogen oxides (NO_x vs. HNO_3 and N_2O_5) limits the reaction rate. Does your suite of measurements lend any insight into which of these, or other processes, limit a more complete conversion of the alkaline mineral components?

There are many more recent laboratory studies regarding the heterogeneous chemistry of mineral dust particles, including the conversion of calcite particles into soluble hygroscopic calcium nitrate, and the importance of mineralogy for these reactions (Krueger et al., 2004; Liu et al., 2008), as well as field observations of processed calcite particles (Laskin et al., 2005; Matsuki et al., 2005; Shi et al., 2008; Sullivan et al., 2007a).

p. 8473, line 16. Citing a model study by Bauer et al. (2007) to describe the mass

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coating and hygroscopicity of aged mineral dust seems odd to me. There are several recent in situ field measurements regarding the hygroscopicity of mineral dust that could be referenced (Carrico et al., 2003; Perry et al., 2004; Roberts et al., 2006; Shi et al., 2008).

p. 8473 line 20. I found the discussion regarding the hygroscopicity and CCN activity of mineral dust particles to be very confusing. What does “Activation of “completely insoluble” dust particles in the 0.6–2.0 μm size range is facilitated by the presence of slightly soluble compounds (Kelly et al., 2007).” mean? I think this discussion could be greatly improved if one of the single hygroscopicity parameters was used. For example, replacing 5% by volume of insoluble calcite with soluble hygroscopic calcium nitrate increases the particle’s hygroscopicity (κ) from 0.0011 to 0.027. A 500 nm particle with this composition will have a critical supersaturation of 0.064% compared to 0.237% for the unreacted calcite particle (Sullivan et al., 2009).

p. 8473, line 30: “These findings are supported by field measurements (Matsuki et al., 2009) which show that calcite-containing particulate are likely acting as CCN.” Shi et al. (2008) measured the hygroscopicity of aged Asian mineral dust particles. Twohy et al. (2009) observed Saharan mineral dust particles in cloud droplet residuals over the Atlantic Ocean.

p. 8474, line 8: “Dust particles larger than $\sim 0.2 \mu\text{m}$ are all effective cirrus cloud ice nuclei (Archuleta et al., 2005)” is incorrect. The IN properties of mineral dust are well known to be a strong function of mineralogy, with aluminosilicate clays typically displaying the best IN ability, and calcite and gypsum mineral phases displaying relatively poorer IN ability (Eastwood et al., 2008; Zimmermann et al., 2008). Mineral dust particles have also been observed to be some of the most efficient heterogeneous IN from ambient measurements, e.g. (DeMott et al., 2003a; DeMott et al., 2003b; Stith et al., 2009).

p. 8475, line 28. Many more recent studies of the chemical composition of Asian

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mineral dust particles exist, e.g. (Arimoto et al., 2004; Claquin et al., 1999; Jeong and Chun, 2006; Jeong, 2008; Mori et al., 2002; Nishikawa et al., 2000).

Page 8487, line 12. Was the contribution to Ca^{2+} from sea salt accounted for?

Page 8487, line 12. Many more measurements of the mass fraction of calcite in Asian loess exist, I have included some references above. The derivation of an average 11% calcite mass in the suspended Asian dust is a valuable measurement, but is there any difference between the dust aerosol size modes?

Page 8488, line 8. The interesting discussion regarding the partitioning/sequestration of sulphur and nitrogen oxides to dust would really be improved if the size range of aerosol chemistry used was mentioned. Along those lines, are there any indications of size-segregated chemistry in the reacted dust, from the AMS for example? Single-particle analysis of aged dust during ACE-Asia at sea level found that ammonium and sulphate were enriched in submicron (Fe/Al-rich) dust, while chloride and nitrate were enriched in supermicron (calcite-rich) dust particles (Sullivan et al., 2007a).

p. 4893, line 5. Secondary production of nitrate in the dry lake bed “dust” was observed during MILAGRO (Moffet et al., 2008).

Fig. 5: How is “dust mass” measured/calculated?

p. 8498 line 9, and 8499 line 5. I am again confused by what aerosol size range is being measured and used to derive these results.

p. 8500, line 13. Again, CaSO_4 is not soluble.

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