Response to comments of Anonymous Referee #1

We thank Anonymous Referees #1 for his/her valuable comments. I realized how deep and thoughtful his/her review is on our manuscript. I would like just respond to the reviewer's comments in the raised order, comment-by-comment. As this is the first review on our manuscript, please allow us the revision of our manuscript which reflects all the suggestions made by the reviewers after getting the second review.

*** Reviewer's summary:** This article "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 Song et al. investigates the chemical composition of particles collected in springtime dust storms. The group has previously reported on an overview of samples collected from 2000-2006. One of these samples (from one day in Nov 2002) was unique in that calcium-containing particles were the most abundant particle type. This article investigates the single particle composition and mineralogy for 109 particles. Their combination of EPMA and ATR-FTIR spectroscopy was sufficient to extract mineralogy of the samples. In addition to their extraction of mineralogy information, the main results of this study are that (1) amorphous calcium carbonate was found in four particles and that (2) the paper states that this is the first field observation of CaCl2 particles converted from CaCO3 in a sample collected in the boundary layer.

I think this is a very interesting study, as single particle analyses are needed to understand more details of the aging process than can be obtained through bulk studies. I have a number of questions that are listed below, but I feel that with minor corrections, this article would be a good contribution to *Atmospheric Chemistry and Physics*.

Before my questions, however, I want to indicate a few rare, but very valuable pieces of information that the authors have included in their manuscript and supporting information. Specifically, the authors have included a table that includes all particles and their compositions as determined individually from the two techniques. This is a wonderful resource for laboratory researchers. Within the text itself, the figures of FTIR and EPMA data for "representative" particles are clear and well laid out. I want to commend the authors for including this level of detail in the figure set and supporting information.

Response: We appreciate the reviewer's very positive evaluation of our work.

*** Reviewer's questions:**

(1) Much of the discussion of mineralogy depends on the observed FTIR transitions. The text would be much clearer if a table of wavenumber regions for different functional groups in FTIR was listed, perhaps by mineralogy. If hydrocarbons were the only type of compound discussed, I wouldn't find this necessary, but it would clarify the results for me for these mineral compounds.

Response: Our previous work showed extensive FTIR spectra for 24 different minerals (Anal. Chem. Vol. 82, pp. 6193-6202, 2010). On the other hand, following the reviewer's suggestion, a table of FTIR peaks for minerals discussed in the text will be added in revised Supporting Information.

(2) I know that it is common to analyze particles collected on filters during field studies. From using impactors, however, I also know that collection efficiencies can be poor and can depend on the composition of the particles. I'd like to know how representative their distribution of particle compositions is compared to the particles that were in the dust storm. Also, with SEM, the authors are limited to investigating super-micron particles. Could they give a sense of whether the sub-micron particles have a similar distribution of compositions? Do the particles in the other 6 impactor stages have similar composition?

Response: As given in the text, this sample was analyzed three times including this work. In our previous paper (J. Geophys. Res. Vol. 110, D23201, 2005), we presented the results for 5 impactor stages of this sample, which showed relatively similar chemical compositional data among the impactor stages. As this sample was found to have experienced extensive chemical modification, the detailed second measurement for the stage 3 sample using low-*Z* particle EPMA was performed to understand the nature of the chemical modification better (Atmos. Environ. Vol. 40, pp. 3869-3880, 2006). After the development of the combined use of EPMA and ATR-FTIR imaging for 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.

Generally speaking, the representativeness in the single particle analysis can be valid for particles of major chemical species if the number of analyzed particles for a sample is ~150 or more as shown in our previous work (Anal. Chim. Acta vol. 389, pp. 151-160, 1999). Indeed, ATR-FTIR imaging is not good for the analysis of submicron particles, due to its poor spatial resolution, and that is why this combined application of two single particle analytical techniques were applied to supermicron particles.

Lastly, some reported that chemical compositions are somewhat different among super- and sub-micron Asian Dust particles, however, this is beyond our research scope of this work.

(3) How do the authors know that no modification of the particle composition occurred between 2002 when the particles were collected and 2012?

Response: After collecting the samples, the samples were immediately put in plastic boxes and the boxes were sealed by insulating tapes and stored in the refrigerator, minimizing the influence on the samples from ambient environment. We notice that the chemical compositional distribution of particles is similar between the previous analyses in 2002 and 2005 and the present analysis.

(4) The authors mention that amorphous $CaCO_3$ could originate from biogenic or soil origin, but the emphasis in the paper is on the fact that it could be biogenic. There are several sentences about biogenic amorphous calcium carbonate before the authors seem to backtrack and say that it is more likely that the amorphous compound came from soil. I think the authors should state in the first sentences about amorphous $CaCO_3$ that it could have a biogenic or soil origin, but that it more likely comes from soil.

Response: Thank the reviewer for his/her careful reading. Our manuscript will be modified in the way suggested by the reviewer.

(5) The paper states that this is the first field observation of $CaCl_2$ particles converted from $CaCO_3$ in a sample collected in the planetary boundary layer. I don’t understand the claim because the Sullivan et al. 2007b measurements were ship-based and as a result, they were also collected in the lower troposphere.

Response: Until now, there are just two report about $CaCl_2$ formation from $CaCO_3$ (Sullivan et al. 2007b and Tobo et al. 2010), which were observed in marine boundary layer. In the text, we want to say this is the first inland observation on $CaCl_2$ formation from $CaCO_3$. 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.

(6) It’s unclear to me why the authors characterize COO^- as being indicative of humic-like organic compounds. On pg 27309, the authors make the qualification that these spectral signatures could also be from oxygenated carboxylic carbonyl compounds. In other places, the authors just refer to humic acid.

Substances like oxalic acid (a carboxylic acid) have been found to be internally mixed with mineral dust aerosol (Sullivan and Prather, ES&T, 2007). Should all indications of humic be qualified as humic or oxidized organics? Also, in the table in the supporting information, sometimes the authors write “organic”, “organic (CH, humic)”, “organic (CH, COO-)”, “organic (humic)”, etc. The differences between these should be explained.

Response: Table S1 in Supporting Information contains three columns for describing chemical species in the individual particles; i.e. based on X-ray spectral data, ATR-FTIR data, and the combined use of two techniques. In the column of chemical species from ATR-FTIR data, we tried to analyze organic functional groups as much as possible. Accordingly, in this column, we indicated IR peaks of CH, COO, humic, etc. However, it is difficult to clearly define detailed organic chemical species based on ATR-FTIR data, so our final assignment in the last column was “organic” species. Regarding the use of “humic” and “oxygenated carboxylic carbonyl compounds” words in the text, we will use one of the words consistently in the revised manuscript.

(7) In the silicate particles, I am surprised the authors don’t see aluminosilicate clay minerals like illite and kaolinite, especially since illite is mentioned in the article as being found in Chinese loess. Are they able to differentiate, for example, between kaolinite and muscovite? If so, how?

Response: Our ATR-FTIR spectral library consists of ATR-FTIR spectra of both bulk and single particles of clay minerals frequently observed in airborne particles which includes montmorillonite (SWy-1, $(Ca_{0.12}Na_{0.32})[Al_{3.01}Fe_{0.41}Mg_{0.54}][Si_{7.98}Al_{0.02}]O_{20}(OH)_4$), kaolinite (KGa-1b, $Al_4Si_4O_{10}(OH)_8$), illite (IMt-1, $Mg_{0.09}Ca_{0.06}K_{1.37})[Al_{2.69}Fe_{0.82}Mg_{0.43}][Si_{6.77}Al_{1.23}]O_{20}(OH)_4$), muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$) and so on. In our previous study (Anal. Chem. Vol. 82, pp. 6193-6202, 2010), it was shown that we can clearly distinguish these minerals from each other by the combined use of low-*Z* particle EPMA and ATR-FTIR imaging. For example, elemental concentrations and their ratios obtained from EDX are clearly different for muscovite and kaolinite. Muscovite contains K while kaolinite does not. In addition, ATR peak positions and peak patterns are different e.g., structural OH band exhibits three sharp peaks at 3687, 3646, and 3626 cm^{-1} in kaolinte while one broad peak at 3620 cm^{-1} in muscovite. If a larger number of particles are analyzed, the probability of encountering illite and/or kaolinite will be higher.

*** Minor Corrections:**

(1) FT-IR is not a typical abbreviation of FTIR. The text should be changed to ATR-FTIR.

(2) In the supporting information, could the major and minor FTIR peaks be indicated in the table of particle composition?

(3) In the figures in the manuscript, I think that once the figures are reduced in size for the published manuscript, some of the fonts will be too small. The elemental composition, legends, and axes, for example, are likely to not be visible. The axes of the FTIR data should be labeled with words and units, not just units.

(4) Pg 27303 line 8 “on the other hand” should be changed to “in addition”.

(5) Figure 1 needs a scale bar.

(6) Did the authors study 178 particles (pg 27300) or 109 particles (everywhere else in the manuscript)?

(7) Pg 27314 line11 “without containing” should be changed to “that did not contain”

(8) Pg 27316 line 24 I think the authors mean that the carbonate minerals are a minor mineral component, in which case “their minor mineral” should be changed to “a minor mineral”

(9) In the table in the supporting information “MOx” should be “MOx” where M = metal (Al, Fe, etc.)

Response: Regarding the minor correction #6, when we mentioned our previous work, we said that 178 particles were studied. In this work, 109 particles were investigated. Although the other corrections are minor, I realize how thoughtfully the reviewer made a review – and I thank the reviewer again. Those minor corrections will be employed in the revised manuscript.