

Interactive comment on “Change of iron species and iron solubility in Asian dust during the long-range transport from western China to Japan” by Y. Takahashi et al.

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We thank the referee for the constructive comments. Our replies to the comments are listed below.

All the corrections are shown in the pdf file uploaded as a supplement.

=== Comment 1 === Although the results of this paper are undoubtedly profound, the authors tend to overstate the significance of their findings. For instance, the estimated difference between ferrihydrite content in Asku (desert) and Tsukuba (Japan) samples is 105% and 245%, respectively, which is attributed to a 7% increase in iron aerosol solubility (in rainwater, Table 1). This increase in iron solubility of Asian dust due to an-

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thropogenic chemical processing is minor compared to results reported in other studies (1–80% increase) (Mahowald et al., 2005). Therefore, it may be difficult to argue that changes in iron speciation of Asian dust during long-range transport are a “significant” source of bioavailable iron to the ocean. The authors should ultimately tone down the conclusions concerning the significance of this mechanism throughout the manuscript.

Reply 1: We acknowledge the comment. We toned down the effect of the mechanism in this study as shown below.

Original sentence in Abstract: Our findings suggested that ferrihydrite secondarily formed during the transport is an important source of soluble iron species, which can be more soluble than clay minerals initially contained in the mineral dust such as illite and chlorite. Revision: Our findings suggested that secondary formation of ferrihydrite during the transport should be considered as one of important processes in evaluating the supply of soluble iron to seawater.

Original sentence in Conclusion: The results of our observation suggested that the transformation of chlorite to ferrihydrite in aerosols during the long-range transport can increase the solubility of Fe in dusts to seawater. Revision: The results of our observation suggested that the transformation of chlorite to ferrihydrite in aerosols during the long-range transport can be one of important factors that can control the solubility of Fe in dusts to seawater.

=== Comment 2 === Abstract and conclusion: Quantitative iron solubility and clay mineral and ferrihydrite content should be reported in both sections.

Reply 2: We added the results in the abstract and conclusion.

=== Comment 3 === Pg. 19551, Methods, The authors use XAFS techniques to probe iron mineralogy of dust. In the method section it is specifically noted: “The samples appearing on the filter as dark spots (spot size: 0.5–2mm) were directly exposed to the incident X-ray beam.” Throughout the manuscript, it is not clear whether the authors

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took several “single particle” measurements of iron mineralogy or bulk iron mineralogy using XAFS techniques. If the former, what did the authors do to ensure that single particle XAFS spectra were representative of the entire sample?

Reply 3: Our measurement was not single particle analysis. To avoid the misunderstanding, two sentences were added at the beginning of the Section 2.3 in the Method section.

Sentence added: Iron speciation was conducted by Fe K-edge XAFS. In our analysis, we used mm size X-ray beam used for the sub mg aerosol particles collected on the filter, showing that Fe speciation data in this study are bulk analysis in our study.

=== Comment 4 === Pg. 19552, Line 1-5, In this study, XAFS energy spectra were fit to a number of iron standard spectra to determine mineralogy. A few details on XAFS fitting were left out of the discussion paper. For example, what XAFS analysis software was used for linear combination fittings? Did the authors do an initial principal component analysis (PCA) to infer which standards were most appropriate for the linear combination fitting analysis? A table including the PCA and multiple LCF results (with R values) would greatly support their XAFS fits.

Reply 4-1: Names of the softwares REX 2000 (Rigaku, Japan) and Athena (Ravel and Newville, 2005) used were added in the Method section.

Reply 4-2: We conducted PCA analysis for the spectra measured in fluorescence and electron yield modes. The results showed that three or four components are needed to fit XANES and EXAFS measured in this study (Fig. S3 and Table S3 in Supporting Materials). Since we already found that chlorite and illite as main Fe species in the samples collected in Aksu and Qingdao, the two species can be the end members of the Fe species. In addition, there should be Fe oxide fraction including ferrihydrite, goethite, and hematite as suggested from CBD method and oxalate method. The comparison of the two methods suggested that ferrihydrite can be main Fe oxide species in our samples. This is consistent with the absence of goethite and hematite in the XRD

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results. Thus, we decided to employ illite, chlorite, and ferrihydrite to fit all the XANES and EXAFS spectra in our samples. The fitting procedure was also shown in Fig. S2 in Supporting Materials showing that the three end members are needed to explain the spectra measured. In addition, all the Fe speciation data with R values were given in Table S2 in Supporting Materials. This discussion was added into the Section 3.2.

New paragraph in Section 3.2. Further support for the fitting results was obtained through statistical data for the XANES and EXAFS fitting. Principle component analysis (PCA) in such fitting has been often used to estimate the number of end members required to fit the spectra. The PCA for all the XANES spectra for the Aksu, Qingdao, and Tsukuba samples measured both in FY and CEY modes showed that the number of independent end members can be three or four (Fig. S3 and Table S3 in Supporting Materials). Given that chlorite and illite are main Fe species in the samples collected in Aksu and Qingdao, these two species are likely the end members of the Fe species. In addition, the Fe oxide fraction should contain ferrihydrite, goethite, and hematite as suggested by the CBD and the oxalate method. The comparison of the two leaching methods suggests that ferrihydrite is the main Fe oxide species in the samples. This is consistent with the absence of goethite and hematite in the XRD results. Thus, we decided to employ illite, chlorite, and ferrihydrite to fit all the XANES and EXAFS spectra in our samples. The fitting procedure was also shown in Fig. S2 in Supporting Materials, showing that the three end members can account for the spectra recorded.

=== Comment 5 === Pg. 19558, Line 12-15, Can you clarify why physical weathering decreases the Fe(III) oxide content?

Reply 5: The sentence can be misleading. We would like to mention that chemical weathering that can produce Fe(III) oxide is more important in soils compared with desert sand in arid area and that the Fe(III) oxide content in dust mainly from desert sand in arid area can be smaller than that in dusts from soils formed in humid area.

Revision (Section 3.2): Since physical weathering rather than chemical weathering is

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important for the formation of desert sand in the arid area, it is possible that Fe(III) oxide contents cannot be high as those in the aerosols originated from soils formed under humid climate.

=== Comment 6 === Pg 19559, Line 12-14, The authors mention that the dissolution rate of chlorite is far greater than that of illite at pH 4. However, aerosol acidity appears to be mostly basic (pH 9 in Asku) to neutral (pH 6 in Takusba) during transport. As most iron minerals have variable solubility properties at different pH values, there may be reported differences in solubility properties of chlorite reported at pH 6. If so, what is the expected amount of chlorite that will dissolve at the pH 6? A short discussion on the amount of chlorite that will dissolve and subsequently form ferrihydrite under these atmospheric conditions (e.g. aerosol acidity and atmospheric transport time) would be useful.

Reply 6: The pH value was given in this discussion to show the effect of anthropogenic effect on the aerosol samples during the transport. However, the pH value does not show the in situ pH value for the small amount of water phase at the aerosol surface. The pH measurement was conducted for 10 mL water in contact with about 1-5 mg of aerosol. Since the amount of water phase at aerosol surface is very small, in situ pH can be much lower than that measured by the method in Takahashi et al. (2009). In addition, the pH value includes the effect of dissolution of alkaline salts such as carbonate remaining in the aerosols into the solution. However, it has been suggested that Fe-rich particles are often externally mixed with carbonate (Sullivan et al., 2007) and Fe-rich particles experience low pH condition during the long-range transport (Ito and Feng, 2010). Thus, it is likely that in situ pH condition was low during the alteration of chlorite in the aerosol. The discussion above was added in Section 3.3 in the revised version.

=== Comment 7 === Pg. 19560, Line 20-23. Once again, a principal component analysis coupled to linear combination fits would support your CEY-XAFS results. A table either in the manuscript or supplement showing these results would support their

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results.

Reply 7: As shown in the reply to the comment 3, the PCA analysis and fitting results with R values were shown for CEY-XAFS results in Table S2 in the Supporting Materials.

=== Comment 8 === Pg 19561, Line 1-13. This argument needs some clarification. It is not clear why these results point to formation of ferrihydrite nanoparticles. Please add a few sentences to further explain this argument.

Reply 8: The larger ratios of ferrihydrite in CEY mode than in fluorescence mode can be due to either (i) selective formation of ferrihydrite at the surface of the particle or (ii) finer particles sizes of ferrihydrite than other Fe species in the samples. This sentence was added into the Section 3.4.

=== Technical comments === - Pg. 19548, Line 11, Change to 2.1. Sample collection and characterization - Pg. 19560, Line 16, Change to (ii) alteration of chlorite - Figure 1 and Figure 9, Increase the font size for axis label and legend

Reply: These points were corrected in the revised version.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/11/C10758/2011/acpd-11-C10758-2011-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 19545, 2011.

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