

## ***Interactive comment on “Role of dust alkalinity in acid mobilization of iron” by A. Ito and Y. Feng***

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We thank the referee for his/her constructive suggestions for improving the paper.

Comment: 1) The chemical speciation of iron included in the model is based on previous experiments which assume that the predominate iron species are iron oxides, specifically hematite [Luo et al., 2005]. However, recent work has called into question the veracity of these assumptions (e.g. [Journet et al., 2008; Schroth et al., 2009]). I recommend that the authors include a third experiment where they investigate how iron dissolution from clays and/or from a better speciated Goethite:Hematite:Ferrihydrite mixture for Asia dust affects the deposition of iron near the source and in the remote North Pacific after long-range transport.

Response: An important difference from previous studies and a new finding of our paper is that only a small fraction (< 0.2%) of iron dissolves from the acid mobilization of

C6399

dust aerosols with the inclusion of alkaline dust, even though we assume hematite as the predominate iron oxides for the fine mode in our base simulations. Recent laboratory studies suggest that iron in clays in the atmosphere may potentially represent a significant source of soluble iron in acidic environments, but the dust is not always in acidic conditions as indicated by recent field observations. So, the alternative mechanism was examined, based on the individual particle analysis.

In modeling studies, the chemical speciation of iron could be simplified from the experimental data, as the reviewer pointed out. We are aware of the importance of chemical specificity of iron-rich dust, therefore, added two more simulations (Exp 3 and Exp 4) in the revised manuscript to explore the sensitivity of the soluble iron deposition near the source and in the remote North Pacific Ocean due to the assumption about the mineralogy of iron. In the sensitivity studies, we assume that illite, instead of hematite, is the main iron-containing species in the fine-mode dust. Accordingly, dust aerosols in our model simulations have lower iron content but the dissolution constants of iron are faster or slower than that of hematite, depending on the fraction of total oxide dissolved. Our results demonstrate that the iron solubility is sensitive to the chemical specification of iron-containing minerals in dust, especially when the iron-containing minerals are externally mixed with carbonate minerals - a mixing state which we found in this study most likely for fine-mode dust particles. We have thoroughly revised our paper to clarify our findings and future works.

The following is now added in the section 2.2, last paragraph:

“However, the assumption of hematite as the solely important source for dissolved iron may need to be revisited, as more comprehensive experimental data for chemical specificity of iron-rich dust become available (Cwiertny et al., 2008; Journet et al., 2008; Schroth et al., 2009; Fu et al., 2010). Here, the illite dissolution is also considered for specification of “structural iron”, which is trapped in the crystal lattice of aluminosilicate minerals (RS4 in Table 1).”

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Also in section 3:

“In the last two experiments (Exp3 and Exp4), we explore the sensitivity of iron solubility to the iron mineralogy, because of the importance of chemical specificity of iron-rich dust. The dissolution rate of illite (Table 1) and abundance of iron in dust (1.8%) are taken from literature values (Journet et al, 2008; Nagy, 1995; Skopp, 2000; Tessier, 1990). The mixing state with alkaline dust is also examined for internal and external mixing in Exp3 and Exp4, respectively”

and the section 3.3, last paragraph:

“Finally, we present the sensitivity of iron solubility in the fine-mode dust to the mineralogy of iron in simulations of Exp3 and Exp4. The faster dissolution rate of illite is partly compensated by the lower abundance of iron in dust. As a result, average soluble iron deposition ( $\text{pg m}^{-2} \text{s}^{-1}$ ) to the ocean from dust source for hematite internally mixed with the alkaline dust (Fig. 8a) is comparable to that for illite internally mixed with the alkaline dust (Fig. 8c). On the other hand, when the buffering effect of alkaline dust minerals is excluded, a higher iron fraction in dust and a faster dissolution rate at the second dissolution stage with the assumption for hematite lead to substantially higher soluble iron deposition (Fig. 8b) than that for illite externally mixed with the alkaline dust (Fig. 8d). These results demonstrate that the iron solubility is sensitive to the chemical specification of iron-containing minerals in dust, especially when the iron-containing minerals are externally mixed with carbonate minerals.”

Comment: 2) Despite being limited to simulating the April 2001 time period, the manuscript does not present any quantitative comparisons to the ACE-Asia or TRACE-P data sets - other than comparison of iron fractional solubility and soluble iron concentrations. Given the wide range of reported iron solubilities it is not inconceivable that the soluble iron concentrations could be reasonable accurate but that the simulated concentrations of anthropogenic aerosol and mineral dust are not well simulated (i.e. right answer but for wrong reasons). At least one, preferably multiple comparisons

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should be undertaken, in particular verification that the simulated concentrations of anthropogenic and mineral dust aerosols in boundary layer and the FT are accurately simulated.

Response: The IMPACT model has been thoroughly evaluated in previous studies, focusing on ozone chemistry (Ito et al., 2007, 2009; Rotman et al., 2004), anthropogenic and dust aerosol (Feng and Penner, 2007; Liu et al., 2005). The simulated concentrations of aerosol have been also evaluated under the AEROCOM exercises. In the revised manuscript, we added more quantitative comparisons of simulated anthropogenic sulfate and mineral dust aerosols to the ACE-Asia data set including a new figure (figure 2), as the reviewer suggested.

The following is now added at the beginning of section 3:

“The concentration, chemical composition and transport of mineral dust along with the East Asian continental outflow have been previously studied by a number of investigators, notably during the ACE-Asia field campaign (Huebert et al., 2003). Here, we focus on the processes and factors that affect the iron dissolution. Vertical distribution of simulated aerosol concentrations is compared with measurements from the total aerosol sampler (TAS) aboard the C-130 aircraft for the non-sea-salt sulfate (Fig. 2a and 2b) and soluble calcium (Fig. 2c and 2d) in April 2001 (Huebert et al., 2003; Kline et al., 2004). The model results are averaged over the selected regions and the periods of sampling time in the aircraft flights, which covered large areas. The model demonstrates the ability in simulating the vertical structure of the observed anthropogenic sulfate and mineral dust aerosols. The absolute concentration of soluble calcium ( $2 \pm 3 \mu\text{g m}^{-3}$ ) is lower than the aircraft measurements ( $4 \pm 6 \mu\text{g m}^{-3}$ ), but the difference is within a standard deviation. More importantly, the model simulates the non-sea-salt sulfate concentrations well ( $8 \pm 10 \mu\text{g m}^{-3}$  for model vs.  $8 \pm 7 \mu\text{g m}^{-3}$  for measurement), which drives the acid mobilization in the absence of alkaline dust. This sets the stage for investigating the iron solubility. ”

C6402

Comment: Specific arguments which support the need for these revisions are included below. Page 10401; lines 3-5 The dissolution of dust minerals strongly depends on solution pH during the chemical processing of hematite-containing mineral dust by sulfuric acid formed from oxidation of SO<sub>2</sub>. Page 10405; lines 10-11 The hematite dissolution is also treated explicitly as a kinetic process, after Meskhidze et al. (2005). Page 10405; line 27 to Page 10406; line 3 Currently, the iron-containing mineral in dust aerosol is treated as hematite, following previous studies (Luo et al., 2008; Meskhidze et al., 2005; Solmon et al., 2009). Thus the chemical composition of dust aerosols is assumed to be: 11% CaCO<sub>3</sub>, 5.5% MgCO<sub>3</sub>, and 5% Fe<sub>2</sub>O<sub>3</sub> (59 Tg Fe per year). [Meskhidze et al., 2003] state “Since most of the Fe in surface soils of the gobi deserts is found in the form of hematite (α-Fe<sub>2</sub>O<sub>3</sub>) [Hseung and Jackson, 1952; Claquin et al., 1999], we focus here on hematite dissolution”. In [Claquin et al., 1999] the authors state “In soil studies and in dust analysis, the most common forms of iron oxides, hematite and goethite, are often considered together because they usually have a limited abundance. As far as mineral aerosols are concerned, hematite and goethite have close radiative properties, and, in this work, we consider them together.” In [Ito and Feng, 2010] we are not considering ‘radiative properties’ but chemical properties. Their limited abundance and speciation is therefore potentially important. Furthermore, in Figure 4 of [Claquin et al., 1999] there are only two data points compared, in a log-log plot. They point out “The correlation coefficients are not indicated for the [Hematite:Quartz] ratio because of lack of enough data”. Also note the comment in [Cwiertny et al., 2008] “mineralogical considerations will likely have to extend beyond generalized classification schemes such as Fe oxide phases or Fe-containing aluminosilicates, as our dissolution data suggest that solubility predictions based solely upon the abundance of iron oxide phases in a material may not be sufficient”. Asian dust is dominated by goethite not hematite [Lafon et al., 2004; Lafon et al., 2006]. Furthermore, the solubility product of goethite is ~1 order of magnitude greater than hematite (Table 1; [Kraemer, 2004]). [Meskhidze et al., 2005] explicitly state “the assumption that hematite is the only Fe-containing mineral in soils is not strictly valid” and then claim “the Fe content in

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clay minerals is usually small and thus for the purposes of this study can be neglected”. However, [Schroth et al., 2009] (a reference cited in this manuscript but unavailable to Meskhidze et al. [2003, 2005]) appear to disagree with this assumption when they state “the ubiquity of ferrihydrite and low abundance of haematite (routinely differentiated and quantified by extended X-ray absorption fine structure (EXAFS) analyses; Supplementary Fig. S1) in these samples suggests that ferrihydrite must be considered by the ocean modeling community as a common Fe phase associated with atmospheric deposition, as it differs substantially in solubility and chemical structure compared with haematite, which is often assumed the dominant iron form in dust input from arid regions”. Page 10410; lines 14-19 This simulation (Exp1), however, underestimated the mass fraction of soluble iron in the fine mode to the total soluble iron concentration (54% for Exp1 vs. 79% for measurement in Table 3) over the Pacific Ocean. If we combine the iron deposition for fine particles from Exp2 (aluminosilicate-rich dust) with that for coarse particles from Exp1 (calcite-rich dust), we would be able to obtain a better agreement in the mass fraction (75%) with the observation. Page 10410; lines 23-28 The mass fraction of dust in the fine-mode aerosols is small near the source regions, so that the resulted increases in iron deposition are small near the continents. However, it is noteworthy that the deposition of soluble iron from this scenario would become predominantly high (10–15 pgm<sup>-2</sup> s<sup>-1</sup>) over the eastern North Pacific Ocean, due to a longer residence time of smaller particles. The work of [Journet et al., 2008] was not available to Meskhidze et al. [2003, 2005]. Journet et al., focused on analyzing African dusts, however, similar to African samples, Asian dusts are also dominated by Illite clays. In their conclusions they state “Our results therefore suggest that the use of iron (hydr)oxides and particularly hematite in biogeochemical models, might induce an underestimation of the dissolved iron supply and hence an overestimation of atmospheric chemical processes contribution as in the increase of the solubility during dust transport. The impact of this trend in Fe solubility will be to smooth out the strong gradients in atmospheric iron supply to the ocean, with proportionately less soluble Fe delivered to areas close to major dust sources and more to remote areas, relative to

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most current models, which use a fixed value for aerosol Fe solubility.” Thus though Ito and Feng, [2010] propose using a combination of Exp1 and Exp2 in order to explain the observations, [Journet et al., 2008] propose an alternative hypothesis for the simulated results, namely that the exclusive use of hematite as the iron bearing mineral (rather than Fe in illite clays) is causing the discrepancy. I recommend Ito and Feng explore this alternative hypothesis, confirm it or rule it out, and discuss its possible implications to their conclusions. This might be in the form of a third study (Exp3) which evaluates the effect of updated iron speciation compared to Exp’s 1 & 2 using the hematite assumption.

Response: We thank to the anonymous reviewer for encouraging us to conduct additional simulations, as was shown above. We are interested in collaborative studies to explore more sensitivity in future simulations.

Comment: Page 10407; line 18 In [Solmon et al., 2009] the veracity of the GEOS-Chem simulations in East Asia was evaluated in Figure 5 as well as in separate publications [Fairlie et al., 2007; Heald et al., 2006]. The simulations by the IMPACT model presented in [Ito and Feng, 2010] do not include a similar discussion of the reliability of the model in predicting the concentrations of pollution or dust. Perhaps more importantly, how well does the model replicate the vertical distribution of pollution, mineral dust and the relative proportions of acid and basic species? Because dust events of April 2001 are so well documented, I recommend that Ito and Feng undertake ground- and free troposphere-truthing of the simulations by including at least one and preferably multiple comparisons to the ACE-Asia data sets (Gosan, R/V Ron Brown data, C-130 data, and the MP02 cruise [Hand et al., 2004]).

Response: We have added the results of comparison with observations from C-130 data, as was shown above.

Comment: Page 10407: Section 3.1 While the results presented in this section appear to support observations, the discussion of calcium solubility is totally incorrect.

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The solubility of calcium compounds, from least to most soluble is:  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{CaCl}_2$ ,  $\text{Ca}(\text{NO}_3)_2$  Thus the line 7,8 statement “the soluble calcium (i.e. sum of calcite and calcium ion) is being converted to solid forms” is misleading and should read “relatively insoluble species are being converted to more soluble compounds” Similarly, the line 17,18 statement “the percentage of the modeled soluble calcium is reduced from 90–100% near the source region to 60–70% at a regional sampling site (GOSAN)” should read, “insoluble calcium carbonate accounts for 90-100% of the calcium near the source but only 60-70% after transport to the GOSAN site.” Finally, lines 20-23 “large fractions of the mineral dust (80–90%) remain as soluble calcium over Japan, and then only 20–40% of the soluble calcium is converted to solids ( $\text{CaSO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$ , and  $\text{CaCl}_2$ ) over the eastern North Pacific” also needs to be amended, as the statement implies that  $\text{CaSO}_4$ ,  $\text{CaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$  are less soluble than  $\text{CaCO}_3$ . They are not.

Response: In our model, we assumed that once the secondary compounds were formed, they were precipitated out. Thus the “modeled soluble” calcium represents the  $\text{CaCO}_3$  and  $\text{Ca}^{2+}$ . However, it is very confusing when they are compared with the observation of “water soluble” calcium. In the revised text and figure, we corrected to the secondary compounds formed from the reactions of calcium carbonate with inorganic acids.

The following is now corrected at the section 3:

“the calcite is converted to the secondary compounds (i.e. sum of  $\text{CaSO}_4$ ,  $\text{CaCl}_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ) formed from the reactions of calcium carbonate with inorganic acids”

“the percentage of the modeled secondary compounds are increased from 0–10% near the source region to 20–30% over south of the Korean Peninsula”

“only 20–30% of the calcite is converted to the secondary compounds ( $\text{CaSO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$ , and  $\text{CaCl}_2$ ) over the eastern North Pacific”

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Figure caption: Spatial distribution of the secondary compounds (i.e. sum of CaSO<sub>4</sub>, CaCl<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>) in total calcium (%) in (a) the surface air and (b) the free troposphere during April 2001.

#### Additional Acknowledgments

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