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

Anonymous Referee #2

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Summary The Ito and Feng, 2010 manuscript summarizes model simulations of the deposition of iron to the North Pacific by examining the effects of acidic anthropogenic gases on iron-bearing mineral aerosol, the buffering capacity of Asian dust, as well as contribution of iron derived from anthropogenic combustion sources – a very comprehensive approach. The article is timely as simulations of iron deposition to the North Pacific are needed to better constrain the impacts of natural and anthropogenic emission on the biogeochemistry of the North Pacific. The article is relevant for publication in ACP as a determination or iron deposition throughout the North Pacific can only be estimated by using climate models with chemically resolved gas- and aerosol-phase species.

However, I cannot recommend it be published in ACP until the following 2 major revisions are considered.

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.

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 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.

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 SO2.

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% CaCO3, 5.5% MgCO3, and 5% Fe2O3 (59 Tg Fe per year).

[Mezkhidze et al., 2003] state “Since most of the Fe in surface soils of the gobi deserts is found in the form of hematite (a-Fe2O3) [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 $\sim$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 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”.

âĂČ Page 10407: Section 3.1 While the results presented in this section appear to support observations, the discussion of calcium solubility is totally incorrect. The solubility of calcium compounds, from least to most soluble is:

CaCO3, CaSO4, CaCl2, Ca(NO3)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 (CaSO4, Ca(NO3)2, and CaCl2) over the eastern North Pacific” also needs to be amended, as the statement implies that CaSO4, CaCl2 and Ca(NO3)2 are less soluble than CaCO3. They are not.

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−2 s−1) 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 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.

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]).

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