Responses to Reviewer’s comments: Reviewer 3

General Response: We have addressed all the reviewer comments and made appropriate adjustments to the text. Where this has not been appropriate, we have explained why below. In particular we have added a paragraph in the Introduction dedicated to describe in more detail the previous work and to make clearer the novelty of this study. We have also expanded the discussion somewhat by discussing in more detail our data in the context of previous relevant literature. Finally, we have also added the experimental details to clarify the conclusion of this work.

Comment 1:
P26209, L16: the large variability of iron solubility in aerosols is attributed to atmospheric processes during transport but also to the presence of anthropogenic iron (e.g. Sedwick et al., 2007): it needs to be specified.

Response:
We now have mentioned this more specifically and changed the sentence to: “These variations suggest that atmospheric processes (including dust atmospheric processing and mixing with anthropogenic and biomass burning aerosols) during long-range transport strongly affect and increase the measured Fe solubility in aerosols (Mahowald et al., 2005; Sedwick et al., 2007).” The “atmospheric processes” in our initial manuscript indeed include the physical mixing processes.

Comment 2:
P26210, L20: Journet et al. (2008) and Schroth et al. (2009) can be cited and their results should be discussed since they emphasized the presence of different Fe-bearing minerals and the importance of clay as supplier of soluble Fe which will be important to discuss further results of this paper.

Response:
We have added two sentences to take into account this comment : “I In addition, data in Cwiertny et al (2008), Journet et al. (2008), Schroth et al. (2009) and Fu et al. (2010) suggested that speciation and mineralogy of Fe in the dust/soil affects the rates and amount of Fe dissolution. A recent modelling study also suggested that the predicted Fe solubility is sensitive to the type of Fe-containing minerals (i.e., hematite or illite) in the dust (Ito and Feng, 2010).
Note that, this is the final response the reviewer comments. We slightly changed our response in Response to comments by Reviewer 2.

Comment 3:
P26210, from L23: In this paragraph, authors disregard the works on Fe dissolution kinetics on dust in atmospheric conditions (Spokes and Jickells, 1996; Desboeufs et al., 1999; Mackie et al., 2005; Deguillaume et al., 2010), useful for the discussion of the results. Moreover, this would lead believe for the readers that your approach is innovative.

Response:

In response to this comment, we have now added an additional paragraph in the Introduction to describe in more detail previous work. Much of this information was already included in our discussion but we accept it is better to create a specific paragraph bringing it together at the beginning of our manuscript as suggested by this reviewer. We note that we could not have cited the Deguillaume et al. (2010) because it was published at the same time when we submitted this manuscript. This has now been added.

Fe dissolution rates have been measured in dust or soils at a variety of pHs and dust/liquid ratios (grams or milligrams of dust per litre of solution) previous to this study. Spokes et al. (1994) and Spokes and Jickells (1996) showed that Fe solubility in a Saharan dust increases with time at pH 2 but decreases when pH was increased to 5-6. This decrease in Fe solubility was confirmed to be caused by Fe nanoparticle precipitation by Shi et al. (2009). Desboeufs et al. (1999) measured Fe dissolution in Saharan dusts at relatively high pH (pH 3.8 to 5.3) at diluted conditions (5 mg L^{-1}*) for 2 h. They found that a rather small fraction of the total Fe (< 0.1%) is dissolved under these conditions. Mackie et al. (2005) measured the Fe dissolution rates of an Australian dust over a larger pH range (pH 2.15 to ~7) for up to 120 h. They concluded that Fe is significantly mobilized below a threshold of pH ~3 which is a typical pH of aerosols in the atmosphere outside of clouds. Spokes and Jickells (1996) and Mackie et al. (2005) also showed that Fe dissolution rate is not dependent on dust/liquid ratio at diluted conditions (i.e., <40 mg* L^{-1}*) at low pH (e.g., ~2). Cwiertny et al. (2008) and Fu et al. (2010) investigated the Fe dissolution behaviour of a series of soil or loess samples from pH 1 to 3 at a dust/liquid ratio >2 g* L^{-1} *for up to 30 h. They demonstrated that temperature, type of acids, photo-radiation and the nature of the dust all affect Fe dissolution rates. In all of these studies Fe dissolves very fast initially and then slower and Fe dissolution rates are strongly pH dependent. However, for those experiments carried out at the low pH conditions (e.g., <3) found in atmospheric aerosols, the Fe dissolution curves are far from reaching equilibrium plateaus. These studies did not model the kinetics of Fe dissolution over the entire relevant pH/time range for dust. Deguillaume et al. (2010) has modelled the dissolution behaviour of aerosol particles at pH 4.7 to simulate the cloud conditions but the material they used was an urban particulate matter sample which is fundamentally different to dust (Desboeufs et al., 2005).*

Comment 4:

P26211, L23: The protocol by wet-sieving, even in MilliQ water, enables the release of the most soluble iron in water. Could you specify the protocol of freeze drying? During drying, dissolved Fe precipitates to the surface of Tibesti-PM20 forming a new pool of Fe. How do you take into the precipitated Fe-pool (probably ferrihydrite) account? Do you quantify the part of this new Fe-pool in comparison of the natural Fe-containing minerals in dust samples? These points are important for the discussion on the fresh or dry ferrihydrite in the part 3.5.

P26211, L25: The wind tunnel production of fine fraction of dust is very different of the protocol by sieving. The aeolian processes of erosion (saltation and sandblasting) are reproduced in the wind-tunnel that it is not the case for the sieving, in particular for wet-sieving. In consequence the conclusions of Lafon et al. (2006) are not adapted to your protocol.

Response:
In response to these two comments, we have added the following paragraph to section 2.1 to explain in more detail exactly our experimental protocols. "Less than 50 ml of MQ water were used for sieving more than 100 g dust and that water was included in the freeze drying process. The results by Desboeufs et al. (1999) showed that less than 0.06% of Fe is released into solution in a Saharan dust at pH 4.7 in 40 min. Therefore, the dissolution of Fe from large particles should be minimal because the contact time of water with 20-63 um soils was less than 20 min and the pH is much higher in the solution due to acid buffer capacity of the dust. The wet sample suspension was frozen to <-40 °C and then freeze dried and later gently disaggregated before use. This process is widely used in geochemistry to minimize the potential change to properties of the original material during dehydration."

We re-checked Lafon et al. (2006) and found that they also used a liquid separation technique for PM20. Our data further supported our argument that the freeze drying and wet sieving procedure did not significantly affect Fe speciation. (1) Fe dissolution kinetics of PM10 and PM20 are very similar in general but noticeably different to that of PM2.5; (2) Table 2 shows that the first Fe pool in PM10 is 18 umol/g and that in PM20 is 10.5 umol/g. If there is significant amount of Fe nanoparticles precipitated as mentioned in the reviewers comment, there should be more in first Fe pool in the PM20. However, this is not the case. Finally, the results of the Tibesti-PM20 and that of the Beijing dust are consistent, which further supported our conclusions.

Comment 5:
P26213, L18: Even if the long-range transport of dust is around several hundred hours, the dissolution of dust take place during the cloud phase, i.e. about ten or so minutes (Warneck et al., 1998). On this basis, how do you justify the choice to work on timescale about several hundred hours to use the dissolution kinetics in the atmospheric modeling?

Response:
First, the reviewer misunderstood that Fe dissolution only occurs in the cloud phase but not in the aerosol phase. As detailed in the paper, we explained that low pHs are more likely to occur in the aerosol phase, not in the clouds. This whole paper is to discuss how Fe will dissolve in the aerosol water at low pHs with an aim to provide a better understanding for parameterization of the Fe acid mobilization in dust (Meskhdize et al., 2005; Luo et al., 2005; Fan et al., 2006; Solmon et al., 2009; Ito and Feng, 2010).

Second, as shown in the papers listed in this reviewers comments (Desboeufs et al., 1999; Deguillaume et al., 1999; Machie et al., 2005), Fe dissolution in the dust at high pH (>3.8) is extremely slow and reaches plateau in less than an hour to hours. Only a very small fraction of Fe could be dissolved at high pHs (e.g., <0.1%) in the dust under those conditions. Atmospheric models (e.g., Meskhdize et al., 2005; Luo et al., 2005; Fan et al., 2006; Solmon et al., 2009; Ito and Feng, 2010) are not designed to address this process because it has little effect in enhancing Fe solubility during dust transport.

Third, the purpose of this work is to understand the underlying factors to control Fe dissolution kinetics in dust aerosol water at low pHs. To this purpose, we have to have the dissolution kinetics at much longer timescale (ideally to reach plateau) to properly simulate the dissolution curves and then to understand the Fe dissolution processes in the dust. Therefore, the timescale we have chosen is fully justified.

Comment 6:
P26214, L11: The dissolution experiments are carried out in batch reactor which do not enable to control the saturation limit, is it possible that the solubility product FeIII with respect to crystalline oxo hydroxy salts (e.g. ferrihydrirte) is reached at 1000 mg.L-1? (Figure 7 for 60 mg/L)

Response:
The log of the solubility product at 1000 mg L-1 is about 3 even when all the Fe is dissolved. At 20 h, only 40 umol L-1 of Fe is dissolved in the solution (it is log value is 4.4). Assuming 40% of Fe can be dissolved at 1000 mg L-1, log value of dissolved is about 3.5. Both these values are much lower than the solubility product of ferrihydrite and nano-goethite at pH <2.

Comment 7:
Paragraph "3.2 Fe dissolution kinetics": The results presented in this section are used to develop the parameterization of dissolution kinetics (part 3.3). I think that it is important to replace these results in a general context by comparing these data with others works on this subject. For example, the dissolution kinetics observed in this study (fast then slow dissolution kinetics) have been already determined by Desboeufs et al., 1999 et 2005; Mackie et al., 2005 or Deguillaume et al., 2010. In order to emphasize the interest of your work on kinetic models, it needs to show that your results are not an exception. In the same way, the section dealing with the effect of the ratio dust/liquid on iron dissolution has been already showed by Bonnet et Guieu, 2004.

Response:
We have added new text where this can clarify and add to our existing argument. We also note below that some of the references which the reviewer asks us to consider are not directly relevant to this manuscript.

Thus we have now added two sentences after P26615, line 27:
"*The results reported here are based on long-term Fe dissolution experiments in dusts at low pHs. These are consistent with previous Fe dissolution experiments at similar pH conditions on dust and/or soils at shorter time scale (12 h to 120 h) which showed that Fe dissolution rates in dust or soils are strongly ph dependent and that Fe dissolves faster initially (Spokes et al., 1994; Spokes and Jickells, 1996; Mackie et al., 2005; Cwiertny et al., 2008; Fu et al., 2010).*"

We also added two sentences after line 8 (page 26616): "*These results agree with the findings by Spokes and Jickells (1996). Our data are also consistent with Mackie et al. (2005) in general although a more direct comparison is difficult because of the low sampling frequencies by the latter authors.*"

At the end of the paragraph 1 of section 3.6, we also directly compared our data with the most relevant previously published data and added a paragraph:

"*Mackie et al. (2005) derived a zero-order dissolution equation of Fe solubility with time based on dissolution of Australian dust at similar dust/liquid ratio (55 mg* L^{-1}*) and pH (2.15) to that used in this study (60 mg L-1 and pH =2). Using their calculated relationship, the predicted Fe concentration was considerably higher for the initial 10 min of dissolution but up to two times lower at 10 min to 200 h than those of the Tibesti-*PM_{20} *and Beijing dust samples measured in this study. Therefore, their equation is not applicable to Saharan and Asian dust (see also Spokes et al., 1994; Cwiertny et al., 2008; Fu et al., 2010). As mentioned below, this difference may reflect the difference in weathering and Fe mineralogy of Australian versus Asian and Saharan dusts (Mackie et al., 2008; Shi et al., 2010).* …"

The rates reported by Deguillaume et al. (2010) were derived from dissolution from an urban particulate matter sample at pH 4.7. This cannot be directly compared to our data which are derived from Fe dissolution at lower pHs in dusts.

We did not find any dissolution rates in Desboeufs et al. (2005) paper and therefore it is not immediately relevant. Bonnet and Guieu (2004) reported the effect of dust/liquid ratio on iron dissolution in seawater. The pH conditions and the mechanisms are very different from the situation being studied here. .

Comment 8:
P26622, L2: It is maybe necessary to cite the recent papers which show the relative invariance of the size distribution with time after 1–2 days of transport (e.g. Reid et al., 2008).

Response:
We understand that this paper could be useful for a paper discussing Fe solubility change during dust transport. But for the purpose of our discussion in this manuscript , it is not immediately relevant.

Comment 9:
P26623, L8: I wonder myself if the question of the mineralogical source of the "intermediate" pool is not an artifact associated to your choice of using 3 Fe-pools? The kinetic constant k of this intermediate pool seems to be an average of the two other pools. Deguillaume et al. 2010, who consider a first-order kinetic for Fe dissolution from urban particles to estimate dissolved Fe in atmospheric models, use only two pools of Fe (labile and refractory but on a period of 2h). Their "intermediate" kinetic is the sum of the kinetics of labile and refractory pool. Considering the results of Shi (2009 & 2010) on the increase of dissolution in presence of nano-sized Fe

oxides, I think that these nanoparticles are very reactive and constitute probably the "fast" pool with ferrihydrite.

Response:
The reviewer is missing the point. We did not arbitrarily choose a 3 pool model. This was the simplest way to describe the data we have over the entire relevant range. It was not possible as we showed to create a 2 pool model which worked.
We agree that the "fast" Fe pool is probably highly reactive ferrihydrite (p26622).

We could not comment on Deguillaume et al. (2010) because the original dissolution data are not presented and we could not see how good are the fitting. We also noticed the fundamental differences in the experimental conditions in Deguillaume et al. (2010) and ours (pH, source of material, dust/liquid ratio).

P26212, L11: Table 1
Response: We have now changed this text.

P26216, L6: suggesting
Response: We have now changed this text.

P26220, L24; P26224, L8 and P26225, L5 & L9: Mackie et al., 2005
Response: We have now changed it.

Figure 7: at replaces @
Response: We have now changed it.