

Interactive comment on “Iron dissolution kinetics of mineral dust at low pH during simulated atmospheric processing” by Z. Shi et al.

Anonymous Referee #3

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This manuscript investigates the dissolution kinetics of Fe from dust samples in acidic conditions on time period of 1000h. Major findings are: (1) the initial rate of dissolution is fast and become slower with time, (2) the Fe dissolution kinetics is pH-dependant, (3) the Fe dissolution kinetic is liquid/dust ratio dependant (4) the dissolution kinetics could be parameterised as 3 successive first-order kinetics related to 3 Fe-pools: ferrihydrite or poorly crystalline oxides, (hydr)oxide/clay. This paper concludes that dust/liquid ratio and pH are fundamental parameters controlling Fe dissolution kinetics in the dust.

The manuscript is generally well-written, logically organized, and adequately illustrated. Abstract is succinct and accurate.

The results are interesting for the estimation of soluble iron supply to the world's oceans and consequently for studying nutrient dynamics and carbon biogeochemical cycling.

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However, the findings (1), (2), (3) and hence the conclusion are not new and the discussion of the corresponding literature is not detailed enough, weakening the point (4) which is the key point of this paper. Some experimental points need also to be specified to clarify the conclusions of this work.

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.

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.

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.

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

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your protocol.

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?

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. ferrihydrite) is reached at 1000 mg.L⁻¹? (Figure 7 for 60 mg/L)

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.

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).

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

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(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.

Minors corrections:

P26212, L11: Table 1

P26216, L6: suggesting

P26220, L24; P26224, L8 and P26225, L5 & L9: Mackie et al., 2005

Figure 7: at replaces @

References:

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- Desboeufs, K. V. and G. Cautenet (2005). "Transport and mixing zone of desert dust and sulphate over Tropical Africa and the Atlantic Ocean region." *Atmos. Chem. Phys. Dis.* 5: 5615-5644.
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