

Interactive comment on “Chemistry and mineralogy of clay minerals in Asian and Saharan dusts and the implications for iron availability” by G. Y. Jeong and E. P. Achterberg

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Reply to the comments by anonymous referee #2

We appreciate the referee's comments.

General comments

Comment: Authors are very careless in their definition of dissolved Fe. Iron biogeochemical cycle presents unusual difficulties, as fluxes cannot be described solely in terms of the fractional iron solubility (%Fes). As a matter of fact, from oceanic point of view, and I think this is where the authors are going with this article, %FeS of mineral

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dust is an irrelevant parameter. Iron can be transported as colloids (defined as < 1 μm in diameter), nanoparticles (defined as <0.1 μm in diameter) and aqueous species (operationally defined as passing through 0.02 μm filter) (Raiswell and Canfield, 2012). So each investigator using different measurement methodologies will report different values. While the data reported in the current paper is consistent with the measurements of Buck and collaborators, it may not be consistent with others (e.g., Baker et al., Cwiertny et al., and many others).

Reply: Our manuscript deals with the mineralogy of atmospheric dust, and in particular focuses on the importance of clay minerals for transfer of Fe to the surface ocean. We infer a link between clay minerals and Fe supply and its dissolution through the strong observed relationship reported in literature between Fe and Al or Si release in leaching experiments. We are surprised about the strong focus by referee #2 on dissolved Fe and how it can be transported in different physical forms. This is not of direct relevance to our manuscript, which deals with the importance of clay minerals in dust for Fe transfer. We are also surprised by the focus by referee #2 on the measurement methodologies employed by others. In fact, numerous investigators measured the "soluble" iron fraction of dust (Sholkovitz et al., 2012), but almost none of them measured "soluble" Al and Si in leached solutions. Since Fe is hosted in clay minerals (which are aluminosilicates) as well as Fe-(hydr)oxides, Fe release from clay minerals can be estimated from the concentrations of Al and Si. Although we have done extensive search for published leaching data of mineral dust, only Buck et al. (2006, 2010) presented reasonable data including dissolved Al as well as Fe concentration in leached solutions (even they did not measure Si in 2006 paper). They also presented Al, Si, and Fe contents of their dust samples. The referee cites "Baker et al., Cwiertny et al., and many others". "Baker et al." may be Baker and Jickells (2006). From their supplementary Tables, average Fe/Al molar ratio in the leached solution was 0.12 (fine aerosol) and 0.9 (coarse aerosol) when aerosols was reacted with 1.1 M ammonium acetate (pH 4.7). These values are significantly lower than the 0.26 and 0.25 obtained for their fine and coarse aerosols, respectively and could not be explained given that Al was almost exclusively

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released from minerals in dust. In addition, iron (hydr)oxides release only Fe. Thus we have not included the data of Baker and Jickells (2006) in our Table 3. "Cwiertny et al." may be either Cwierthy, Baltrusaitis, . . . et al. (2008) or Cwierthy, Young, and Grassian (2008). Since Cwierthy, Young, and Grassian (2008) is a review paper, we assume that "Cwiertny et al." is Cwierthy, Baltrusaitis, . . . et al. (2008). Cwiertny et al. (2008) performed leaching experiments of dust but only measured Fe concentration of the leached solution without providing Al and Si concentration data. The referee recommends to see "many others". However, we could not find other leaching data including Al and Si concentrations in addition to Fe concentration. We did our best to collect existing data, but unfortunately the only reliable data were those presented by Buck and collaborators. The referee stated that "So each investigator using different measurement methodologies will report different values". The relevant reports on dust leaching including Al and Si concentrations are too limited, so we hardly understand the meaning of the statement.

Comment: (A) Improved knowledge of mineralogical and elemental composition of clay minerals in dust particles is important. (B) However, previous work has shown that the range in Fe solubility measurements (0.001 to 80%) is considerably higher than the uncertainty in total Fe content. (C) Since authors did not measure dissolved iron directly, no attempt should be made to infer %Fes by comparing Fe/Si, Al/Si, and Fe/Al to limited number of measurements. Such comparison can lead to erroneous conclusions. (D) Moreover, analysis methodology for the data selected for the comparison is inconsistent.

Reply (A): Chemist and modelers assume simple mineralogy and chemical composition of dust particles, often overlooking complex nature of the natural dust particles. There is no paper presenting Fe and other elemental composition of each clay mineral directly measured in natural dust. When modeling climatic effects by iron-bearing minerals, iron contents and type of clay minerals are assumed based on literature (commonly illite, e.g. Johnson and Meskhidze, 2013). Of course, analysis of individual clay

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minerals mixed in dust particles is extremely difficult. However, we have overcome this difficulty, and done successful analysis of representative clay minerals (not only illite but also illite-smectite mixed phases and chlorite) as well as the average Fe content of clay minerals. We think that this is a major accomplishment of our study.

Reply (B): The wide range in Fe solubility measurements (0.001 to 80%) is ascribed to the wide range of dust sample types subjected to analysis. Anthropogenic dusts with low total Fe content have higher Fe solubility, while natural dusts with high total Fe content have lower Fe solubility. In this manuscript, we have dealt with natural dust. We have analysed Asian dust transported to North Pacific Ocean, and Saharan dust transported to Atlantic Ocean. Our samples were collected on the transport pass of Asian and Saharan dust: Korea and Cape Verde, respectively.

Reply (C): We think that leaching experiments for our dust samples are not essential in our in-depth mineralogical and microchemical work. Our main achievements are the detailed properties of clay minerals in individual dust particles: clay mineral types, microscopic occurrence, and Fe and other elemental compositions with clay contents of the dusts. As a spontaneous extension of our research, we compared analytical data of clay minerals to published data to get some implications to the role of clay minerals in Fe supply. Of course, we agree with the referee in that strong conclusion on the role of clay minerals is somewhat risky because published leaching data including dissolved Al and Si concentrations are few. We will revise the strong relevant conclusion to moderate one. This issue will be further refined by additional leaching experiments.

Reply (D): Since the leaching data are those by Buck et al., "inconsistent analysis methodology" in the referee comment may refer the elemental compositions of several bulk dusts selected from literature. We do not understand why we have to consider published data obtained by the same method. Everybody uses his/her analytical method to determine elemental compositions of bulk dust: ICP-MS, WD/ED-XRF, Synchrotron XRF, SEM-EDS, PIXE, Time-Of-Flight mass spectrometry, etc. However, they reach the similar results if they use reliable standards, calibration, and instrumentation. We

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think that the data published in high-standard journals are consistent despite inconsistent methodology. The different elemental ratios in the data shown in Table 3 are mostly related to the sample particle sizes (fine PM_{2.5}, medium PM₁₀, and coarse TSP). We have discussed this matter in the text. Fe/Al ratio is higher in the clay-rich fine dust samples. The difference in the elemental ratios is not caused by the different analytical methodology, but almost by the size characteristics of the dust sample.

Comment: (A) 1. Buck et al., 2006 used DI water leaching into pH 3.3 solution. 2. Elemental analysis of Arimoto et al. (2004) are based on ICP-MS and contain no information on dissolved Fe. (B) 3. As far as I can tell, data for Al and Si are not reported in Buck et al. (2010).

Reply (A): In Table 3, we compared elemental composition determined by TEM-EDS analysis to previous reports on the bulk chemical composition by ICP-MS. Chemical analysis of individual clay minerals in mixture in dust particles should be done only by microbeam methods using TEM-EDS. Because there are no similar reports, we have compared with the elemental composition of bulk dust. Since elemental composition cannot be compared directly, elemental ratios should be compared. We reached the conclusion that our TEM-EDS analysis is valid. Although there are some reports on chemical composition of bulk dust, we have only few cases of leaching data including Al concentration.

Reply (B): Dissolved Al and Si concentration data of leached solution of Saharan dust in the Atlantic Ocean are reported in Table 1 of Buck et al. (2010, *Marine Chemistry*, v. 120, 57–70).

Comment: Overall, I would like to emphasize that because Fe/Al/Si ratios reported by few authors for “water soluble” fraction agree or disagree with the ones measured in this study tell nothing about the sources of the iron and should not be used as a justification that “the dissolved Fe and Al originated from the clay minerals, which suggests that the major source of leached Fe is not Fe (hydr)oxides, but clay minerals.”

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Reply: Leaching data including Al and Si are rare. Nevertheless, elemental ratios of clay minerals determined in our study agree with existing leaching data (Buck et al. and collaborators). We do not understand whose data disagree with our data.

Comment: Unfortunately, I find little of any scientific value in the manuscripts findings related to dissolved iron content of mineral dust. That said though, I think results of the current study could be of interest to geologists. However, if decided to resubmit to more appropriate journal, I think the paper will benefit from comparison to number of studies currently available (e.g., Cwertny et al., 2008).

Reply: The novelty of our manuscript is the first direct mineralogical and chemical analysis of clay minerals which are most abundant and important in representative natural dusts (Asian and Saharan dusts). We cannot find modelers using realistic clay mineralogy and their Fe contents in natural dust. The analysis of individual clay minerals in mixture in dust particles is extremely difficult. However, we have done this, presenting Fe contents of several clay mineral types. Comparing our data to existing leaching data is a subsidiary extension of our research, and the agreement with existing leaching data supports the contribution of clay minerals to available Fe source. If we have not done this, some referees question the role of clay minerals in Fe supply: Why didn't you compare with leaching data? We accept the referee's comment that our conclusion about the contribution of clay minerals in Fe supply was too strong because the published leaching data including Al and Si are few. We will moderate the related conclusions. We think the journal “*Atmospheric Chemistry and Physics*” is the appropriate for our work as it is a forum for advanced mineral dust research and provides a fast exchange of recent information. Our manuscript is the first to report on types, abundance, and Fe and other elemental composition of clay minerals in individual particles of Asian and Saharan dust, and therefore suitable to the scope of the journal.

Specific comments

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Comment: Pg. 15738, ln 4. Please remove the discussion of Fe complexation. I do not see how organic ligands in seawater can affect %Fes during long-range atmospheric transport.

Reply: We will remove the discussion on Fe complexation.

Comment: Pg. 15738 Please include the reference to Johnson and Meskhidze (2013) who looked at the contribution of clay minerals to the total dissolved iron in mineral dust.

Reply: This is a recent and best paper on the modeling of the contribution of mineral dust, and also an example of modeling study having a simplified view to clay minerals. We will cite Johnson and Meskhidze (2013) in revised version. They assumed clay minerals as illite. However, clay minerals in dust particles are more diverse: illite-smectite mixed phases, smectite, chlorite, and kaolinite with diverse Fe contents. Although they calculated the release rate of Fe from illite, a Fe content of illite in their study is uncertain. Throughout reading the paper, we found that they adopted the Fe content of one commercial illite (3.38% Fe, AP135, Fithian, Illinois) presented in Paris et al. (2011). The commercial illite collected from the rock in one locality does not represent clay minerals in natural mineral dust derived from diverse bedrocks and soils. The Fe content (3.38%) of the Fithian illite is consistent with 2.8% of our illite (group B in Fig. 6). However, as shown in Table 1 and Figure 1–5, the Fe content (group A, 5.8%) of more reactive and abundant nanocrystalline illite-smectite series clay minerals are much higher than illite. In addition, we should consider chlorite (14.8% Fe) which is generally not included in modeling. It is evident that realistic clay mineral makeup and their iron content obtained from natural dust is essential, highlighting our study.

Comment: Pg. 15770, Fig. 6. Plotting Fe against K could be misleading. As pointed out by Arimoto et al. (2004) considerable amount of K, even during large dust storms, may be attributed to anthropogenic activities. I believe plotting Fe concentration vs. particle diameter (see Cwertny et al., 2008) is more appropriate.

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Reply: This is likely a misunderstanding of our analytical procedure. We dissected individual dust particles, and used electron beam probe that can be reduced down to 50 nm to analyze the inner part of the target clay grains. There is little chance of contamination by other anthropogenic grains which is identifiable in the TEM observation. K is essential element for chemically discriminating clay minerals types (illite, illite-smectite mixed layers, smectite, chlorite, and kaolinite). However, plotting Fe concentration vs. particle diameter does not provide mineralogical information.

Sincerely

On behalf of authors

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