MS No.: acp-2014-449
Title: Chemistry and mineralogy of clay minerals in Asian and Saharan dusts and the implications for iron supply to the oceans

Authors: G. Y. Jeong, E. P. Achterberg
MS Type: Research Article

We appreciate valuable comments by two anonymous referees. We replied to all the comments and revised carefully the manuscript considering the comments by the referees. We deleted section 5 in the original manuscript, added a short section, and slightly changed the title.

Reply to the comments by anonymous referee #1

Referee #2 pointed out that we have not carried out Fe dissolution experiment for our dust samples, and raised a serious question on the discussion (section 5) about the Fe availability. Thus, we have deleted the section 5 "Data supporting a strong contribution of clay minerals to dissolution of Fe" and Table 3. We added a short section about the usefulness of our data on clay minerals and analytical procedure on the evaluation of Fe supply.

Comment 1: Page 15740, line 18. I think the year of the last dust sample in this should be 2014

Reply 1: "2013" was replaced by "2014".

Comment 2: P 15741, lines 8 & 26. The length units here should not be squared (i.e. "3mm x 4mm" and "6um x 6um").

Reply 2: Thanks. We have not found the errors created probably during the copy editing. The length units in line 8 and 26 were corrected to "3 mm × 4 mm" and "6 μm × 6 μm", respectively.

Comment 3: P 15753, lines 21-22. Please check that all the cited manuscripts are present in the reference list. Two at least (Alastuey et al., 2005 and Klaver et al., 2011) appear not to be.

Reply 3: Thanks. However, they are not needed anymore as a part of deleted section 5. We checked again all the references.

Comment 4: P 15753, lines 28-. This appears to be a mis-citation. I can find no such information in Baker & Jickells 2006.

Reply 4: Although this was not discussed in the text of Baker and Jickells (2006), such information can be found in the Supplementary Tables provided by them. Average Fe/Al molar ratio of 0.12 in a leaching test and the 0.26 for the corresponding fine aerosol were derived from the Supplementary Tables ts02 and ts03, respectively. Anyway, we deleted the section 5 including the sentence.

Reply to the comments by anonymous referee #2

We think that the major achievement in our study is the determination of clay mineral composition and chemistry in Asian and Saharan dust. Although clay minerals are major components in natural dust, detailed mineralogy and Fe chemistry of individual clay minerals have not yet been reported. The referee raised questions about the discussion on the role of clay minerals in the Fe availability. Since we have not performed the dissolution experiment of our dust samples, we accept the referee's major comment, and deleted the section 5 "Data supporting a strong contribution of clay minerals to dissolution of Fe" and Table 3. We added a short section about the usefulness of our data on clay minerals and analytical procedure on the Fe supply.

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 dust is an irrelevant parameter. Iron can be transported as colloids (defined as < 1 um in diameter), nanoparticles (defined as <0.1 um in diameter) and aqueous species (operationally defined as passing through 0.02 um 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: We deleted the section 5 "Data supporting a strong contribution of clay minerals to dissolution of Fe" and Table 3. We also present our replies to the referee comments in bracket.
[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. 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.
Referee #2 focused 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 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. Thus, 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.]

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: Since we have not measured dissolved Fe from our dust samples, we agree with referee. We deleted the section 5 "Data supporting a strong contribution of clay minerals to dissolution of Fe" and Table 3.

[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 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.

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. 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 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 PM_{10}, 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: We deleted the section 5 "Data supporting a strong contribution of clay minerals to dissolution of Fe" and Table 3.

[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 noting 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."

Reply: We deleted the section 5 "Data supporting a strong contribution of clay minerals to dissolution of Fe" and Table 3.

[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).]

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: We deleted the section 5 "Data supporting a strong contribution of clay minerals to dissolution of Fe" and Table 3. We think the journal "Atmospheric Chemistry and Physics" is 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.

[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. 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.]

Specific comments

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 removed the sentence 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 cited and discussed 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.

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 are 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.

<Changes in the revised manuscript>

We have revised following the comments by referees.

- We deleted Section 5 in original manuscript "Data supporting a strong contribution of clay minerals to dissolution of Fe" and Table 3.
- We added new Section 5 "Implications to the evaluation of iron supply to oceans".
- Title was slightly modified to "Chemistry and mineralogy of clay minerals in Asian and Saharan dusts and the implications for iron supply to the oceans".
- Changes in the manuscript are highlighted with yellow color below.

Chemistry and mineralogy of clay minerals in Asian and Saharan dusts and the implications for iron ==supply to the oceans==

Abstract: Mineral dust supplied to remote ocean regions stimulates phytoplankton growth through delivery of micronutrients, notably iron (Fe). Although attention is usually paid to Fe (hydr)oxides as major sources of available Fe, Fe-bearing clay minerals are typically the dominant phase in mineral dust. The mineralogy and chemistry of clay minerals in dust particles, however, are largely unknown. We conducted microscopic identification and chemical analysis of the clay minerals in Asian and Saharan dust particles. Cross-sectional slices of dust particles were prepared by focused ion beam (FIB) techniques and analyzed by transmission electron microscopy (TEM) combined with energy dispersive X-ray spectroscopy (EDXS). TEM images of FIB slices revealed that clay minerals occurred as either nano-thin platelets or relatively thick plates. The nano-thin platelets included illite, smectite, illite–smectite mixed layers and their nanoscale mixtures (illite–smectite series clay minerals, ISCMs) which could not be resolved with an electron microbeam. EDXS chemical analysis of the clay mineral grains revealed that the average Fe content was 5.8% in nano-thin ISCM platelets assuming 14% H_2O, while the Fe content of illite and chlorite was 2.8% and 14.8%, respectively. In addition, TEM and EDXS analyses were performed on clay mineral grains dispersed and loaded on microgrids. The average Fe content of clay mineral grains was 6.7% and 5.4% in Asian and Saharan dusts, respectively. A comparative X-ray diffraction analysis of bulk dusts showed that Saharan dust was more enriched in clay minerals than in Asian dust, while Asian dust was more enriched in chlorite. ~~The average Fe/Si, Al/Si and Fe/Al molar ratios of the clay minerals, compared to previously reported chemistries of mineral dusts and leached solutions, indicated that dissolved Fe originated from clay minerals.~~ Clay minerals, in particular nanocrystalline ISCMs and Fe-rich chlorite are ==probably== important sources of Fe to remote marine ecosystems. Further detailed analyses of the mineralogy and chemistry of clay minerals in global ==mineral dusts== are required to evaluate the inputs of Fe to surface ocean microbial communities.

1. Introduction

Iron dissolution from aerosols has been represented by fractional Fe solubility (%Fe_S), and varies strongly depending on the aerosol source (Mahowald et al., 2005; Sholkovitz et al., 2012). Sholkovitz et al. (2012) compiled total Fe loading (Fe_T) and %Fe_S for a global-scale set of aerosol

samples, and found a hyperbolic trend in the %Fe$_S$ as a function of Fe$_T$, which was explained by the mixing of mineral dusts of high Fe$_T$ and low %Fe$_S$ and anthropogenic aerosols of low Fe$_T$ and high %Fe$_S$. However, mineral dust is an important supply of soluble Fe to the remote ocean, particularly during dust events originating from desert sources. Ito and Feng (2010) demonstrated using model simulations that, compared to Asian dust, soluble Fe from combustion sources contributed a relatively small amount to the soluble Fe supply to the North Pacific Ocean during spring periods. An enhancement of dust %Fe$_S$ occurs during long-range transport. The factors responsible for this increase in %Fe$_S$ are not yet fully understood, and include the type of Fe-bearing minerals of dust and their reactivity (Cwiertny et al., 2008; Journet et al., 2008), ~~Fe complexation by organic ligands in seawater (Kraemer et al., 2005),~~ the photoreduction of Fe in dust particles (Siefert et al., 1994; Hand et al., 2004; Fu et al., 2010), reactions between dust particles and water during cloud processing (Desboeufs et al., 2001; Shi et al., 2009), reactions with acidic gases in the atmosphere (Zhuang et al., 1992; Meskhidze et al., 2003), and changes in particle size during long-range transport (Jickells et al., 2005; Baker and Croot, 2010).

Information regarding dust mineralogy enables the %Fe$_S$ of mineral dust to be better understood, as highlighted by Cwiertny et al. (2008) after an extensive literature review. The mineralogical factors related to %Fe$_S$ include solubility, reactivity with atmospheric acids, grain size, Fe content, and the Fe oxidation state of the minerals. Despite numerous articles on the measurements of %Fe$_S$ (Sholkovitz et al., 2012 and references therein), the modeling of dust input (Mahowald et al., 2005, 2009; Johnson and Meskhidze, 2013), and the determinations of the aqueous geochemistry of Fe (Baker and Croot, 2010 and references therein), basic data are still lacking on the properties of Fe-bearing minerals in dust. Iron oxides/hydroxides are an important source of available Fe. However, the quantities of Fe (hydr)oxides in mineral dust are much lower than the quantity of Fe-bearing silicates. Mineralogical analyses have shown that clay minerals are the most abundant phases followed by quartz, feldspars, and calcite in the long-range transported dusts (Glaccum and Prospero, 1980; Avila et al., 1997; Jeong 2008; Jeong et al., 2014). The crystal structures of clay minerals can accommodate a significant quantity of Fe in their octahedral sites. Thus, both the clay minerals and Fe (hydr)oxides should be considered when investigating their roles in Fe availability (Raiswell and Canfield, 2012). Journet et al. (2008) reported a higher Fe solubility of clay minerals compared with Fe oxides, emphasizing the significant role of clay minerals in Fe availability. However, in the experiments performed by Journet et al. (2008), dissolution work was conducted for a limited set of clay minerals and Fe (hydr)oxides obtained from rocks. Clay minerals in atmospheric dust particles have diverse origins and a wide range of chemical compositions and particle sizes, depending upon the lithology, geological setting, and physical/chemical weathering process in their source regions. The contribution of clay minerals to

Fe availability should be considered on the basis of the physical and chemical characteristics of the different clay mineral types in the natural dust. For example, the Fe content of clay minerals in dust for modeling and dissolution experiments is typically not known. The separate determination of the Fe content of each clay mineral species is almost impossible for bulk dust because of the agglomeration of many silicate mineral grains (Falkovich et al., 2001; Shi et al., 2005; Jeong, 2008; Jeong et al., 2014). This is in contrast to the exact determination of Fe content in the form of Fe (hydr)oxides using an established selective extraction procedure, such as the method of Mehra and Jackson (1960). However, the chemical composition of submicron grains of clay minerals can be determined by energy dispersive X-ray spectrometry (EDXS) induced by an electron microbeam. EDXS attached to a transmission electron microscope (TEM) is an excellent technique for the chemical and physical characterization of individual clay mineral grains.

In this study, we report the mineral species, nanoscopic occurrence, and chemical compositions of the clay mineral grains in individual Asian and Saharan dust particles obtained by the combined application of TEM and EDXS. Analyses of clay minerals mixed in particles were conducted on cross-sectional slices of individual dust particles prepared by focused ion beam (FIB) milling. Clay mineral grains loaded on microgrids by a conventional procedure were also analyzed by TEM and EDXS. We furthermore present the mineral compositions of bulk dusts obtained by X-ray diffraction (XRD) analysis. The chemical compositions of the clay minerals were compared to the reported chemistry of the bulk dust and their leached solutions to assess the contribution of clay minerals to Fe availability.

2. Dust samples and methods

The Asian dusts were sampled using a Thermo Scientific high-volume total suspended particulate (TSP) sampler fitted with Pallflex teflon-coated borosilicate glass-fiber filters (8×10 in.) or Whatman® No. 1441-866 cellulose filters. The 2012 dust was sampled on a mountain peak at Deokjeok Island (190 m above sea level, 37°13′59″N, 126°08′57″E) off the western coast of Korea for 24 h (09:00 31 March–08:00 01 April) at a flow rate of 250 L min^{-1}. The 2009, 2010, and 2014 Asian dusts were sampled using the same procedure on the roof of a four-storey building at Andong National University (36°32′34″N, 128°47′56″E) over a 12–h period (09:00–21:00 17 March 2009, 20:00~08:00 19 March 2010, and 10:00–22:00 18 March 2014).

X-ray diffraction (XRD) analysis was conducted to obtain information on the mineral composition of bulk samples using a Rigaku Ultima IV diffractometer. A portion of the filter was cut and immersed in methanol in a 10–mL glass vial. The filter was agitated in an ultrasonic bath to

remove dust particles from the filter. During the agitation, dust particles were disaggregated into clay minerals and other silicate grains. The suspension was sieved through 270 mesh sieve to remove cellulose fibers and dried on the glass plate. Then, dust was collected by razor blade. Several milligrams of dust samples (2–10 mg) were loaded on the 3 mm × 4 mm cavity of an aluminum plate. The analytical conditions were 60 s counting per 0.03º step in the scan range of 3–65° 2θ, Cu Kα radiation, and 45 kV/35 mA. Because the quantity of the samples was small, the patterns obtained were not suitable for precise quantification. Thus, the compositional analysis was deemed semi-quantitative. Mineral compositions were derived using a SIROQUANT software package (version 4). Since intensity loss was significant in the lower angle region due to the small sample size irradiated with X-rays, the high angle region (24.5–65° 2θ) was used for the simulation of the observed XRD pattern. After the XRD analysis of the bulk dusts, the samples were subjected to ethylene glycol and heat treatments for detailed identification of clay minerals. The samples were wetted with water, smeared, and dried on a glass slide, and subsequently treated with ethylene glycol vapor at 60°C in a desiccator for 2 days followed by heating at 350°C for 30 min.

Electron-transparent thin slices of dust particles (2009, 2012, and 2014 Asian dusts; 28–31 Dec, 2007, 18–23 Jan, 23–26 Feb, 29 Feb–04 Mar, 12–14 Mar, 2008 Saharan dusts) were prepared for TEM analysis of clay minerals. Hereafter, the term "particle" refers to individual solid objects suspended in the atmosphere, while the term "grain" refers to the constituents of the particles. Thin slices (ca. 100 nm in thickness) of about ca. 6 μm × 6 μm size were cut from dust particles using a SII NanoTechnology SMI3050TB and a JEOL JIB4601F FIB instrument for Asian and Saharan dusts. Prior to using the FIB, the dust particles were transferred onto adhesive carbon film and characterized using a JEOL JSM 6700F field emission gun scanning electron microscope (SEM) equipped with an Oxford EDXS system at 5 kV acceleration voltage and 8 mm working distance after being coated with platinum for electrical conductivity. Dust particles were selected for FIB work on the basis of mineralogical characteristics identified by SEM-EDXS analysis as reported in Jeong (2008) and Jeong et al. (2014). Individual Asian dust particles could be selected and prepared as thin slices by FIB milling because the particles were sufficiently separated from each other on the filters. However, the Saharan dusts considered in this study were highly concentrated and aggregated on the filters. Thus, the original atmospheric particles for FIB milling could not be identified with confidence. However, the purpose of the TEM analysis undertaken in this study was not to reveal the structures of individual original dust particles as reported by Jeong and Nousiainen (2014), but to analyze the chemistry and mineralogy of clay mineral grains. Thus, we prepared thin slices using FIB milling from the Saharan dust samples.

4. ~~Iron dissolution from~~ Clay minerals as iron carrier

5. Implications to the evaluation of iron supply to oceans

Global dust distributions and oceanic Fe deposition are modeled assuming the Fe content of bulk dust being equivalent to the average Fe content of the Earth crust (3.5%) (Mahowald et al., 2005, 2009). A recent modeling study on Fe supply to the oceans progressed to include dust mineralogy and Fe content of clay minerals (Johnson and Meskhidze, 2013). Mineral compositions were predicted from available soil data (Claquin et al., 1999; Nikovic et al., 2012; Journet et al., 2014). However, mineralogical and chemical compositions of world soils are certainly variable and poorly constrained. Particularly, the analytical data on the chemical composition (including Fe) of fine clay minerals in local soils are hard to find in literature, because the analytical measurements are as difficult as the analysis of clay minerals in dust. The modeling study on the Fe supply to global oceans by Johnson and Meskhidze (2013) highlighted the importance of mineralogical data of dust in the deposition of dissolved Fe to the global oceans. They adopted mineral compositions of dust derived from a soil database of Nikovic et al. (2012) and Fe content of a commercial illite reported by Paris et al. (2011). However, their model sensitivity analysis showed large variations of dissolved Fe fluxes to the oceans, associated with the uncertainty in the dust mineralogy and Fe content of constituent minerals. They emphasized that realistic data of dust mineralogy and Fe content within individual Fe-containing minerals are essential for the improvement of the description of the Fe biogeochemical cycles in climate models. Although the chemical analysis of clay minerals in individual dust particles as carried out in this study is challenging, detailed analysis of representative global dust samples is likely an efficient approach to obtain information on Fe mineralogy in dust. Long-range transported dust has the average mineralogical and chemical properties of fine soil particles lifted from the wide source regions of varying soil mineralogy. In addition, the mineral composition and chemistry in dust from the major source regions do not show significant inter-event and annual changes (Jeong, 2008). Further analytical works for dust samples transported over long distances from major source regions will allow the establishment of realistic mineralogical database for the evaluation of Fe inputs to the remote ocean.

~~5. Data supporting a strong contribution of clay minerals to dissolution of Fe~~

~~The dissolution of Fe from clay minerals can be investigated by the simultaneous measurement of Al, Mg, and Si concentrations in solutions subjected to dust addition. Unfortunately, the~~

concentrations of Al, Mg, and Si in solution have rarely been reported in previous studies. Buck et al. (2006) determined both the Fe and Al concentrations in leached solution after the reaction with aerosols collected on cruises in the north-west Pacific Ocean. Although Buck et al. (2006) did not discuss the mineralogical implication of the Fe and Al concentrations, their data provide an insight into the source of the dissolved Fe. The average Fe/Al molar ratio for whole data set ($n = 60$) was 0.53 for aerosol concentrations ranging from very low (264 pmol Fe m^{-3}) to high (48 945 pmol Fe m^{-3}). However, particular attention should be given to aerosol samples obtained during dusty periods to evaluate the Fe solubility of desert dust, because the high Fe/Al molar ratios in aerosols collected during periods of low loadings are influenced by a contribution from anthropogenic aerosols that contain large amounts of soluble Fe (Sholkovitz et al., 2012). Fe/Al molar ratios of 0.25–0.31 in solution after leaching with deionized water were obtained from four samples collected during a dust event (>20 000 pmol m^{-3} Al of filtered air, Table 1; Buck et al., 2006) originating from Mongolia. The average Fe/Al molar ratio of 0.29 is consistent with the average ratio of 0.31 obtained from the TEM-EDXS analysis of clay mineral grains of Asian dust in this study ($n = 514$, microgrid samples; Table 3). This indicated that all 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.

The dissolution of Fe from clay minerals in Asian dust is further supported by the chemical composition of fine particles in the Asian dust. The Fe/Si, Al/Si, and Fe/Al molar ratios of PM$_{2.5}$ (<2.5 µm) samples collected in Zhenbeitai near the Chinese desert (Arimoto et al., 2004) were 0.14, 0.51, and 0.28, respectively (Table 3), which strongly agrees with the average molar ratios 0.16, 0.52, and 0.31 of the clay minerals obtained using TEM-EDXS analysis in this study. The fine particles of the Asian dust (<2.5 µm) from Zhenbeitai were likely to be dominated by clay minerals relatively that were enriched in Fe and Al in comparison to coarse particles. TSP and PM$_{10}$ samples included coarse dust particles. The Fe, Al, and Si concentrations in TSP samples used in dissolution experiments were also determined by Buck et al. (2006). The average Fe/Si, Al/Si, and Fe/Al molar ratios were 0.10, 0.37 and 0.28, respectively for four aerosols generated by dust events (>20 000 pmol m^{-3} Al of filtered air in the Table 1; Buck et al., 2006). The lower Fe/Si and Al/Si ratios of TSP samples analysed by Buck et al. (2006) were due to the high quartz content of coarse TSP samples (Table 3). Nevertheless, the Al/Fe ratio was similar to that in the fine Zhenbeitai dust and that resulting from our TEM-EDXS analysis, indicating the incorporation of Fe and Al into the structure of clay minerals. The Fe/Si and Al/Si molar ratios of the TSP samples reported by Buck et al. (2006) are consistent with the respective molar ratios of PM$_{10}$ (0.10, 0.36, and 0.27) samples from Asian dusts (Jeong, 2008) and Zhenbeitai TSP dust (0.06, 0.25, and 0.25) (Zhang et al., 2003) (Table 3). This elemental data for the aerosols indicate that Fe and Al are largely incorporated in clay minerals.

In Saharan dusts collected from the Atlantic Ocean, Buck et al. (2010) reported high Fe and Al concentrations in aerosols collected in the region between 13.4° and 24.4°N. The source of the aerosols was traced to the Saharan desert. The average Fe/Al molar ratio was 0.30 in aerosols and 0.29 in deionized water reacted with the aerosols from four samples with a high concentration of dust (>20,000 pmol m^{-3} Al). These ratios are consistent with those reported in other studies (Alastuey et al., 2005; Paris et al., 2010; Klaver et al., 2011) (Table 3). The average Fe/Al molar ratio of clay minerals determined by TEM-EDXS analysis in this study was 0.22, which was lower than that in aerosols. This is partly due to the high concentration of kaolinite with a low Fe content in our aerosol samples. Unlike our observations for Asian dusts, Fe/Si and Al/Si molar ratios did not differ between coarse and fine dust samples (Alastuey et al., 2005) (Table 3), which is consistent with the clay-rich characteristics of Saharan dusts.

The evaluation of existing elemental data and comparisons to the corresponding dissolution data suggests that dissolved Fe and Al are largely derived from the clay minerals in the aerosols. Although anthropogenic Fe contributes to the Fe leached from aerosols, it is the Fe associated with clay minerals in mineral dusts that dominates the leached Fe present in remote ocean environments, particularly during dusty seasons.

6. Summary and Conclusions

Mineral composition of bulk dust samples, Fe content of constituent minerals, and their grain sizes form essential data for the evaluation of Fe supply to remote surface oceans. Particularly, the properties of clay minerals are important because of their abundance in mineral dust and high Fe contents, relative to other silicates. We presented for the first time mineralogical and chemical data of clay minerals in individual dust particles from several Asian and Saharan dust samples, following analyses by TEM and EDXS. The total clay content of Asian dusts determined by XRD analysis was lower than that of Saharan dusts. TEM analysis of thin cross-sectional slices of the dust particles revealed that nano-thin platelets of ISCMs (illite, smectite, and illite–smectite mixed layers) were most abundant in association with illite, chlorite, and kaolinite occurring as thicker plates. Asian dusts were enriched with chlorite relative to Saharan dust, while Saharan dusts were relatively enriched with kaolinite. Kaolinite in Saharan dust occurred as hexagonal plates that were better crystallized than in Asian dust. The average Fe content of the ISCMs in Asian dusts as determined by EDXS was 5.8% assuming 14% H_2O, while the contents of illite and chlorite were 2.8% and 14.8%, respectively. The average Fe content of the EDXS data of the clay mineral grains dispersed and loaded on the microgrids was 6.7% and 5.4% in Asian and Saharan dusts,

respectively. ~~Molar elemental ratios of the long-range transported mineral dusts and leached solution indicated that dissolved Fe mostly originated from clay minerals. Iron-bearing clay minerals are a major source of Fe in remote marine environments compared to Fe (hydr)oxides.~~ The Fe dissolution from clay minerals is thought to be enhanced by the nanocrystallinity of ISCMs, and furthermore, Fe-rich chlorite susceptible to acids may enhance dissolution of Fe. The establishment of realistic mineralogical data sets from global dust samples is important to reduce the uncertainty in the prediction of iron inputs to oceans using geochemical and meteorological models.

References

~~Alastuey, A., Querol, X., Castillo, S., Escudero, M., Avila, A., Cuevas, E., Torres, C., Romero, P. M., Exposito, F., García, O., Diaz, J. P., Dingenen, R. V., and Putaud, J. P.: Characterisation of TSP and PM2.5 at Izaña and Sta. Cruz de Tenerife (Canary Islands, Spain) during a Saharan dust episode (July 2002), Atmos. Environ., 39, 4715–4728.~~

~~Arimoto, R., Zhang, X. Y., Huebert, B. J., Kang, C. H., Savoie, D. L., Prospero, J. M., Sage, S. K., Schloesslin, C. A., Khaing, H. M., and Oh, S. N.: Chemical composition of atmospheric aerosols from Zhenbeitai, China, and Gosan, South Korea, during ACE-Asia, J. Geophys. Res., 109, D19S04, doi:10.1029/2003JD004323, 2004.~~

Claquin, T., Schulz, M., and Balkanski, Y.: Modeling the mineralogy of atmospheric dust sources, J. Geophys. Res., 104, 22243–22256, 1999.

Johnson, M. S., and Meskhidze, N.: Atmospheric dissolved iron deposition to the global oceans: effects of oxalate-promoted Fe dissolution, photochemical redox cycling, and dust mineralogy, Geosci. Model Dev., 6, 1137–1155, 2013.

Journet, E., Balkanski, Y., and Harrison, S. P.: A new data set of soil mineralogy for dust-cycle model, Atmos. Chem. Phys., 14, 3801–3816, 2014.

~~Klaver, A., Formenti, P., Caquineau, S., Chevaillier, S., Ausset, P., Calzolai, G., Osborne, S., Johnson, B., Harrison, M., and Dubovik, O.: Physico-chemical and optical properties of Sahelian and Saharan mineral dust: in situ measurements during the GERBILS campaign. Q. J. R. Meteorol. Soc., 137, 1193–1210, 2011.~~

~~Kraemer, S. M., Butler, A., Borer, P., and Cervini-Silva, J.: Siderophores and the dissolution of iron-bearing minerals in marine systems, Molecular Geomicrobiology. Rev. Mineral. Geochem., 53–84, 2005.~~

Nickovic, S., Vukovic, A., Vujadinovic, M., Djurdjevic, V., and Pejanovic, G.: Technical Note: High-resolution mineralogical database of dust-productive soils for atmospheric dust modeling,

Atmos. Chem. Phys., 12, 845–855, 2012.

Paris, R., Desboeufs, and Journet, E.: Variability of dust iron solubility in atmospheric waters: investigation of the role of oxalate organic complexation, Atmos. Environ., 45, 6510–6517, 2011.