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

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We appreciate comments by referees. We replied to all the comments and revised the manuscript considering the comments by the referees.

Reply to the comments by anonymous referee #1

Comment 1: The level of certainty implied by the statement on the occurrence of illite-smectite series clay minerals (ISCM) in the Abstract (lines 37-39) is rather higher than suggested by the discussion of their occurrence in the main body of the text (lines 239-256). In particular, the main text implies that ISCM occurrence has been inferred from the results of other studies, rather than from those of the present work (lines 239-241). The authors might consider rewording the Abstract to clarify this point.

Reply 1: Unambiguous layer-by-layer identification of illitic and smectitic clay minerals in nano-scale mixtures is challenging issue because lattice-fringe spacings of smectite layers are almost same as that of illite. Even the nano-scale analysis of clay minerals is generally not possible because of severe damage of clay minerals by finely focused electron beam. We hope to solve this issue by adopting special sample treatments and conditioning TEM instruments. Although we have cited previous works in lines 239–241, in this study we have also identified the presence of smectite in both the Asian and Saharan dust. In the line 374–376 of the manuscript, we stated that "XRD analysis of the preferentially oriented specimens of both the Asian and Saharan dusts showed 17Å peaks of smectite." We have reworded the sentence based on the level of certainty in the text from "The nano-thin platelets included…." to "Chemical compositions and lattice fringes of the nano-thin platelets suggested that they included….".

Comment 2: A very minor point, but the authors might like to check that the reference to Table 1 on line 361 is correct. The rest of this paragraph refers to Table 2 and this one reference to Table 1 seems out of place.

Reply 2: "Table 1" was changed to "Table 2".

Reply to the comments by anonymous referee #2

Comment 1: Soluble, dissolved, bioavailable, filterable, aqueous, etc. (some of which are just operationally defined) have been interchangeably used in the literature. However, considering that a portion of aeolian iron can be directly acquired from the dust particles by ocean biological organisms like dinitrogen-fixing cyanobacterium Trichodesmium (Rubin et al., 2011), it is more appropriate to use "bioavailable" on Line 74 instead of "soluble".

Reply 1: We have changed "soluble" on Line 74 instead of "bioavailable".

Comment 2: Please reword discussion on Line 412 regarding Fe(II). Even if Fe(II) is easier to be taken up by microbial organisms, there is no Fe(II) in the ocean and the lifetime of Fe(II) delivered through atmospheric pathways is less than 20 min.

Reply 2: We have changed the statement from "The most bioavailable Fe for microbial organisms is thought to be Fe(II) (Shaked et al., 2005; Baker and Croot, 2010" to "Whilst Fe(II) is a bioavailable form of Fe for microbial organisms (Shaked et al., 2005; Baker and Croot, 2010), its concentration is low due to rapid oxidation to Fe(III) and low supply rates. Microorganisms therefore have a range of alternative Fe uptake strategies (e.g. Rubin et al., 2011)."

<Changes in the revised manuscript>

- 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. Chemical compositions and lattice fringes of the nano-thin platelets suggested that they 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. 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

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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 ==bioavailable== 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), 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).
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3.3. Mineralogical properties of bulk dust

Mineral compositions determined by XRD analysis are presented in Table 2. Due to the small quantity of samples and low X-ray counts, the data in Table ==2== are at best semi-quantitative. However, mineralogical differences are evident between Asian and Saharan dusts. Although the quantity of each mineral has a large uncertainty, the sum of the mineral groups is more reliable. The mineral compositions of three Asian dusts were compared to the compositions determined by single particle analysis using SEM and EDXS (Table 2). Despite the differences in analytical methods and their semi-quantitative nature, the mineral compositions determined by both methods were well matched, supporting the reliability of the mineral composition data for small bulk dust samples presented in this study. ISCMs and discrete thick illite grains could not be distinguished in the XRD

method adopted in this study. Thus, sum of ISCMs and discrete illite is presented in Table 2.

4.2. Chlorite

Chlorite has received little attention in previous studies. Fe-rich chlorite is easily decomposed by acids (Ross, 1969; Kodama and Schnitzer, 1973; Brandt et al., 2003; Lowson et al., 2005). In Chinese loess, chlorite is weathered much faster than other silicate minerals (Jeong et al., 2011). Chlorite should be considered in studies of Fe dissolution from mineral dust. Chlorite content of Asian dusts was ca. 4–6% as determined using single particle analysis (Jeong et al., 2014) and 5–7% in XRD analysis (this study). In Saharan dusts, the chlorite content was lower at ca. 3% as determined by XRD analysis (this study). Although the chlorite content in dust is much lower in comparison to ISCMs, the release of Fe from chlorite is likely to be significant because its Fe content is 3–6 times higher than in the ISCMs and illite. Takahashi et al. (2011) suggested that chlorite could possibly be transformed into soluble ferrihydrite, after cloud processing during long-range atmospheric transport. Although we did not determine the oxidation state of Fe, the structural Fe present in chlorite is known to be dominated by Fe(II) (Newman, 1987). In contrast, the structural Fe in the fine ISCMs (dioctahedral illite, smectite, and their mixed layers) is dominated by Fe(III) (Weaver and Pollard, 1975; Newman 1987). Thus, trioctahedral clay minerals including chlorite may be an important source of soluble Fe(II). Whilst Fe(II) is a bioavailable form of Fe for microbial organisms (Shaked et al., 2005; Baker and Croot, 2010), its concentration is low due to rapid oxidation to Fe(III) and low supply rates. Microorganisms therefore have a range of alternative Fe uptake strategies (e.g. Rubin et al., 2011). Fe(II) dissolved from dust is commonly considered to be derived from the photochemical reduction of Fe(III). However, Cwiertny et al. (2008) suggested that Fe(II)-substituted aluminosilicates may be an important alternative source of soluble Fe(II), particularly after the reaction of dust with atmospheric acids. Chlorite grains occur in a diverse size range from individual large flaky particles of several micrometers (Jeong, 2008; Jeong and Nousiainen, 2014) to nano-thin platelets mixed with nano-thin ISCMs (Fig. 2b-3). Nano-thin chlorite plates are probably most effective in releasing Fe from dust particles following reaction with atmospheric acids.