MS No.: acp-2014-45
Title: TEM analysis of the internal structures and mineralogy of Asian dust particles and the implications for optical modeling

Authors: G. Y. Jeong, T. Nousiainen
MS Type: Research Article

We appreciate valuable comments by four anonymous referees during both the quick and ACPD reviews. We replied to all the comments and revised carefully the manuscript considering the comments by the referees.

<Reply to the comments in Open Discussion>

Reply to the comments by anonymous referee #1

From the line numbers in the comments, they are based on the original submission manuscript. The revised version of the original submission is now posted on ACPD website.

General comments

Comment: "This manuscript present **(1)** a detailed analysis of 9 slices of large (>10 micron) Asian dust particles collected from a receptor site in Korea. The authors use the high resolution imaging obtained with transmission electron microscopy to develop generalized models to be used in optical modeling. I commend the authors for a detailed and innovative approach to particle imaging. However, I raise a few questions about the validity of this approach. **(2)** First, how can the authors ensure that they are imaging an individual particle as it was present in the atmosphere and not an agglomeration that formed on the collection filter? **(3)** Second, I have doubts that such generalized models can be of much use for radiative calculations and remote sensing considering they were developed on the basis of a few particles. **(4)** A good portion of the manuscript is devoted to implications; I did not feel like this section added much to the paper as it was speculative and qualitative in nature. Based on these comments I suggest the authors perform major revisions to the manuscript to focus on the detailed analysis of particles. I think **(5)** more information can be added to the experimental to be clearer about the statistical nature of their measurements. **(6)** Perhaps more focus can be placed on the chemical composition as it relates to the source and atmospheric processing (or lack thereof). These general comments are based on specific points listed below."

Reply (1) The number of slices analyzed by TEM is not 9 but 35. We prepared 35 slices from 35 dust particles. Of these 26 slices were fully analysed by high resolution TEM analysis, but 9 slices were partly analysed because of the physical damage during the handling of micron-size slices. Since we could not present all the data, 12 particles of high quality covering diverse types were chosen and their data were presented in Figs. 2–13. A detailed reply is given below.

Reply (2) We confirm that they are not agglomerated on the collection filter. A detailed reply is given below.

Reply (3) We prepared 35 slices from 35 dust particles. The 35 dust particles were carefully selected from thousands of particles which had been already classified into mineral and mineral groups by scanning electron microscopy and energy dispersive X-ray spectrometry. Thus, the internal structures in this study are representative of the Asian dust particles. A detailed reply is given below.

Reply (4) The atmospheric radiative effects were one of the major motivations for this study.

Reply (5) Further information was already added in ACPD version, and will be added in final version..

Reply (6) This study focused on the internal structures of dust particles. Chemical composition of dust is not a main concern.

Specific comments

Comment Line 36 (original manuscript): “particles” is misspelled

Reply Line 36: It has been already corrected for the current paper in ACPD website.

Comment Lines 39-40 (original manuscript): The authors state that “There have been many reports on the microphysical characterizations of mineral dust, but no investigations of the internal structures or mineral composition of individual dust particles” Microscopic measurement of individual aerosol particles has been around for some time now. This is stated in the introduction so it is contradicting.

Reply Lines 39-40: In the revised version, we deleted “or mineral composition”.

Comment Lines 58-59 (original manuscript): The authors should state how the inclusion of this detail will improve radiative transfer modeling. The authors state it is important to include this detail, but is never proven that the detail is needed.

Reply Lines 58-59: The single-scattering properties are necessary input to radiative transfer simulations of systems exhibiting small particles. Because the single-scattering properties are potentially quite sensitive to the internal structure of dust particles, the radiative transfer simulations may also be. The question is largely about the degree of change in the single-scattering properties. Because this is pioneering work to investigate dust particle internal structures, we do not have existing models to quantify the impacts of the discovered structures. Past research tells us, however, that internal structure has potential to influence the single-scattering properties quite considerably (see, e.g., Vilaplana et al. 2006; Lindqvist et al. 2009, 2011; Nousiainen et al. 2011a, 2011b).

We understand the interest towards quantitative estimates. We, however, believe that it is better to address these issues in a separate study. To carry out a quantitative analysis, we first need to develop morphological models for the structure. We then need to carry out the necessary simulations, which require for us to use brute-force numerical methods such as the discrete-dipole approximation, otherwise the structures cannot be realistically accounted for in the simulations. A thorough set of such simulations probably takes several months to carry out. To include in the current manuscript the details of the development of the morphological models, the description of the simulation setup and the analysis of the obtained results, the manuscript would probably triple its length and the revision would require about a year to complete. We do not consider this reasonable.

As an alternative, we could obviously carry out some simplistic sensitivity studies. But this would not offer the requested proof. Instead, it would simply open the floor for the next set of questions about how realistic our treatment was, and how would the results be different, had we used a more realistic approach. In fact, it would add little to what can be learned from past sensitivity studies by Vilaplana et al. and Lindqvist et al., for example. Those studies clearly demonstrate the potential for considerable impacts in the single-scattering properties, and offer indications of how different single-scattering properties might be affected.

To address the Referee comment, we have added some explicit examples about the impacts of different types of inhomogeneity to single-scattering properties in Section 3.3.1.

Comment Line 91 (original manuscript): The authors need to be more specific about the sort of mass spectrometry: I suggest changing "time of flight mass spectrometry" to "single particle mass spectrometry".

Reply Line 91: We changed "time of flight mass spectrometry" to "single particle mass spectrometry".

Comment Paragraph starting on line 85 (original manuscript)): The word "microphysical" is used without any precise definition. Later on in the conclusions it is stated that microphysical properties are different than "single scattering" properties. Microphysical properties include single scattering properties. The authors need to be more clear about what they are trying to say here.

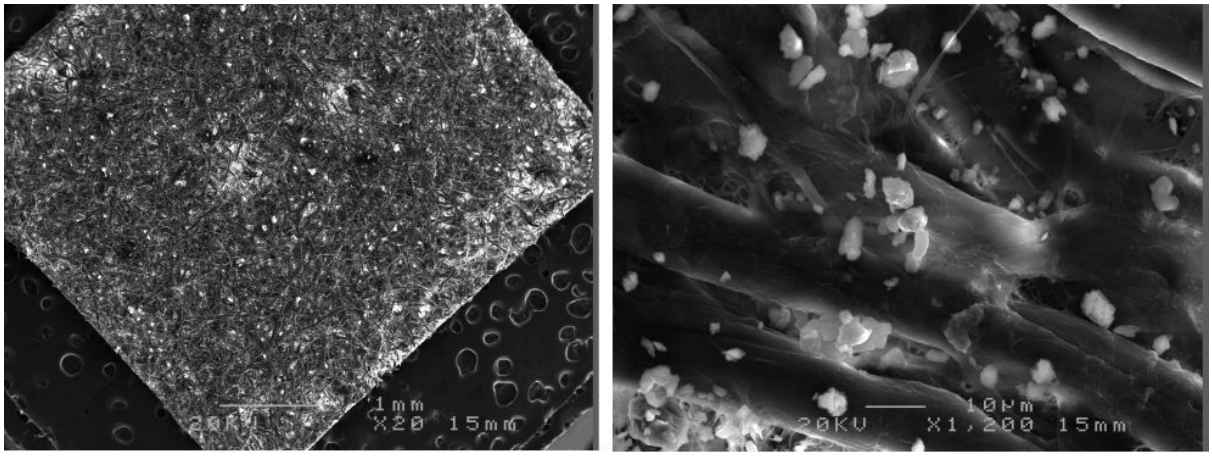
Reply Paragraph starting on line 85: We have never seen this as a problem; rather typically it is considered that the purpose of the single-scattering modelling is to establish the linkage between the physical and optical (or single-scattering) properties of particles. Of course, electrodynamics is a branch of physics, so obviously the single-scattering properties are also physical quantities. To explain our terminology, what we call the physical properties are input to single-scattering models, and what we call the single-scattering properties are the output. To clarify our terminology, we added the following sentence to the end of the paragraph mentioned: "Hereafter, we will denote the particle size, shape, composition and internal structure as microphysical properties, which are input to single-scattering models that produce the optical (single-scattering) properties as output." We also made some other minor changes to the paragraph in question to improve its clarity

Comment Experimental (original manuscript): **(1)** How can the authors be sure that these particles were present as individual particles in the atmosphere? Isn't it possible that these particles agglomerated on the filter? **(2)** In the process of the sample preparation (Pt coating, carbon "welding" of "loose agglomerates" (line 152)) it seems possible to more permanently "stick" these particles together. **(3)** Along these lines of thought: did the authors ever obtain closure of their SEM derived size distributions with size distribution measurements obtained in real time (e.g. with an aerodynamic particle sizer or the like)? **(4)** It is clear that 35 total slices were taken and 9 of those slices were utilized for a high resolution analysis. Later in the paper these high resolution analyses are used to develop generalized models. I do not believe that enough sampling was undertaken to make such generalizations. **(5)** How many total particles were used to derive the 35 slices?

Reply Experimental **(1)**: It is correct that the possibility of agglomeration on the filter should be tested. This is important and always considered by every single particle analyst. However, we confirm that the structures presented in this study were not formed by agglomeration. Since 2004, the first author (GYJ) has long experiences of SEM & EDXS analysis of dust particles collected on filter as published in Jeong (2008) and Jeong et al. (2014). Total number of particles analyzed by SEM may exceed several ten thousands including unpublished results. The particles on original filters are enough separated each other as shown in **Suppl. Fig. 1**. The flow rate and filtering time should be adjusted to avoid possible agglomeration depending on the dust concentration. Of course, some of the particles are ambiguous whether they are original or agglomerate during the filtering. These ambiguous dust particles should be excluded from FIB milling.

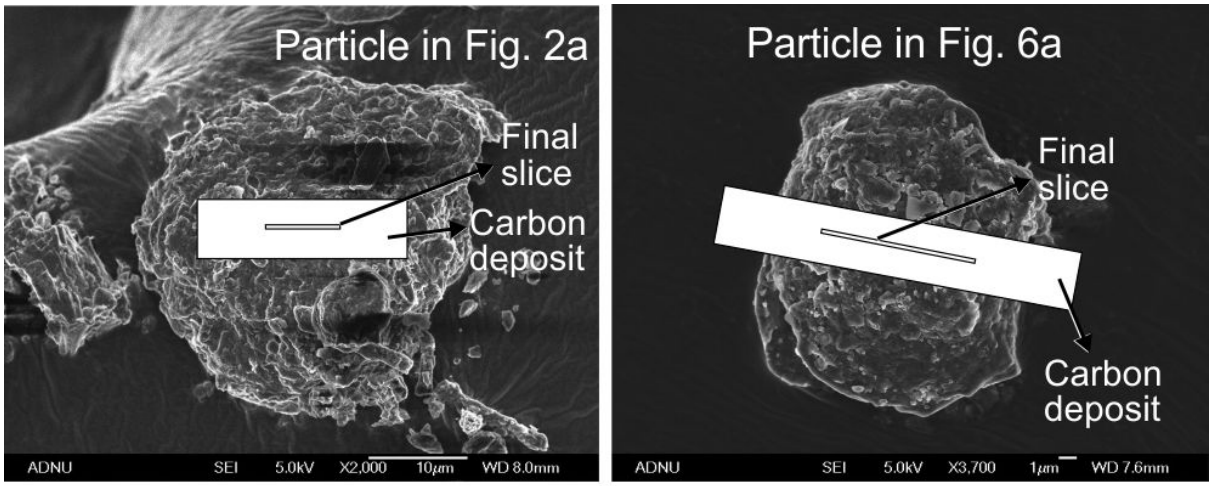
Mineral dust particles are normally micron-size particles. However, mineral grains constituting individual dust particles in the Fig. 2–13 are commonly submicron- and nano-size. It is not reasonable that numerous submicron and nano-size grains were tightly and locally agglomerated on filter to form larger particles which are separated from each other as shown in **Suppl. Fig. 1**.

There is addition and modification in revised version to clarify this issue.



Suppl. Fig. 1. SEM images of dust particles collected on cellulose filter (2009 dust).

Reply Experimental **(2)**: Thin Pt coating (several tens nanometer) is applied on whole area of SEM stub to facilitate conduction and avoid charging during the SEM observation. Carbon deposition (or platinum depending on laboratory options) is applied on the selected rectangular area of 10–20 µm× 5 µm before step-by-step FIB milling. Carbon (or Pt) deposition is always applied on target area before FIB milling because intense Gallium (Ga) ion beam damage target area. Thus, carbon deposition is only applied to the surface of particle surface, thus, normally does not affect the interior of the particles. Carbon deposition is also a bonus fixing grains loosely exposed on the particle surface. Most of the internal structures presented in this study are not welded by carbon deposition. However, in some case, carbon entered large pore and filled as shown in Fig. 3c. FIB milling commonly applied to flat surface in material sciences (e.g. semiconductor). Since our natural dust particles are 3D particle and natural agglomerates of many submicron to nano-size grains often with pores, FIB milling is technically more difficult object consuming more time. The carbon deposit should be thicker than in other application to avoid curving, spalling, and disruption of the slices during the milling. The carbon deposit increases the strength of dust particles. After the final step of milling, the slices of (5~12) µm (length) ×ca. 100 nm (thickness) × (5~6) µm (depth) are prepared. We have not saved the image of every step of FIB milling. However, the carbon deposition was done for single dust particles as shown in **Suppl. Fig. 2**.



Suppl. Fig. 2. Carbon deposition area (white) on the surface of individual dust particle and location of final slice.

Reply Experimental **(3)**: Size distribution of 2009 dust was not measured, but the size distribution of

2012 dust was measured both by SEM particle analysis and optical particle counter (Jeong et al. 2014). Here it should be noted that particle size measured by SEM single particle analysis is not matched with optical particle counter due to different measurement basics (Reid et al., 2003).

Reply Experimental **(4)**: The important thing is the number of particles analyzed by TEM. The number of slices for a high resolution TEM analysis is not 9 but 26. We wrote in the original manuscript: "Altogether 35 slices were prepared and analyzed by TEM. Of these, 26 slices had a good flatness and a wide area sufficient for the TEM analysis. However, only a limited analysis of a small area was possible in nine slices." We prepared 35 slices from 35 dust particles. Of these 26 slices were fully analysed, but 9 slices were only partially analysed because of the physical damage during the handling of micron-size slices. Since we could not present all the data, higher quality and representative data of 12 particles were chosen and presented in Figs. 2–13. We clarified this matter in revised version. In the **Suppl. Fig. 1** added in the finally revised version, we attached the TEM images of other 14 slices with additional two slices which have been included in Jeong et al. (2014).

Reply Experimental **(5)**: TEM of FIB slices is the best method imaging internal structures of dust particles with the least damage of original structure. Unfortunately, FIB slicing cannot be applied to numerous particles as done by statistic SEM-EDS analysis of particles because the process needs rather careful and complex operation, particularly for irregular, weak agglomerate particles, and is expensive method. However, the 35 dust particles considered for FIB work in this study were carefully selected from thousands of particles which had been already classified into mineral and mineral groups based on their morphology, chemistry, and mineralogy using SEM and EDS as done in Jeong et al. (2014) and Jeong (2008). For example, three clay-rich dust particles in Fig. 2, 3, and 4 were selected from the particles classified into the abundant ISCM group in Table 2 of Jeong et al. (2014). Thus, we think that the internal structures found in this study are representative of the Asian dust particles. We revised experimental section to clarify particle selection.

Comment Line 152 (original manuscript): How was the carbon deposited? What form is the carbon in? Amorphous, organic, elemental, graphitic?

Reply Line 152: In FIB milling, carbon or platinum layer (1~2 μm thick) is deposited on the target area. It is a kind of chemical vapor deposition (CVD) method. The carbon layer is amorphous. The main role of carbon layer is to protect samples (which will be milled to thin slices) from energetic Ga (gallium) ion beam, and avoid spalling and disruption of agglomerate samples during the FIB milling.

Comment Line 165 (original manuscript): What does it mean for identification to be "delicate"? I suggest that the authors mean "difficult".

Reply Line 165:"delicate" was changed to "difficult".

Comment Line 169 (original manuscript): Is it possible for there to be other minerals that have the same chemical composition and lattice spacing?

Reply Line 169: The phases of the same chemical composition and same lattice (crystal structure) are same mineral. When using TEM, minerals are identified on the basis of EDXS (chemical composition) and lattice fringe imaging and electron diffraction (crystal structure). Since smectite and vermiculite are different in chemical composition, they should be identified by EDXS. However, in practice this is impossible for a close mixture of nano-thin smectite and vermiculite because the diameter of electron microbeam used for EDXS is normally larger than the size of individual grains of nano-thin smectite or vermiculite.

Comment Line 212 (original manuscript): **(1)** Is there a reference describing the dehydration behavior of minerals in vacuum? **(2)** What effect might the FIB have had on the sample? Is it possible the beam disrupted the sample?

Reply Line 212 **(1)**: In the field of clay-mineral research, the dehydration of smectite in the high vacuum of TEM chamber is a common phenomenon. Please see Peacor (1992, see page 338, Diagenesis and low-grade metamorphism of shales and slates, in Minerals and reactions at the atomic scale: Transmission electron microscopy, Reviews in Mineralogy, 27, 335–380).

Reply Line 212 **(2)**: In the current version of manuscript posted at the ACPD website, the referee can see an added paragraph (Artifacts reported ….. mineral growth/dissolution) regarding artifact problem to the experimental section.

Artifacts reported during the FIB slicing are surface amorphization, Ga contamination, and curtain effect (Ishitani et al., 2004; Kato, 2004; Mayer et al., 2007). Surface amorphization by the Ga ion sputtering and Ga contamination are important issues in thin film and semiconductor analysis, but not problems for mineral dust particles because our FIB slices showed sufficiently clear images with microstructural details and lattice fringes. If significant amorphization occurred, structural details and lattices were destructed. We think that surface amorphization was restricted in the very thin surface region and had almost no influence on the quality of image. Ga contamination was detected by EDXS along the boundary between carbon deposits and dust particle. Weak curtain effects (stripes of light and dark contrast) due to topography and phase property (pores, mineral composition, and density) can be seen in Figs. 5c, 7c, 9c, 10c, and 11d. However, those curtain effects did not degrade image quality.

In traditional ion milling, Ar ions bombard the sample surface at higher angles, making a large hole in the center. The thin edges around hole are observed by TEM. In this type of ion milling, preferred erosion is common along the weak parts of the samples such as grain boundary and poorly crystalline phases, thus small holes can be produced in some parts around center hole, particularly for polyphase specimens. However, in FIB milling, Ga ions are bombarded almost parallel to the sample surface, and do not produce such artifact pores in most cases. This is one of the most important advantages of FIB milling of geological samples compared to traditional ion milling. For example, we can see the curtain effects (dark contrast stripes behind goethite grains) due to the density difference between goethite and pore within chlorite (Fig. 11d, please see Figure in the reply to referee #4 in the quick review below). However, the delicate large and small lens-shaped pores forming by goethite crystal growth are well preserved in FIB slices. We cannot see any modification by FIB milling. The large pore in the center of plagioclase (Fig. 7c) is evidently dissolution cavity formed during the weathering in the source soil on the basis of the occurrence of halloysite which is a common weathering product of plagioclase. Triangular pores in Fig. 5d, 5e, 7g, and 9d are original ones formed by morphological mismatch between larger round grain and stacks of fine platy grains. As written in text, some linear cracks with matching walls, e.g. those in Fig. 4c, can be formed during laboratory sample drying, but even those are not relevant to FIB milling. Thus, almost all the pores observed in the images were not formed by FIB milling. Our long experience in using FIB slicing and TEM observations support our conclusion that the pores were present in dust particles before FIB milling. Of course, some were formed by dehydration and were not necessarily present in the atmosphere, as indicated in the text.

We have added and modified experimental section.

Comment Line 242 (original manuscript): For the submicron goethite grains: I suggest the authors show the EDX spectra for these inclusions as evidence.

Reply Line 242: EDX spectra was added in finally revised version.

Comment Line 331-332 (original manuscript): Types I, II, and III need to be indicated on figs 14 and

15.

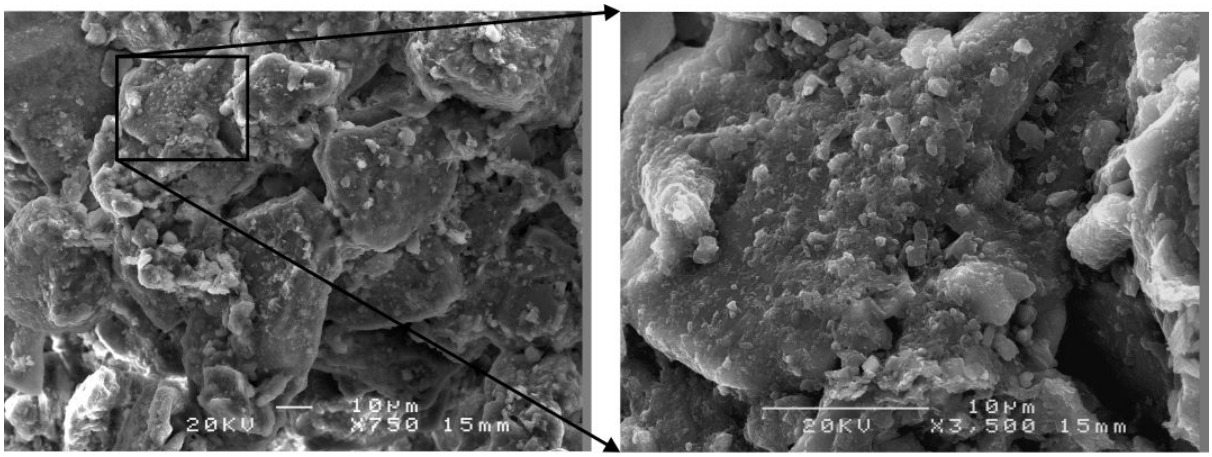
Reply Line 331-332: Types was indicated in Figs. 14 and 15 in revised version.

Comment Line 334 (original manuscript): How is abundance quantified? In order to undertake the sort of modeling the authors call for, these results need to be quantified.

Reply Line 334: It must be emphasized that this is pioneering work. In this early stage of internal structure research, it is difficult to derive the relative proportions of structural types in bulk dust from the analysis of 35 particles. Nevertheless, since we know the relative proportions of the mineral and mineral groups of dust particles from which samples for FIB were selected, the types of internal structure can be integrated with statistical data obtained by SEM single particle analysis for the simulation of optical properties in future. However, it should be noted that the simulation of optical properties of even one type of internal structures requires heavy computations. Thus, there may be long steps toward the optical simulation of bulk dust composed of several structural types. First we can model optical properties of each structural type, and then progress to model whole bulk dust considering the relative abundance of the structural types. We added some sentences regarding this issue in experimental section (Combined application …..representative of the Asian dust particles) and at the end of section 3.4 (Even though the present …….of the structural types).

Comment Line 342-343 (original manuscript): Provide a reference for the formation of the clay coatings.

Reply Line 342-343: Desert and arid land surface soils (in our case, Gobi desert in Mongolia and northwestern China) are mixed when disturbed by wetting in intermittent rainfall and subsequent drying. Bulky soils can be eroded and deposited by surface flow when heavy rainfall comes. Colloidal soil grain moves along the pores and accumulates there (eluviation and illuviation). Plant roots and bugging insects disturb soils. Freezing and thawing also induce the mixing of soil particles. In all these soil process, coarse and fine mineral particles are mixed. Coarse particles are always coated with clay mineral grains which have surface charges and tend to adhere on the other mineral surfaces. The first author has no experience in other dust source soils, but has extensive microscopic data of Gobi soils which are Asian dust source. **Suppl. Fig. 3** is an example where every coarse mineral grain (commonly, quartz and feldspars) is coated with tiny clay mineral grains. The image data are also presented in Figs. 3 and 4 of Jeong (2008). Birkeland (1999)'"Soils and Geomorphology" is helpful to get a general concept of soil process. Since there are few available data on this subject (cloud processing and any possibility of clay coating formation), some uncertainty is inevitable. Thus, we deleted ", and do not form in the atmosphere through, for example, cloud processing."



Suppl. Fig. 3. SEM of Gobi desert soil. Coarse grains (several tens micrometer) are coated with fine clay mineral grains <1~2 µm.

Comment Section 3: This section is too speculative. The authors have performed not calculations to prove that the detail provided by the measurements will have implications for radiation models. I suggest that this section be removed or bolstered with calculations. The application of the structural models presented in section 3.2 to detailed models of light scattering would be one way to accomplish this, however, it is not clear how abundant those types are.

Reply Section 3: As disclosed in our response to the first comment, quantitative estimation of the effects would require much additional work, would require about a year, and probably triple the length of the manuscript. Adding simplistic sensitivity would require less work and time to accomplish, but would not serve to quantify the effects, and besides, would offer little to augment studies already reported in the literature (see, e.g., Vilaplana et al. (2006), Lindqvist et al. (2011), Nousiainen et al. (2011)). Those studies are sufficient for establishing the potential for the internal structures found to considerably influence the single-scattering properties. To quantify the impact, sophisticated simulations with equally sophisticated morphological models for the particles are required, which we plan to publish separately once completed. Removing Section 3 altogether is, of course, an option, but undesirable, as the atmospheric radiative effects were one of the major motivations for this study. We have, however, added some details and quantitative examples from the literature to the section.

Comment Conclusions (original manuscript): It is stated: "All microphysical properties, including size distributions, particle morphology, and composition should be known and accounted for to allow for realistic optical single-scattering treatment". I think this is not feasible for current models, which is why parameterizations and process models are developed. To try and model everything perfectly is beyond the scope of many modeling studies. Also it is stated: "when computing bulk properties, averaging should in principle be performed for single-scattering properties rather than for microphysical properties; what is averaged matters, because the microphysical properties and the resulting single scattering properties are not linearly proportional" Technically, single scattering properties are microphysical properties. The distinction between microphysical properties and single scattering properties needs to be distinguished. But more generally, I think the authors need to be specific about what they mean here: what single scattering properties? Cross sections, phase functions? What microphysical properties are averaged?

Reply Conclusions (original manuscript): We agree that there is a limit what can and is even reasonable to be accounted for in models. The models should be as simple as possible and as detailed as necessary. This means that all important aspects should be included, but nothing more. It is important to know quantitatively the internal structure of dust in order to quantify its importance:

whether it is one of those characteristics that should be included. And this of course depends on the application of interest. Regarding modeling capabilities, volume-integral methods such as the discrete-dipole approximation can handle almost any kind of model particles. These models can be run with reasonable computational expenses only for particles not much larger than the wavelength.. For many applications, sizes beyond the reach of such methods will be relevant. Still, these simulations can be used to assess the importance of these features for the single-scattering properties of wavelength-scale particles, as well as the size dependence of their importance within the range where the computations are possible. This will provide a good basis for estimating in which applications internal structures would be important. In addition, they may provide suggestions as to how their impact could be parameterized, if explicit computations are not possible.

Regarding averaging, we have rewritten the part in Conclusions where this was discussed to improve its clarity. The point is, one can only average additive quantities, and composition is not additive. Because the single-scattering properties depend on the size and shape of the particles in a composition-dependent way, and for mineral dust the composition varies from particle particle, one cannot obtain the true bulk optical properties by using bulk composition. In fact, because shape and composition are not independent either, one truly needs to model each particle individually. Of course, this is not to say that the bulk optical properties derived from bulk compositions would be significantly in error. This is simply not known until it has been done properly to provide a reference.

The issue about the terminology regarding microphysical and single-scattering properties was already addressed by our response to the second comment. Regarding which single-scattering properties will be affected, we cannot readily think of one that would not be. It is supposed to be generic. Of course, different single-scattering properties will be differently sensitive to different characteristics.

Comment Line 499 (original manuscript): It is stated that Goethite was the dominant iron oxide. How was this quantified? How statistically relevant is this? Was this determined from the few slices of the few particles that they analyzed? Or, was this measured elsewhere?

Reply Line 499: It is correct. In revised version, we deleted the phrase because we have not done any quantitative estimation. We positively identified goethite grains in many slices, but rather rarely hematite. Our estimation was qualitative.

Reply to the comments by anonymous referee #2

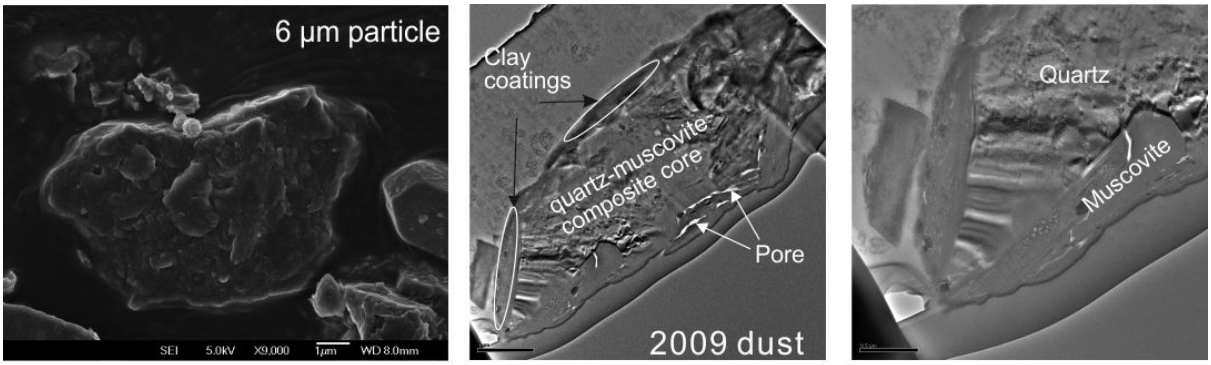
Major comments

Comment 1: Throughout the manuscript, the descriptions of particle mineralogy are detailed but, I believe, most readers in the atmospheric field have little knowledge about mineralogy. The mineralogical descriptions should be written in general terms so that readers in atmospheric science can understand. For example, I suggest writing general chemical formula of each mineral so that readers can have idea about their chemistry.

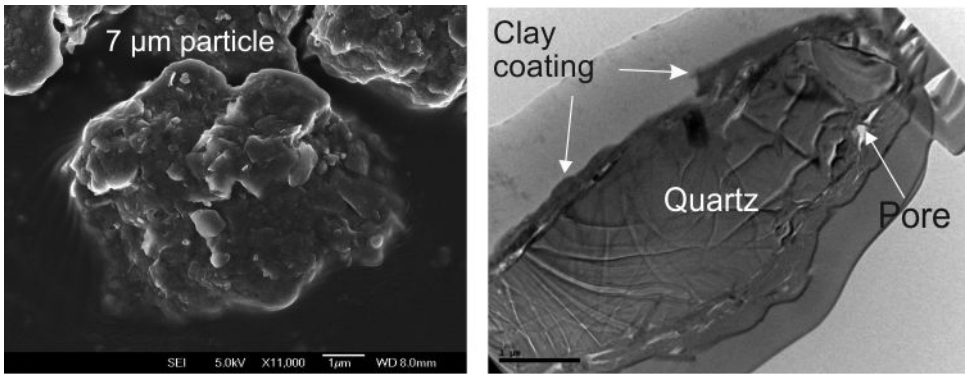
Reply 1: In the final version after the end of discussion forum, we added a short Supplementary Table of the general chemical formulas which are based on the literature and our EDXS analytical data. We inspected the manuscript again and revise the mineralogical terms for readers in atmospheric sciences.

Comment 2: This manuscript shows examples of selected Asian dust particles, most of which are larger than 10 micrometer. The discussion in this manuscript mainly based on such large dust particles, although they are small number fraction within all dust particles (Jeong et al., 2014; ACP). **(1)** I question the significance of these large particles having relatively small number concentrations to the atmospheric aerosol optical properties. In general, atmospheric number concentrations are important as well as volume concentrations. Also, dust particles with several micrometer or smaller were more abundant in their samples (Jeong et al., 2014) and **(2)** may not neither have pore nor polycrystal structure that are proposed in the current paper. I believe further discussion regarding particle sizes including smaller but more abundant dust particles will be needed to clarify the implication of this study to ambient optical modeling.

Reply 2: **(1)** Although the diameter of the particle shown in Fig. 5a is ca. 5 μm, the internal structure shows quartz core coated with thin clay layers similar to the structures observed in larger particle (Fig. 6). We have prepared FIB thin slices from two dust samples collected in 2009 and 2012. The sizes of the dust particles collected in 2012 (Jeong et al., 2014) were larger those in 2009. More images were selected from the image data of 2012 dust particles, because they were up-to-date data prepared on the basis of further FIB experiences and improved skill of our FIB team. Another reason is that the larger particles are technically more suitable to FIB handling than small particles. The larger particles are rather stably attached to adhesive substrate, while smaller particles are often not stable because large portion of their rough bases with high curvature was often floated on substrate. Nevertheless, we have observed internal microstructures of some micron-size particles. Here we show two examples (**Suppl. Figs. 4 and 5**).



Suppl. Fig. 4. Internal structures of ca. 6 μm dust particle showing quartz-muscovite polycrystal with clay coatings.



Suppl. Fig. 5. Internal structures of ca. 7 μm dust particle showing quartz core and clay coatings.

(2) We have to pay much more attention to the dust particles of representative sizes in future research by overcoming technical difficulty. However, we think that particles of several micrometers also have

structural features similar to larger particles. In the surfaces of desert or arid soils, fine particles are formed by the repeated jump, impact, and fragmentation of particles during the wind erosion. As shown in **Suppl. Fig. 2 in final revised version**, coarser particles can be divided into finer particles of diverse internal structure types (Fig. 14–16 in text). We have not annotated scale bars on Figs. 14–16, because the models for internal structures could be generally applied to common dust particles. Of course, further attention should be given to the finer particles in next steps of research to refine the internal structure models. The models of internal structures can be certainly improved by the continued investigations for dusts from other sources and diverse size fractions in the next stage of study. We revised the final version considering above discussion.

Comment 3: I am unsure if small pores (< 1 micrometer) within such large particles (> several tens micrometer) indeed have an effect to their optical properties. When dust particles are large enough (tens micrometer), the solar radiation may not be able to penetrate inside the particles. A simple core-shell calculation suggests that small core (pore) within large particles have negligible effects on the optical properties of the entire particles, depending on the choice of refractive index. Note that discrete dipole approximation (DDA) method (Page 6639 line 22) will not be available for large particles such as those used in this study (Draine and Flatau, 1994). As author said further investigations do need to confirm the effects, I would like to see more quantitative discussion.

Reply 3: We agree that one submicron pore inside a particle tens of microns across would most likely not have a substantial impact on the optical properties. However, some of the particle cross sections show tens of percent of the area are occupied by pores. This would certainly have a considerable impact. As to the penetration of the solar radiation inside the particle, the question is unfortunately complicated by the fact that dust particles tend not to be homogeneous but are mixtures of different minerals. Some species, such as calcite or quartz, have so low imaginary parts of the refractive index that even crystals tens of centimeters across are transparent. Whether radiation can penetrate a few tens of micrometers depends obviously on the composition, but most mineral species typically encountered in dust are relatively weakly absorbing. Mixed with them are some highly absorbing species, such as iron oxides, but they are seldom evenly distributed. If we, for example, take a quartz particle that has isolated grains of hematite with the total vol% of a few percent, the particle interior will definitely be exposed to radiation. If we take the same amount of quartz and hematite and mix them evenly, the amount of radiation penetrating the particle will be much less. The impact of pores on radiation will therefore depend not only on the size of the pore and the size of the particle, but also on the composition of the particle.

The Referee is also correct that the DDA method will not be applicable to dust particles few tens of micrometers across at solar wavelengths. The practical upper limit for computing orientation-averaged optical properties will be somewhere in the size parameter range of 20–30, which corresponds to a particle diameter of 4-6 micrometers at 628 nm wavelength. For considerably larger size parameters, we cannot think of any method that would allow taking into account the irregular particle shape and the inhomogeneity. The coated sphere model can be applied, but mineral dust particles are not spheres, nor are the pores arranged in concentric layers. Understanding obtained using coated-sphere model would therefore be quite limited and possibly misguided. For particles few micrometers across, the DDA could be used, and indeed we plan to carry out such investigations. Such investigations are however time consuming, and we prefer to conduct them as a separate study. Needless to say, it would be desirable to obtain data on micrometer-scale particles for this purpose.

Minor comments

Comment 1: P6620, L6-8: This sentence contradicts to that in P6622 (L1-6). For example, Jeong et al (2014) reported mineralogical composition of individual particles. In abstract, it says there have been many reports on the microphysical characterization, whereas in Introduction, it says the microphysical

properties of individual particles have not been fully resolved.

Reply 1: In revised version, we deleted “or mineral composition” in Line 7.

Comment 2: P6620 L 25-28: “likely have a great impact”: This statement is qualitative, and no evidence is shown if they have a great impact. Please see Major comment 3.

Reply 2: We have changed the sentence and it now reads “In particular, the observed internal structures of dust particles such as clay coatings, preferred orientation, embedded grains in clays, and pores, have potential to considerably impact light scattering of dust particles.” This claim is not wholly speculative, but supported by results from the past sensitivity studies cited.

Comment 3: P6623 L18-19: I think there is at least one report by Jeong et al. (2014), who reports internal structures of dust particles.

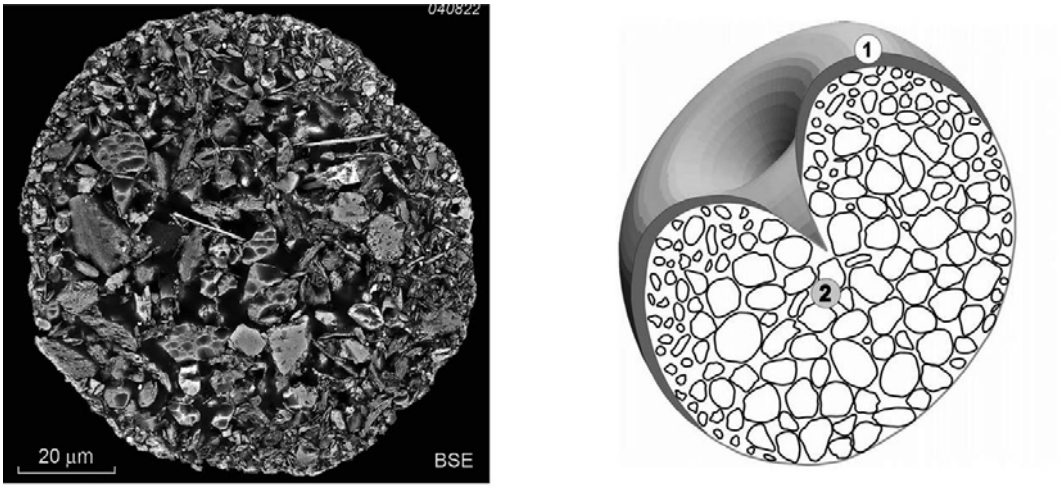
Reply 3: Jeong et al. (2014) is one of a series of papers organized by the first author (GYJ). The internal structures provided in Jeong et al. (2014) are only small portion of large set of TEM image data which were added to help the readers to better understand particle mineralogy. This paper is in fact the first report dedicated to the systematic investigation of the internal structures of dust particles.

Comment 4: P6627 L25-26: Why they are unlikely to have formed?

Reply 4: Grain arrangement in Fig. 2c is random in overall, but subparallel locally. Long thin lenticular pores in Fig. 2c may have been formed by the dehydration and contraction of subparallel agglomerates. However, the circular pore (arrow in Fig. 2c) cannot be formed by this mechanism, but may have been formed by soil process, particularly repeated wetting-drying and freezing-sawing cycles in the dry and cool sources of Asian dust. We added this explanation to the revised version.

Comment 5: P6632 L19-21: I guess iberulite, which is formed from mineral aggregates within rain droplet in atmosphere, may be one of potential formation process of the clay-rich particles.

Reply 5: Cloud processing deserves to be considered as a possible formation mechanism of clay-rich particles. However, the internal structures of iberulite are quite different from dust particles considered in this study. The morphology and structures of iberulite formed from dust-bearing rain droplet are characterized by high sphericity, vortex depression, outward-fining grains sizes, and porous internal structures with some biological fragments (**Suppl. Fig. 6**). We did not find microscopic features typical of iberulite in the cross-sectional slices of Asian dust particles. However, since there are few available data and inevitably some uncertainty on this subject (cloud processing and any possibility of clay coating formation), we deleted “, and do not form in the atmosphere through, for example, cloud processing.”



Suppl. Fig. 6. Structures of iberulite from Díaz-Hernández and Párraga (2008, Geoochimica et Cosmochimica Acta ,72, 3883–3906).

Reply to the comments by anonymous referee #3

Major comments

Comment 1: Most of the particles presented in this manuscript are very large (this is necessary to use FIB). However, long-range transported dust has a smaller diameter (Zender et al., JGR, 2003, 108, 4416 ; Durant et al., Prog. Phys. Geo., 2009, 33, 88). According to number distribution, most of the long-range transported dust is less than 1 micron in diameter. In this manuscript, many inclusions/coatings/pores are hundreds of nanometers to 1 micron across (with the exception, perhaps, of some of the goethite inclusions). As a result, I would expect that individual particles the submicron fraction are much more homogeneous in structure. Consequently, I would expect that this manuscript is applicable to the optical properties of dust near the source region, but not long-range transported dust, and thus has a lower degree of applicability to retrievals. These points should be addressed in the manuscript.

Reply 1: Larger particles were used, because they are more suitable for FIB milling and provided sufficient areas for TEM analysis of structures and chemistry. Small particles are difficult to mill, because they are often not stably attached on substrate like larger particles. We are aware that TEM data of fine dust particles would be more desirable for atmospheric applications. We will try to obtain enough data from fine particles in future research, but in this pioneering publication we chose to use larger targets more easily handled. We will make a note of this in the revised version.

Further, we wish to point out that, from the radiation point of view, volume/mass concentrations are more interesting than number concentrations. In Zender et al. (JGR, 2003), the mass mode of Saharan dust predicted from their model is 2–3 μm at Barbados (~5000 km from Sahara), while the number mode is submicron. In addition, they stated "As mentioned earlier, recent measurements from the PRIDE experiment [*Reid et al.*, 2003] show that the transport mode of African dust is about D_v= 3.5 μm or larger. This is significantly greater than the D_v= 2.5 μm predicted by DEAD in the Caribbean (Figure 1) and used for our sub-bin distribution (Table 2). A larger transport mode could help to reconcile some of the disparities between DEAD and observations." Mckendry et al. (2008) reported mode of Asian dust as 2–4 μm transported ~10,000 km from an Asian source. The dimensions of most of the FIB slices are around 5~10μm, which is about double of the volume/mass mode of long-range transported dust. We think that this is not so great a difference. We expect that

many structural features observed in coarse particles are inherited to long-range transport finer particles. Please see Suppl. Fig. 2 included in the revised manuscript.

Comment 2: Clarity of figures: The imaging in this paper is beautiful, but I am concerned about the clarity of image interpretation. In particular: 1) not all of the images have scale bars, 2) the words indicating composition will be too small once the figures are the final size (could letters and a legend be used, e. g. Q = quartz, G = goethite, etc.?), 3) the lattice fringes are hardly visible and should be shown at higher magnification (a zoomed in image).

Reply 2: We found lack of scale bars in Fig. 10e and in the electron diffraction patterns of Figs. 12 and 13. They will be added in revised version. Also, the figures reveal many details if zoomed in, so the lack of these features is largely due to the small size of individual panels, which is an issue about presentation rather than the image quality. Figures will be enlarged in the final version for ACP. This is partly caused by the larger horizontal size of the ACPD page. Vertical size of the ACP page is larger than horizontal size. We will see if we can somehow enhance the features to be visible also in smaller panels without zooming. We reconsidered these matters in preparing final version.

Comment 3: Other studies have performed FIB-SEM imaging of aerosol particles, and should be discussed in the introduction (e. g. mineral dust: Conny, Environ Sci Technol, 2013, 47, 8575; organic aerosol: Adler et al., PNAS, 2013, 110, 20414).

Reply 3: We cited these two papers regarding the FIB-SEM images. Particularly, internal structures of urban dust particles imaged by SEM in Conny (2013) are very interesting.

Minor comments

Comment 1: Section 2: Some brief description of the field collections would be useful (were these samples obtained during dust storms?).

Reply 1: In spring season, the author (GYJ) monitors satellite remote sensing data and PM_{10} level in air which are uploaded at the website of Korea Meteorological Administration in almost real time. When dust storm outbreak in Asian dust sources (normally Gobi desert) is identified, we start to operate TSP dust sampler. Dust-laden air mass normally moves eastward crossing Korea, Japan, and North Pacific Ocean. The arrival time of dust is known from the PM_{10} data. We added a short description about the field collection in the final version.

Comment 2: pg 6625 lines 24-26: This sentence is awkwardly worded.

Reply 2: The sentence was modified as “In traditional ion milling, Ar ions bombard the sample surface at higher angles, making a hole in the center. The thin edge around the hole is then analyzed by TEM.”

Comment 2: pg 6627 lines 25-26: Why are the pores unlikely to be formed from dehydration? Are they too large?

Reply 2: Grain arrangement in Fig. 2c is random in overall, but subparallel locally. Long thin lenticular pores in Fig. 2c may have been formed by the dehydration and contraction of subparallel agglomerates of platy clay minerals. However, the circular pore (arrow in Fig. 2c) cannot be formed

by this mechanism, but may have been formed by soil process, particularly repeated wetting-drying and freezing-sawing cycles in the dry and cool sources of Asian dust. We added this explanation to the revised version.

Reply to the comments by anonymous referee #4

Comment 1: Figure 1 would be more complete if not just clays but all important groups of sheet silicates, such as mica were included among the schematic drawings, especially that muscovite and biotite with submicrometer grain sizes are shown in Figs. 4 and 15.

Reply 1: Fig. 1 will be modified to include biotite. However, muscovite is not well distinguished from illite due to their almost identical structure and chemistry in submicron scale. In sheet silicate mineralogy, muscovite and illite are often confused because of their similar structure and chemistry. Illite is distinguished from muscovite by its higher Al, lower K, and often fine grain size. Illite is formed in low-temperature geological environments such as by diagenesis and hydrothermal alteration, while muscovite crystallizes from magma or during high-grade metamorphism. Fine soil fractions of dust are formed by the physical breakdown of bedrock. In such source soils, fine muscovite and coarse illite are often difficult to distinguish. Thus, it is safer to group submicron dioctahedral mica into illite. Thus, we changed muscovite in Figs. 4 to illite.

Comment 2: In the caption of Figure 5: "(e) TEM lattice 767 fringe image of ISCMs. " – I assume the number 767 appears by mistake. "(f) TEM lattice fringe image of ISCM and chlorite."
– please mark chlorite in the image.

Reply 2: In the caption of Fig. 5, 767 should be removed. "and chlorite" is our mistake, and should be deleted. In text, chlorite is not mentioned when explaining Fig. 5f.

Comment 3: Fig. 13. I cannot see any reflections at the positions marked 0.43 and 0.46 nm in the f panel.

Reply 3: We replaced current image with a brightness-enhanced image in revised manuscript

Comment 4: I wish the authors had cited this paper, which I think is highly relevant to the topic since it was the first to describe crystallographically oriented aggregates of clays on other minerals in atmospheric dust: Díaz-Hernández, J. L. and J. Párraga (2008). "The nature and tropospheric formation of iberulites: Pinkish mineral microspherulites." Geochimica et Cosmochimica Acta 72(15): 3883-3906.

Reply 4: We cited Díaz-Hernández, J. L. and J. Párraga (2008) in the revised version.

<Reply to the comments in Quick Review>

Reply to the comments by anonymous referee #2

1) This study reports some case studies of the dust particles without statistic

TEM of FIB slices is the best method imaging internal structures of dust particles with the least damage of original structure. Unfortunately, FIB slicing cannot be applied to numerous particles as done by statistic SEM-EDS analysis of particles because the process needs rather careful and complex operation, particularly for irregular, weak agglomerate particles, and is expensive method. However, the 35 particles considered for FIB work in this study were carefully selected from thousands of particles which had been already classified into mineral and mineral groups based on their morphology, chemistry, and mineralogy using SEM and EDS as done in Jeong et al. (2014) and Jeong (2008). For example, three clay-rich dust particles were selected from the particles classified into the abundant ISCM group in Table 2 of Jeong et al. (2014). Thus, we think that the internal structures found in this study are representative of the Asian dust particles. Furthermore, the mineralogical features of the Asian dust varied little through different events and years. In this early stage of internal structure research, it is difficult to derive the relative proportions of structural types in bulk dust. Nevertheless, since we know the relative proportions of the mineral and mineral groups of dust particles from which samples for FIB were selected, the types of internal structure could be integrated with statistical data obtained by SEM single particle analysis for the simulation of optical properties in future. However, it should be noted that the simulation of optical properties of even one type of internal structures requires heavy computation. Thus, there may be long steps toward the optical simulation of bulk dust composed of several structural types. We added some sentences regarding this issue in experimental section (Combined application …..representative of the Asian dust particles) and at the end of section 3.4 (Even though the present …….of the structural types).

2) The implication of the optical property is not directly relate to the results of this study

We are not entirely sure what the Referee means by the implication of the optical property, but we assume the criticism is against the missing linking of the observed physical properties and the corresponding optical properties. Such a linking is obviously dependent on the wavelength of radiation considered, and needs to be established through single-scattering modeling. To properly carry out such modeling, one should first derive the three-dimensional shape of each particle to be modeled, and then derive their detailed 3D internal structure. This is obviously quite an undertaking, and nothing like this has ever been done. A somewhat simpler approach would be to take a phenomenological approach, where shapes and internal structures that do not match but nevertheless resemble those observed are used. A third, a simplest approach would be to carry out a sensitivity study where some simple basic, fixed shape is assumed for the model particles, and then simplistic internal structures of different types are considered, resembling those observed in the TEM images. Obviously, the last approach would ignore any linking between the shape and the internal structure. Yet, even the simplest approach would take considerable amount of pages to properly explain in the manuscript, and the computations would be quite time consuming (this would require a volume-integral method such as a discrete-dipole approximation or the finite different time domain method to be applied, which are both computationally heavy).

We strongly believe that, instead of trying to squeeze some quick (and potentially dirty) model simulations into the manuscript, a dedicated study focused on the linking between the physical and the optical properties of the particles is much preferable. Still, because the

implications for the optical properties are of great interest, we did not want to ignore the issue completely. Therefore, we added a discussion on what structures we expect to be optically important, based on our past experiences with single-scattering modeling of dust particles. We also point out that there are many publications about dust particle physical properties without any discussion about the implications for the optical properties. Thus, the lack of rigorous simulations on the aforementioned linking cannot be considered a critical flaw. In fact, we believe that a series of manuscripts will be required to cover all the different types of internal structures that will be found, as the structures appear quite diverse, and different types will require different modeling approaches.

Nevertheless, to clarify this issue in the manuscript, we have modified the end of the Conclusions, which now reads:

"The microphysical parameters of individual dust particles considered in this study can be explicitly accounted for in single-scattering modeling if sophisticated methods, such as a discrete-dipole approximation by Draine and Flatau (1994), are used. Such modeling studies can illustrate the means by, and degree to, which microphysical parameters influence dust particle single-scattering properties, and will allow for further investigation of the dust radiative effect and remote-sensing implications. In the future, we plan to both carry out such simulations and to measure the internal structures for more dust particles and from different sources."

Reference:

Draine, B. T., and P. J. Flatau (1994), Discrete-dipole approximation for scattering calculations, J. Opt. Soc. Am. A Opt. Image Sci., 11(4), 1491 – 1499.

3) How or if internal structures affect the optical properties for the relatively large particles.

There have been some sensitivity studies concerning the impact of possible internal structure on the optical properties of large dust particles. For example, Nousiainen et al. (2003) and Muinonen et al. (2009) investigated this using different types of modified ray-optics models. Both conclude that the internal structure is potentially quite significant for the optical properties. Note that these investigations simply assumed random structure within particles, in the absence of observational data. Similar finding have been reported concerning ice crystals (e.g., Macke et al. 1996; Nousiainen et al, 2011b). There is no reason to think that internal structures observed would be insignificant for the optical properties for the particle sizes considered here. As to how the observed structures impact the optical properties, we again emphasize that it needs to be established by appropriate simulations. As this is a considerable undertaking, and even the particle models to be used in the simulations have not been implemented yet, we much prefer to publish the findings separately.

To clarify this issue in the manuscript, we have added the following sentence to the Introduction:

"Likewise, Nousiainen et al. (2003) and Muinonen et al. (2009) found that internal structure, assumed in their studies to be random structure in the absence of observational data, is potentially quite significant for the single-scattering properties of dust particles much larger than the wavelength."

Reply to the comments by anonymous referee #4

1) There is no discussion on possible sample preparation artifacts, such as the amorphization of the surface due to Ga ion bombardment. A crucial point is whether the observed voids were originally present in the aggregates or formed as a result of FIB milling.

→ Artifacts reported during the FIB slicing are surface amorphization, Ga contamination, and curtain effect (Ishitani et al., 2004; Kato, 2004; Mayer et al., 2007). Surface amorphization by the Ga ion sputtering and Ga contamination are important issues in thin film and semiconductor analysis, but not problem in mineral dust particles because our FIB slices showed sufficiently clear images with microstructural details and lattice fringes. If significant amorphization occurred, structural details and lattices were destructed. We think that surface amorphization was restricted in the very thin surface region and had almost no influence on the quality of image. Ga contamination was only detected by EDXS along the boundary between carbon deposits and dust particle. Weak curtain effects (stripes of light and dark contrast) due to topography and phase property (pores, mineral composition, and density) can be seen in Figs. 5c, 7d, 9c, 10c, and 11d. However, those curtain effects did not degrade image quality.

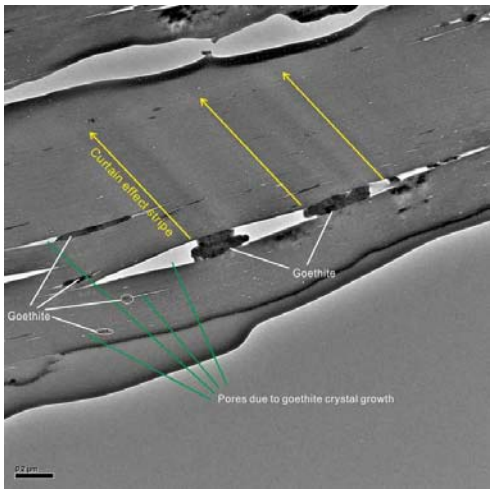
In traditional ion milling, Ar ions bombard the sample surface at higher angles, making large hole in the center. The thin edges around hole are observed by TEM. In this type of ion milling, preferred erosion is common along the weak parts of the samples such as grain boundary and poorly crystalline phases, thus small holes can be produced in some parts around center hole, particularly for polyphase specimens. However, in FIB milling, Ga ions are bombarded almost parallel to the sample surface, and do not produce such artifact pores in most cases. This is one of the most important advantages of FIB milling of geological samples compared to traditional ion milling. For example, we can see the curtain effects (dark contrast stripes behind goethite grains) due to the density difference between goethite and pore within chlorite (Fig. 11d, please see Figure below). However, the delicate large and small lens-shaped pores forming by goethite crystal growth are well preserved in FIB slices. We cannot see any modification by FIB milling. The large pore in the center of plagioclase (Fig. 7c) is evidently dissolution cavity formed during the weathering in the source soil on the basis of the occurrence of halloysite which is a common weathering product of plagioclase. Triangular pores in Fig. 5d, 5e, 7g, and 9d are original ones formed by morphological mismatch between larger round grain and stacks of fine platy grains. As written in text, some linear cracks with matching walls, e.g. those in Fig. 4c, can be formed during laboratory sample drying, but even those are not relevant to FIB milling. Thus, almost all the pores observed in the images were not formed by FIB milling. Our long experiences using FIB slicing and TEM observations support our conclusion that the pores were present in dust particles before FIB milling.

We added a paragraph (Artifacts reported ….. mineral growth/dissolution) regarding artifact problem to the experimental section.

Kato, N. I.: Reducing focused ion beam damage to transmission electron microscopy samples, Journal of Electron Microscopy, 53, 451–458, 2004.

Ishitani, T., Umemura, K., Ohnishi, T., Yaguchi, T., and Kamino, T.: Improvements in performance of focused ion beam cross-sectioning: aspects of ion–sample interaction, Journal of Electron Microscopy, 53, 443–449, 2004.

Mayer, J., Giannuzzi, L. A., Kamino, T., and Michael, J.: TEM sample preparation and FIB-induced damage, MRS Bulletin, 32, 400–407, 2007.



2) Only a single electron diffraction pattern is shown. If the authors have more SAED patterns from the individual grains, they should include them in the paper.
→ We added more diffraction patterns on Figs. 12 and 13. In most cases, EDS and lattice fringe imaging were sufficient for mineral identification.

3) I like the categorization of "structure models" of dust particles for potential modeling applications, this is a good way of making the individual-particle results accessible for modelers (Section 3). Any suggestions on how the relative abundance of the identified structure types could be determined in a dust plume, for example, by remote sensing? It would make the paper stronger if some suggestions for further experimental tests would be included.
→ The 35 FIB slices examined for this study were selected from dust particles which had been already classified into mineral and mineral groups using SEM and EDS. For example, three clay-rich dust particles were selected from particles classified into ISCMs in Table 2 in recent paper (Jeong et al., 2014, ACP, v.14, 505–521). Since we know the number, surface area, and volume % of the ISCM particles, and dust size distribution, it may be possible to integrate structural models of clay agglomerate into quantitative optical modeling. Similarly, since the abundance of other mineral and mineral groups of dust particles are known, we can integrate other structural models into optical modeling. We may approach step by step to model the optical property of bulk dust. First we can model optical properties of each structural type, and then progress to model whole bulk dust considering the relative abundance of the structural types.

line 65: There is an updated version of the cited book chapter by Pósfai and Molnár (2000): Pósfai, M. and Molnár, Á. (2013) Atmospheric aerosol particles: A mineralogical introduction. In Environmental Mineralogy II. European Mineralogical Union Notes in Mineralogy, Vol. 13, D. Vaughan and R. Wogelius eds., European Mineralogical Union

and the Mineralogical Society of Great Britain & Ireland, London, 213-293.
→ Pósfai and Molnár (2000) was replaced by Pósfai, M. and Molnár, Á. (2013)

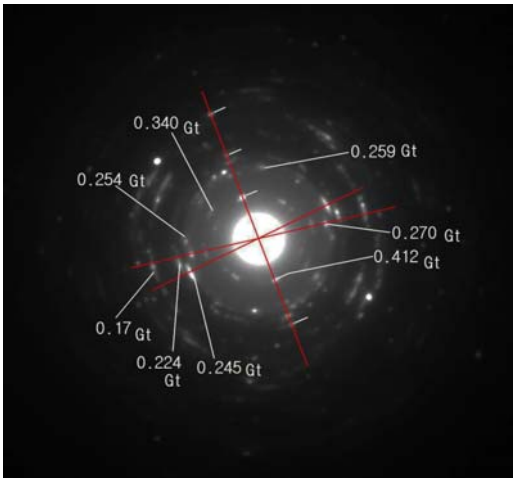
116: „large complex refractive indices" – sounds a bit strange, what does „large" mean for a complex number? Maybe „complex refractive indices with large real and imaginary parts"
→ „large complex refractive indices" was replaced by „complex refractive indices with large real and imaginary parts"

122-123: „no investigations dedicated to the analysis of the internal structures and mineralogical makeup of dust particles have been published so far." – May not be entirely so, in my opinion the studies on iberulite particles did contain information on the internal structures of very large dust particles, see Díaz-Hernández, J. L. and J. Párraga (2008). "The nature and tropospheric formation of iberulites: Pinkish mineral microspherulites." Geochimica et Cosmochimica Acta 72(15): 3883-3906.
→ They investigated the secondary large dust particles by the agglomeration of primary small dust particles via cloud processing to form raindrop. Their Fig. 13 is a type of study similar to ours. Their main structural study shows the association of individual dust particles to form larger particle, but not the internal structures of individual dust particles which is more important in optical modeling. We could not find internal structures of primary African dust particles in literature. Thus, we used word "dedicated". We add word "almost": "almost no investigations dedicated to the analysis of the internal structures…"

166: „lattice fringes of clay minerals perpendicular to the plate (along the c* axis)" – the fringes are probably parallel to the plate and perpendicular to the c* axis (if "plate" is meant as the (001) plane of the clays).
→ It is my mistake. "The lattice fringes of clay minerals perpendicular to the plate (c*-axis)" was replaced by "The lattice fringes of clay minerals parallel to basal plane"

Section 3.1.1: instead of "first", "second" and "third" clay particles, please use something else ("type 1"?) because it sounds as if only three particles were looked at.
→ Since we used "type" in section 3.2, using the word here may confuse the readers. We deleted "first", "second" and "third", and inserted #1, #2, and #3 to keep consistency with Figure captions. "TEM data for three clay-rich particles" was changed to TEM data for three clay-rich particles showing different internal structures."

297: magnetite (200) has also 4.2 A spacing (although I agree that goethite is more likely)
→ Here we show more spacings (nm) which are consistent with those of goethite. We modified the inset in Fig. 12c adding one spacing.



<Changes in the revised manuscript>

We have revised following the comments by referees.
- Addition of two Supplementary Figures and one Supplementary Table.
- Addition of EDXS spectrum of goethite on Fig. 5g.
- Enlargement of some TEM images including lattice fringes.
- Increasing font size of the annotation on the TEM images.
- Changes in the manuscript are highlighted with yellow color below.

Abstract: Mineral dust interacts with incoming/outgoing electromagnetic radiation in the atmosphere. This interaction depends on the microphysical properties of the dust particles, including size, mineral composition, external morphology, and internal structure. Ideally all these properties should be accounted for in dust remote sensing, the modeling of single-scattering properties, and radiative effect assessment. There have been many reports on the microphysical characterizations of mineral dust, but no investigations of the internal structures of individual dust particles. We explored the interiors of Asian dust particles using the combined application of focused ion beam thin-slice preparation and high-resolution transmission electron microscopy. The results showed that individual dust particles consisted of numerous mineral grains, which were organized into several types of internal structure: single and polycrystalline cores of quartz, feldspars, calcite, and amphibole often with oriented clay coatings; individual clay agglomerates of nano-thin clay platelets showing preferred to random orientations commonly with coarser mineral inclusions; and platy coarse phyllosilicates (muscovite, biotite, and chlorite). Micron to submicron pores were scattered throughout the interior of particles. Clays in the coatings and agglomerates were dominated by nano-thin platelets of the clay minerals of illite-smectite series including illite, smectite, and their mixed layers with subordinate kaolinite and clay-size chlorite. Submicron iron oxide grains, dominantly goethite, were distributed throughout the clay agglomerates and coatings. Unlike the common assumptions and simplifications, we found that the analyzed dust particles were irregularly shaped with birefringent, polycrystalline, and polymineralic heterogeneous compositions. Accounting for this structural and mineralogical makeup may improve the remote sensing retrieval of dust and the evaluation of radiation effects, but will also require sophisticated single-scattering modeling. In particular, the observed internal structures of dust particles such as clay coatings, preferred orientation, embedded grains in clays, and pores, have the potential to considerably impact on the light scattering by dust particles. The distribution and size of structural components with contrasting dielectric properties, such as iron oxides, should also be explicitly accounted for.

1. Introduction

Mineral dust interacts with atmospheric incoming/outgoing electromagnetic radiation, contributing to Earth's radiative balance (Sokolik and Toon, 1996; Tegen and Lacis, 1996; Posfai and Molnar, 2000; Formenti et al., 2011). The net radiative effect of natural and anthropogenic mineral dust, sulfate, and organic carbon aerosols is considered to be negative (Forster et al., 2007). In the case of mineral dust, Forster et al. (2007) reported net direct radiative effects ranging from –0.56 to +0.1 W m^{-2}. However, regional observations showed that the direct radiative effect of dust can vary considerably, ranging from –130 W m^{-2} over the ocean off the coast of West Africa (Haywood et al. 2003) to +50 W m^{-2} over land in North Africa (Haywood et al., 2005). The uncertainty associated with the net radiative effect of dust is large (Forster et al., 2007) and is attributed to dust particles' microphysical properties such as particle size, shape, and composition; including inhomogeneity and common birefringence, as well as uncertainties in spatiotemporal global distributions (Nousiainen, 2009). Remote sensing provides detailed information on the atmospheric loading, distribution, migration, particle size, and even some mineralogical properties of dust (Seinfeld et al., 2004; Chou et al., 2008; Kim et al., 2008; McKendry et al., 2008; Chudnovsky et al., 2009; Chen et al., 2011; Haywood et al., 2011; Lenoble et al., 2013). Therefore, it would be ideal for all microphysical properties to be faithfully accounted for when computing the dust single-scattering properties that are applied to radiative effect estimations and remote-sensing retrievals (Sokolik et al., 2001; Forster et al., 2007). For example, an early inversion algorithm for AERONET (AErosol RObotic NETwork) developed by Dubovik and King (2000) assumed homogeneous isotropic spherical particles. However, later applications of the spheroidal particles allowed for more accurate fitting of observed radiation intensity and polarization (Dubovik, 2006).

Extensive microphysical characterizations have been performed for single dust particles to determine their chemical composition (Okada et al., 1990; Anderson et al., 1996; Ro et al., 2005; Gao et al., 2007; Kandler et al., 2007), mineralogical composition (Jeong, 2008; Jeong et al., 2014), and particle size distributions (Reid et al., 2003). Microphysical properties are determined by the laboratory analyses of dust samples on a filter or the real-time analysis of particles through means such as optical particle counting and single particle mass spectrometry, to determine size, morphology, and chemical or mineralogical types (Kulkarni et al., 2011 and references therein). However, a 'single' particle is rarely a single crystal or mineral, but commonly polycrystalline and polymineralic (Falkovich et al., 2001; Jeong, 2008; Jeong et al., 2014). Thus, the microphysical data obtained from 'single' particles are often the result of the numerous mineral grains, composed of different mineral species. Nevertheless, dust particles have usually been grouped into several chemical and mineralogical types based on the resultant properties (Anderson et al, 1996; Gao et al., 2007; Jeong et al., 2014). However, despite the abundant reports, the microphysical properties of individual dust particles have not been fully resolved. While information about the chemistry, mineralogy, external morphology, and size distribution of 'single' particles are needed when modeling the single-scattering properties of mineral dust, they do not offer information about the internal structure of the particles. All these information are needed to yield the true single-scattering properties. Hereafter, we will denote the particle size, shape, composition and internal structure as microphysical properties, which are input to single-scattering models that produce the optical (single-scattering) properties as output.

The geometric characteristics of the internal structure of single dust particles and the varying dielectric properties of the structural components are largely unknown key factors in the evaluation of dust-particle single-scattering properties. For example, Vilaplana et al. (2006) found that the linear polarization of scattered radiation has fundamentally different size dependence and characteristics in terms of absorbing dust particles with or without internal structure. Likewise, Nousiainen et al. (2011a) observed that the single-scattering properties of spheroids with empty cavities could not be mimicked by solid spheroids of varying sizes, shapes and compositions, suggesting fundamentally different single-scattering properties as a result of particle porosity. Similarly, a modeling study by Nousiainen et al. (2011b) found that, for irregular ice crystals, the internal structure had the greatest potential of all the parameters considered to change single-scattering properties. Nousiainen et al. (2003) and Muinonen et al. (2009) found that internal structure, assumed in their studies to be random structure in the absence of observational data, is

potentially quite significant for the single-scattering properties of dust particles much larger than the wavelength. In contrast to considerable efforts expended to investigate how the single-scattering properties of dust particles depend on particle shape (e.g., Nousiainen 2009; Nousiainen and Kandler 2014), relatively little attention has been paid to effects arising from internal structures. Undoubtedly the main reasons for this are the general lack of information regarding the microphysical characteristics of the particle interiors and the limitations imposed by the computational methods needed to solve single-scattering properties.

Iron oxides of complex refractive indices with large real and imaginary parts contribute greatly to the single-scattering properties of mineral dust (Sokolik and Toon, 1999; Lafon et al., 2006; Koven and Fung, 2006; Balkanski et al., 2007; Derimian et al., 2008; Moosmüller et al., 2012). However, calculations have shown that their contributions vary greatly depending on assumptions about the mixing state and mineralogy of iron oxides (Sokolik and Toon, 1999; Lafon et al., 2006). Direct analyses of mixing state and mineralogy were rarely performed for individual particles (Díaz-Hernández and Párraga, 2008; Conny, 2013; Jeong et al., 2014). Díaz-Hernández and Párraga (2008) observed the internal structures of the iberulite, an aggregate of Saharan dust particles wetted in raindrops using a back-scattered electron imaging of polished section. They presented a part of transmission electron microscopic images of ultramicrotome section. Conny (2013) applied focused ion beam (FIB) technique to expose the cross sections of urban dust particles which were analyzed by scanning electron microscopy (SEM). Adler et al. (2013) applied FIB-SEM to analyze the internal pores of organic aerosol. Jeong et al. (2014) combined SEM and transmission electron microscopy (TEM) to characterize the physical and chemical properties of Asian dust particles. A combined application of FIB and TEM is the best method in the high-resolution analysis of mixing state and mineralogy of dust particles. Despite some attempts, almost no investigations dedicated to the systematic analysis of the internal structures and mineralogical makeup of individual dust particles have been published so far. Consequently, the impact of these factors on dust single-scattering properties and radiative effects, as well as on the interpretation of remote sensing data, remains largely uninvestigated, or has otherwise been based on hypothetical models of internal structure (Nousiainen, 2009 and references therein). Yet, these are clearly important factors to consider in radiation-related applications.

In this study, we explored the interiors of individual Asian dust particles using high-resolution TEM. Electron-transparent thin slices were prepared for TEM analysis using an FIB technique. We report the structural and mineralogical details of the Asian dust particles, and discuss the implications of our findings for single-scattering properties and, consequently, for remote sensing and radiative effects.

2. Samples and Method

Asian dust storms occurring in the Gobi desert affect East Asia in Spring (March–May) season. Dust-laden air mass moves eastward crossing Korea, Japan, and North Pacific Ocean. Almost real time satellite remote sensing data of Asian dust are uploaded with PM_{10} level on the website of Korea Meteorological Administration. Dust sampler was operated for several days after dust storm outbreak was identified in the Gobi desert from the remote sensing data. PM_{10} data indicate the arrival time of the Asian dust around the sampling site. Dust particles were collected on a borosilicate glass-fiber filter using a Thermo Scientific high-volume TSP sampler around Seoul on March 31, 2012 and in Andong, Korea, on March 17, 2009. Meteorological, mineralogical, and physical properties of the 2012 dust were previously reported by Jeong et al. (2014). Satellite dust-index images (National Meteorological Satellite Center, 2013) showed that the source of both the 2012 and 2009 dusts was the Gobi desert, situated around northern China and southern Mongolia.

The individual dust particles on the filter were preliminarily examined using a TESCAN LMU VEGA scanning electron microscope (SEM), equipped with an IXRF energy dispersive X-ray spectrometer. The SEM analysis showed that most dust particles were not tightly agglomerated but separated each other. Individual dust particles were able to be identified on the filter. Since the unstable dust particles lying on the porous filter were not suitable for FIB milling, they were

transferred onto a conductive carbon adhesive tape. An SEM stub covered with carbon tape was lightly touched onto the filter surface. After thin platinum coating for 60 s for conduction, the predominant mineralogy of the dust particles was analyzed using energy dispersive X-ray spectrometry (EDXS). High-resolution SEM images were acquired with a JEOL JSM 6700F field emission gun (FEG) SEM.

Dust particles for FIB sample preparation were selected on the basis of the predominant particle mineralogy and morphology determined by EDXS and FEG SEM. We selected only individual dust particles spaced sufficiently from other particles, excluding particles that are too close, forming a cluster. The SEM stub was placed on a SMI3050TB FIB instrument for preparing thin slices of approximately (5~12) × (5~6) μm^2 area and about 100 nm in thickness. Carbon was first deposited on the target particle in a thickness of ~1 μm to protect the loose and porous agglomerates of fine mineral grains from ion beam damage and spalling, and then a gallium ion beam was sputtered to cut one thin slice from each individual dust particle. Amorphous carbon deposition was applied to the surface of target particle, and normally did not affect the interior of particle. However, in some case, carbon entered into and filled large pore probably connected to the surface (Fig. 3c). Altogether 35 FIB slices were prepared from 35 dust particles, and analyzed by TEM. Of these, 26 slices had a good flatness and a wide area sufficient for the TEM analysis. However, only a limited analysis of a small area was possible in 9 slices, which had broken due to the cleavage of minerals or loose agglomeration during the handling of micron-size slices in the FIB instrument or in the TEM chamber. Some of the slices were not suitable for lattice fringe imaging due to their thickness. The FIB slices were imaged using three microscopes: a JEOL JEM 2100F FEG STEM at 200 kV and a JEOL JEM 3010 at 300 kV for high-resolution imaging, and a JEOL JEM 2010 TEM at 200 kV equipped with an Oxford energy dispersive X-ray spectrometer for EDXS analysis. TEM images were recorded using a Gatan digital camera, and processed with Gatan DigitalMicrograph®.

Combined application of TEM and FIB slicing is the best method imaging the internal structures of dust particles. Unfortunately, the FIB slicing cannot be applied to a large set of dust particles because it is expensive and needs complex operation, particularly for irregular, weak agglomerate particles. However, the 35 particles were carefully selected from thousands of particles which had been already classified into minerals and mineral groups based on their morphological and chemical characterization by extensive SEM and EDXS analyses like in Jeong (2008) and Jeong et al. (2014). In addition, the mineralogical features of the Asian dust varied little through different events over many years (Jeong, 2008; Jeong et al., 2014). Thus, the internal structures presented here are representative of the Asian dust particles.

Artifacts reported in the FIB slicing are surface amorphization, Ga contamination, and curtain effect (Ishitani et al., 2004; Kato, 2004; Mayer et al., 2007). Our FIB slices showed sufficiently clear TEM images without the destruction of microstructural details and lattice fringes, indicating that surface amorphization was restricted in very thin surface region, and had little influence on the image quality. Ga was only detected around the boundary between carbon deposit and dust particle by EDXS analysis, but not within the particle interior. Curtain effects (stripes of light and dark contrast) arising from topography and phase property (pores, mineral chemistry, and density) were observed in some of the TEM images (e.g., Figs. 5c, 7d, 9c, 10c, and 11d), with no significant degradation of image quality. Finally, pores found in the particle interiors were not formed by FIB milling. In traditional ion milling, Ar ions bombard the sample surface at higher angles, making a hole in the center. The thin edge around the hole is then analysed by TEM. Thus, preferred erosion may occur along the weak parts of the samples such as grain boundary and poorly crystalline phases, resulting in pore-like features around large center hole. However, in FIB milling, Ga ions are bombarded almost parallel to the sample surface, without forming artifact pores in most cases. This is one of the most important advantages of FIB milling of geological samples compared to the traditional Ar ion milling. Our TEM images discussed in later section 3.1 preserve the large and small pores of delicate shapes, all of which are reasonably interpreted on the basis of grain agglomeration and mineral growth/dissolution.

Mineral identification was based on lattice fringes and EDXS chemical compositions. General chemical formulas of minerals identified in the Asian dusts examined in this study are provided in

the Supplementary Table 1. The identification of non-phyllosilicate and relatively coarse phyllosilicate minerals (muscovite, biotite, and chlorite) was straightforward, but that of nano-thin phyllosilicates (clay minerals) was difficult. The lattice fringes of clay minerals parallel to basal plane were recorded normally above the magnification of ×200,000. The identification of clay minerals was based on the spacings of lattice fringes corresponding to the spacing of repeat units of the crystal structures: 1.0 nm for illite, ~1.0 nm for smectite and vermiculite, ~7.0 nm for kaolinite, and ~1.4 nm for chlorite (Fig. 1). Kaolinite and chlorite were directly identified from their EDXS and lattice fringes (Fig. 1). However, illite, smectite, vermiculite, and illite-smectite (vermiculite) mixed layers could not be positively distinguished from each other because smectite (1.4–1.6 nm unit layers in hydrated state) was dehydrated and contracted under the high vacuum of the TEM chamber, showing ~1.0 nm lattice fringes similar to those of illite (1.0 nm lattice fringe) (Fig. 1) (Peacor, 1992). EDXS can be used for identifying illite and smectite with interlayer cations K and Ca, respectively. However, although illite could form a thick plate and be positively identified from the clear 1.0-nm lattice fringe and high K and Al contents, illite and smectite platelets are normally very thin, consisting of only a few repeat units. They cannot be separately analyzed using EDXS, even when using an electron microbeam that is as small as possible. Additionally, mixed layering of illite and smectite is common in the soil and geological environments (Weaver, 1989, Środoń, 1999). Therefore, in practice, we cannot distinguish between nano-thin illite and smectite. To avoid over-interpretation, nano-thin platelets of clay minerals showing ~1.0 nm lattice fringes with varying K and Ca contents were grouped into illite-smectite series clay minerals (ISCMs). ISCMs are likely nano-scale mixtures of nano-thin platelets of illite, smectite, and illite-smectite mixed-layers.

3. Results and Discussion

In what follows, we will first present the results of our TEM analyses of dust particles. Schematic models for the common structural types observed will then be proposed. Finally, we will discuss the possible implications of the structural features discovered on dust optical modeling and on climate and remote sensing applications. Detailed TEM data of 12 dust particles are presented in Figs. 2–13. TEM data of other 14 particles are summarized in Supplementary Fig. 1.

3.1. TEM observations

3.1.1. Clay-rich particles

TEM data for three clay-rich particles showing different internal structures are presented here because they are the most abundant particle type in Asian dust (Jeong, 2008; Jeong et al., 2014). SEM images of the clay-rich dust particle #1 show a rough surface composed of submicron clay grains (SEM images in Figs. 2a, b). Low-magnification TEM images of the FIB slice prepared from the particle in Fig. 2a show an agglomerate of randomly oriented platelets of clay minerals, which are tightly interlocked with each other (Fig. 2c). EDXS analyses suggest that the clays are mainly ISCM with some chlorite and kaolinite. Minor quantities of submicron iron and titanium oxide grains are also randomly distributed in the clay matrix (Fig. 2c). Confirmation of the specific mineral species of the iron and titanium oxides was not possible because the quality of lattice fringes were poor due to the large slice thickness. The areal fractions of these oxides in Fig. 2c are approximately 0.9 and 0.3%, respectively. High-magnification TEM images of the clay show loose, disrupted, and nano-thin clay platelets (Figs. 2d–f). Lattice fringes confirm ISCMs (Figs. 2e–f) intermixed with coarser platelets of chlorite (Fig. 2e) and kaolinite (Fig. 2f). There are many pores (total 2.2%) of approximately 1 μm in diameter (Fig. 2c). Thin lenticular pores may have been formed through the dehydration of subparallel platelets of expandable clay minerals such as smectite in the high vacuum TEM chamber (Peacor, 1992). However, some of the circular pores (arrow in Fig. 2c) are unlikely to have formed in this way by dehydration. They may have been formed by soil process, particularly repeated cycles of wetting-drying and freezing-sawing in the dry and cool sources of Asian dust.

The clay-rich agglomerate particle #2 also displays a rough surface with micron-to-submicron-sized clay grains (Figs. 3a, b). The mineral grains are at least to some degree preferentially oriented. A TEM image of the slice reveals a large pore size of approximately 4 μm (Fig. 3c), which is certainly not the result of the contraction of expandable clay minerals. The pores (16.3%) are now filled with carbon that was deposited during FIB slicing. The clay matrix is dominated by nano-thin ISCM platelets embedded with rather large packets of chlorite, kaolinite, and discrete illite (Fig. 3c). Non-phyllosilicate particles of quartz, plagioclase, epidote, and iron oxides were also scattered within the clay matrix. Iron oxides are present in minor quantities (0.6%) and approximately 200 nm in size.

The clay-rich agglomerate particle #3 (Figs. 4a, b) has rough surface exhibiting submicron clay particles. The low-magnification TEM image shows highly oriented fabrics (Fig. 4c). Magnified images (Figs. 4d, e) reveal submicron particles of quartz, plagioclase, K-feldspar, biotite, discrete illite, and titanium oxide, the long axes of which were oriented conformably with the fine matrix of oriented nano-thin ISCM platelets. The platelets are generally curved and subparallel to each other (Fig. 4f). Both the lattice fringe imaging and EDXS confirmed that ISCMs are the dominant clay minerals (Fig. 4f). Some long, thin lenticular pores are certainly attributable to the contraction of expandable clay minerals under the vacuum (Fig. 4c). However, the other pores were not formed by dehydration (arrow in Fig. 4c).

The external morphology and surface features of the three clay-rich particles are similar. However, a TEM analysis of the slices shows that the large differences in fabrics depend on the array pattern and sizes of phyllosilicate platelets, pores, and coarser inclusions. Nano-thin ISCM-rich clays are the major constituents of the matrix, scattered with submicron iron and titanium oxides.

3.2. Structural models

To facilitate the optical modeling of mineral dust particles, the internal structures observed in Asian dust particles were grouped into idealized classes. We identified three major types of internal structure: Type I, coarse non-phyllosilicate minerals; Type II, nanocrystalline clay agglomerates; and Type III, coarse phyllosilicate plates.

Type-I dust particles have core grains of non-phyllosilicate minerals including quartz, plagioclase, calcite, K-feldspar, and amphibole in the order of abundance (Fig. 14). They exist as either monomineralic crystals (Figs. 5–9) or polymineralic rock fragments (Fig. 13). The monomineralic particles can also be further described as monocrystalline (Figs. 5, 6, 7, 9) or polycrystalline (Fig. 8). Although some surfaces of the coarser core crystals are directly exposed, almost all the surfaces are covered with nanocrystalline ISCM clay coatings (ca. 0.2–1 μm). Therefore, there are six subtypes, as presented in Fig. 14. In Asian dust sources, all silt-size mineral grains have been observed to be coated with clay minerals according to an electron microscopic analysis of the silty soils as shown in Fig. 4 of Jeong (2008). The clay coatings are features acquired in the source soils via repeated wetting-drying and freezing-thawing cycles.

Type-II dust particles are clay agglomerates composed mainly of nanocrystalline clay minerals (Fig. 15). ISCM is the most abundant mineral group in Asian dust (Jeong et al., 2014). As shown in the Figs. 2d and 4d, the orientations of the nano-thin ISCM platelets are always subparallel in the nano scale. However, at larger scales, fabrics of clay agglomerates are diverse, ranging from complete lamination (Fig. 2c) to random (Fig. 4c). The clay agglomerates often have micron-scale pores of lenticular or irregular shapes (Figs. 2c, 3c, 4c). Agglomerates of pure clays are rare. Many clay-rich agglomerates include larger non-phyllosilicate grains (quartz, plagioclase, K-feldspar, and calcite) and coarser phyllosilicates (muscovite, biotite, and chlorite). Therefore, clay agglomerates could be further classified into eight subtypes (Fig. 15).

Type-III particles are coarse phyllosilicates of muscovite, biotite, and/or chlorite (Fig. 16). The platy morphologies are regulated by the well-developed cleavages along the (001) basal planes. They are commonly coated with ISCM clays. Another feature of the internal structures is the occurrence of goethite (iron-oxyhydroxide) along the cleavages in the weathered biotite and chlorite, which is a feature acquired in the source soils. The lenticular voids occur in the weathered biotite

and chlorite. Although we have not presented the data of muscovite, it is reportedly highly resistant to oxidative weathering due to the absence of iron. Thus, goethite microinclusions and lenticular voids are not expected in the internal structures of muscovite. Coarse phyllosilicates could be further classified into four subtypes, as presented in Fig. 16.

The diameters of the particles milled by FIB in this study are generally large because most of the particles were selected from the coarse Asian dust observed in 2012. In future research to refine the internal structure models, much more attention should be paid to the long-range transport particles with modes around 2–4 μm in equivalent volume/mass diameter (Reid et al., 2003; Zender et al., 2003; McKendry et al., 2008). Nevertheless, we think that particles of several micrometers also have structural features similar to larger particles. In the arid desert soils, fine particles are formed by the repeated saltation, impact, and fragmentation of soil agglomerates by wind. As shown in Supplementary Fig. 2, fine particles derived from coarse agglomerate particles likely have internal structure types summarized in Figs. 14–16.

3.3. Implications for the optical modeling of dust particles

Individual dust particles are often composed of several mineral species. Their mineral grains and pores are arranged to form several types of internal structures, some of which could contribute significantly to the single-scattering properties of mineral dust. Our results imply that the presence of internal structures in natural dust particles is a rule rather than an exception. To quantify their effects on single-scattering properties, sophisticated simulations should be carried out. While this is clearly beyond the scope of the present study, we can nevertheless offer our first impressions and speculate on the possible impacts.

3.3.1. Internal structures

In regards to the geometrical characteristics of the internal structure, the most important factor is the size scale of the structure compared to the wavelength of radiation. This impacts not only the effectiveness of the structure in influencing single-scattering properties (sub-wavelength structures interact with radiation only weakly) but also impacts how it should be accounted for in modeling. If the structures are small compared to the wavelength, and sufficiently randomly located, effective medium approximations (e.g., Chylek et al. 2000) may be used, after which the particle can be treated as a homogeneous material with mean dielectric properties. However, as the example in Sect. 3.3.2 shows, the mixing of dielectrically very different materials can lead to strong effects, and to large errors if all the assumptions are not satisfied. For example, Kocifaj and Videen (2008) investigated errors arising from the use of effective medium approximations for particles that are mixtures of non-absorbing and absorbing constituents, and showed that all single-scattering properties were affected. The backscattering quantities relevant for lidar measurements were most affected. Some of the particles analyzed here also show mixtures of weakly and strongly absorbing constituents. In case of embedded crystals in an ISCM matrix (Fig. 4), the effective medium approximation may perform well, because of the small dielectric constrast between the constituents. Likewise, Kocifaj et al. (2008) reported up to 10 percent error in the asymmetry parameter for coated structures when treated with an effective medium approximation; coated structures are also present in our analyses, e.g., in Fig. 6. For particles with large pores inside, which present large structures with high dielectric contrasts, the effective medium approximations are likely to also fail. Strong effects on single-scattering properties due to internal pores are shown, e.g., by Nousiainen et al. (2011a). Therefore, the pores with fractional areas extending up to 16.3% are clearly significant and should be accounted for explicitly.

Another interesting aspect is that in many particles studied, the internal structure is far from random. Instead, we often see varying types of ordered structure. From the single-scattering point of view, the most important is whether these structures are also preferentially oriented. For example, the embedded constituent crystals may have preferred orientation within the particle (e.g., Figs. 4c–e, Fig 15). Such a structure may act to make the whole particle seemingly birefringent, even if composed of isotropic materials. Whether this is significant for the particles' single-scattering

properties depends on the strength of this structural birefringence and the overall shape of the particle. From Nousiainen et al. (2009) we know that polarization quantities in particles are sensitive to birefringence; whereas, Dabrowska et al. (2012) reports that the effect increases with increasing particle aspect ratio. For example, the preferred orientation of the platelets in clay layers (e.g., Figs. 14 and 16) may give rise to structural birefringence, especially if the particle is elongated, because then there will be more platelets oriented parallel to the longer particle axis than perpendicular to it. Likewise, ordered layered structures, such as those seen in Figs. 10c, 10d, 11c, and 11d, may give rise to structural birefringence. Again, this depends on how preferential the orientations of such structures are in the particle.

3.3.2. Mineralogy

Mineral dust particles can be composed of numerous grains of several mineral species with different refractive indices and sizes. The single-scattering properties of the particles will depend on the internal mixing state, size, and distribution of the constituent grains. For the effect to be substantial, however, the refractive indices of the different grains must vary considerably. Iron oxides are considered to be the most important minerals in this respect, because they are relatively common and the real and imaginary parts of their refractive indices are considerably higher than those for most other mineral species typically encountered in atmospheric dust. There are many reports that even small amounts of iron oxides can be significant for the single-scattering properties of dust. For example, Sokolik and Toon (1999) found that even 1% hematite mixed with kaolinite was sufficient to decrease the dust particles' modeled single-scattering albedo by ~10% when assuming an internal mixture treated with effective medium approximation instead of an external mixture. Similarly, when Balkanski et al. (2007) attempted to constrain dust refractive indices by varying the hematite content in the internal mixture to fit AERONET data, they found that a subtle variation in hematite contents and their mixing state were critical in explaining the observed refractive indices by AERONET, and in evaluating the global net radiative effect. Lindqvist et al. (2013) also found that a few volume percent of hematite was sufficient to impact the simulated single-scattering properties of dust particles.

Confirmations of the specific properties possessed by iron oxides are rare, despite their great importance and many related assumptions. The identification of iron oxide minerals (hematite or goethite) has not been attempted other than by the diffuse reflectance spectroscopic analysis of Lafon et al. (2006). Goethite has different wavelength-dependent refractive indices from hematite (Bedidi and Cervelle, 1993). In addition, the actual impact of iron oxides depends on the grain size and distribution of iron oxides within a particle. For example, widely distributed small iron oxide grains will lead to stronger absorption than a few larger grains of identical total mass.

The results of our study indicate that iron oxides are evenly distributed in the clay agglomerates, normally as submicron-size grains. Lafon et al. (2006), using diffuse reflectance spectroscopy, also showed that goethite was a major iron oxide in dust samples collected near the desert margin of China (38°17'N, 109°43'E). The estimated areal fractions of goethite range from 0.6% to 5.6% for those particles where it was present. The even distribution of submicron goethite particles suggests potentially considerable impacts on the particles' single-scattering properties.

Biotite, chlorite, and their weathered equivalents have also been found above trace quantities in Asian dust (Jeong et al., 2014). Their dark color and iron-rich chemical compositions suggest clearly higher imaginary parts of the complex refractive indices than those of colorless minerals such as quartz, feldspars, muscovite, calcite, or ISCMs. However, their complex refractive indices have not been experimentally measured over a wide range of wavelengths (Mooney and Knacke, 1985). In addition, the grain sizes and spatial distribution of titanium oxides (possibly rutile and anatase) within dust particles are similar to those of iron oxides. Their high refractive indices (Cardona and Harbeke, 1965) may also significantly contribute to the single-scattering properties of dust, which deserve further investigation.

4. Summary and Conclusion

Optical models for the interaction between dust and electromagnetic radiation are important in the evaluation of net radiative effects, and in the processing of remote sensing data. All microphysical properties, including size distributions, particle morphology, and composition should be known and accounted for to allow for realistic optical single-scattering treatment. Of the many uncertainties in bulk microphysical properties, the most uncertain are the properties of individual particles that ultimately govern the radiative effects. Yet, strictly speaking, true bulk optical properties of mineral dust aerosol cannot be obtained without this information, because the single-scattering properties of each particle depend on their size and shape in a composition-dependent way. The use of the same bulk composition for each particle in the single-scattering computations yields correct results only if each particle truly has the same composition, which is not the case. For any heterogeneous particle ensembles, one should compute particle-specific single-scattering properties which, for the additive quantities, can then be averaged. For the most accurate radiative treatments, single-particle microphysical properties are thus needed. In the past, optical models have been based on many assumptions and simplifications of the mineralogical and structural properties of individual particles such as species, size, mixing state, and arrangement of constituent minerals. This study directly explored the interior of individual Asian dust particles, revealing many novel microphysical details of the constituent mineralogy and internal structures.

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Figure captions

Fig. 5. Quartz-rich dust particle #1 from 2009 Asian dust. (a) SEM image of the dust particle. (b) SEM image of the particle surface magnified from the box in (a). (c) Overall TEM image of the FIB slice prepared from the particle in (a). (d, e) TEM images magnified from the box in (c). (f) TEM lattice fringe image of ISCMs. (g) Goethite spheres magnified from the box in (c) with the EDXS pattern of goethite.

Fig. 14. Type-I structural models for single and polycrystals of quartz, plagioclase, K-feldspar, and calcite with clear or clay-coated surfaces. Clay minerals are dominated by ISCMs.

Fig. 15. Type-II structural models for ISCM-clay-rich particles with preferentially or randomly oriented nano-thin clay platelets, and with pores and inclusions of nonphyllosilicates, micas (muscovite and biotite), and chlorite.

Fig. 16. Type-III structural models for plates of micas (muscovite and biotite) and chlorite, which

are either fresh or weathered. Weathered biotite and chlorite contain goethite crystals and lenticular pores.