Atmos. Chem. Phys. Discuss., 14, C1204–C1222, 2014
www.atmos-chem-phys-discuss.net/14/C1204/2014/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "TEM analysis of the internal structures and mineralogy of Asian dust particles and the implications for optical modeling" *by* G. Y. Jeong and T. Nousiainen

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Reply to the comments by anonymous referee #1

We appreciate the referee's valuable comments.

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

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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 will delete “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 question is how the distribution and size of structural components with contrasting dielectric properties will impact the radiative transfer modelling. The short answer is: through the single-scattering properties, which are input to radiative transfer simulations. The question is then how the single-scattering properties

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will be affected, and this depend, on the one hand, on the characteristics of these structures, and on the other hand, how they are accounted for when computing the single-scattering properties. As the examples of the latter, this inhomogeneity can be explicitly accounted for, or some kind of effective refractive index may be derived after which the particles may be treated as homogeneous. It is well known that the use of the effective refractive index can sometimes cause considerable errors. Two cases in particular could give rise to considerable effects on the single-scattering properties that require explicit incorporation of the structure to obtain accurate results: the presence of highly absorbing constituents such as hematite or goethite in the particles, or the presence of porous cavities in the particle. In the former case, explicit treatment is needed, because otherwise the overall absorptivity of the particle will be considerably in error. In the latter case it is needed, because the scattering properties of homogeneous and porous structures may be fundamentally different. A good example is demonstrated by Vilaplana et al. (2006). As for some of our particles, both of these two special cases take place in the same particle, it is obvious that there is a great potential for a considerable effects in the single-scattering properties, the correct estimation of which requires sophisticated modelling. We intend to quantify these effects in a follow-up paper, so that we can do it properly. To include such an investigation into this manuscript would probably almost double the length of the paper and would take months of planning and simulations. Some simple simulations could be carried out quickly and included with little additional space requirements, but as pointed out above, this would not provide us with a correct estimation of the effect. As similar sensitivity studies have already been published in the literature (and cited by us), the additional benefits for the present manuscript of such simulations seem questionable. There will be some modifications to clarify these issues.

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”.

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Reply Line 91: We will change “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 relation 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 suggest to add 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.”

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

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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 & EDX 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 will be addition or modification in revised version to clarify this issue.

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 $\times$ 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

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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) $\times$ ca. 100 nm (thickness) $\times$ (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.

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 will clarify this matter in revised version. In Suppl. Fig. 3, we attach the TEM images of other 14 slices with additional two slices which have been included in Jeong et al. (2014).

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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 will revise 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$\sim$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" will be 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 (crys-

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tal 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 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, min-

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eral 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 Suppl. Fig. 4). 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.

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 will be added in finally revised version.

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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 will be 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 already 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) of current ACPD paper.

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 sawing also induce the mixing of soil particles. In all these soil process,

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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. 5 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 will delete ", and do not form in the atmosphere through, for example, cloud processing."

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: Unless we spend months in doing the said computations and almost double the manuscript length in describing the theory, methodology and results obtained, all we can offer is simple sensitivity tests similar to those already carried out in the literature (see, e.g., Vilaplana et al. (2006), Lindqvist et al. (2011), Nousiainen et al. (2011)). It is our impression that the sensitivity tests carried out in the literature 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 this part is, of course, an option, but undesirable, as the atmospheric radiative effects were one of the major motivations for this study.

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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: For wavelength-scale particles, volume-integral methods such as the discrete-dipole approximation can handle almost any kind of model particles. For larger particles these methods will be too slow. However, as long as those microphysical models are not even known, they cannot be account for except as sensitivity studies. It would be desirable to do such sophisticated simulations even in small scale, for a limited sample, to aid the parameterization work. Regarding averaging, this applies especially to the refractive index, which follows from the mineralogical composition. For example, if there are iron-rich and iron-poor particles in the ensemble, the ensemble will scatter differently to the case where all particles have the same average composition, Further, shapes and compositions and sizes correlate, which will be an issue in sophisticated modelling. The issue about the terminology regarding microphysical and single-scattering properties has been addressed above. 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.

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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 will delete 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.

With the closing of discussion forum, we will prepare final version considering comment and reply above.

Sincerely

On behalf of co-authors

Gi Young Jeong Corresponding Author

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 6619, 2014.

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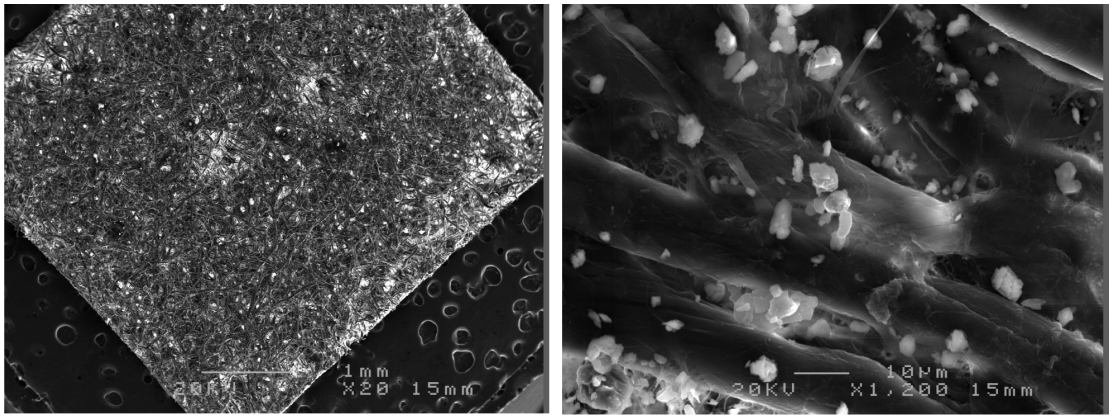
Interactive Comment



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

Fig. 1. Suppl. Fig. 1

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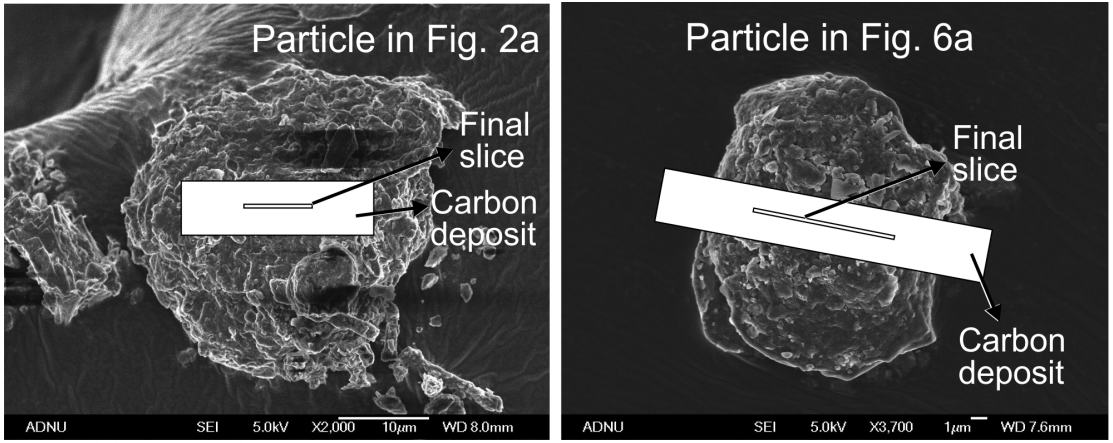

Suppl. Fig. 2. Carbon deposition area (white) on the surface of individual dust particle and location of final slice.

Fig. 2. Suppl. Fig. 2

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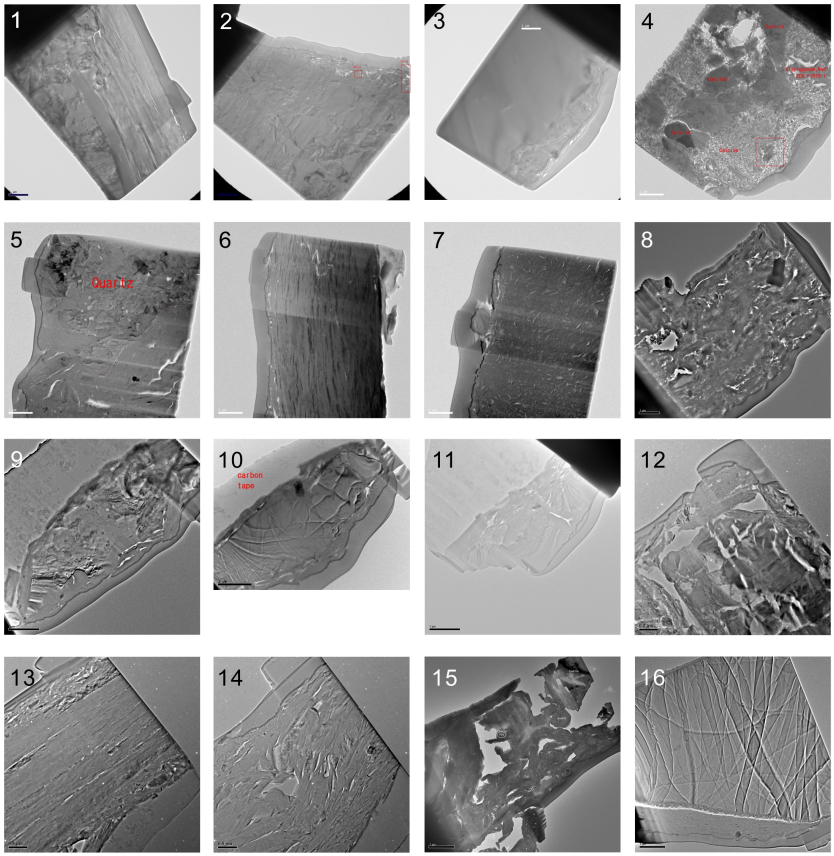

Suppl. Fig. 3. Low magnification TEM images of 14 cross-sectional slices not included in this ACPD paper (1–14). Slice 15 and 16 were included in Jeong et al. (2014)

Fig. 3. Suppl. Fig. 3

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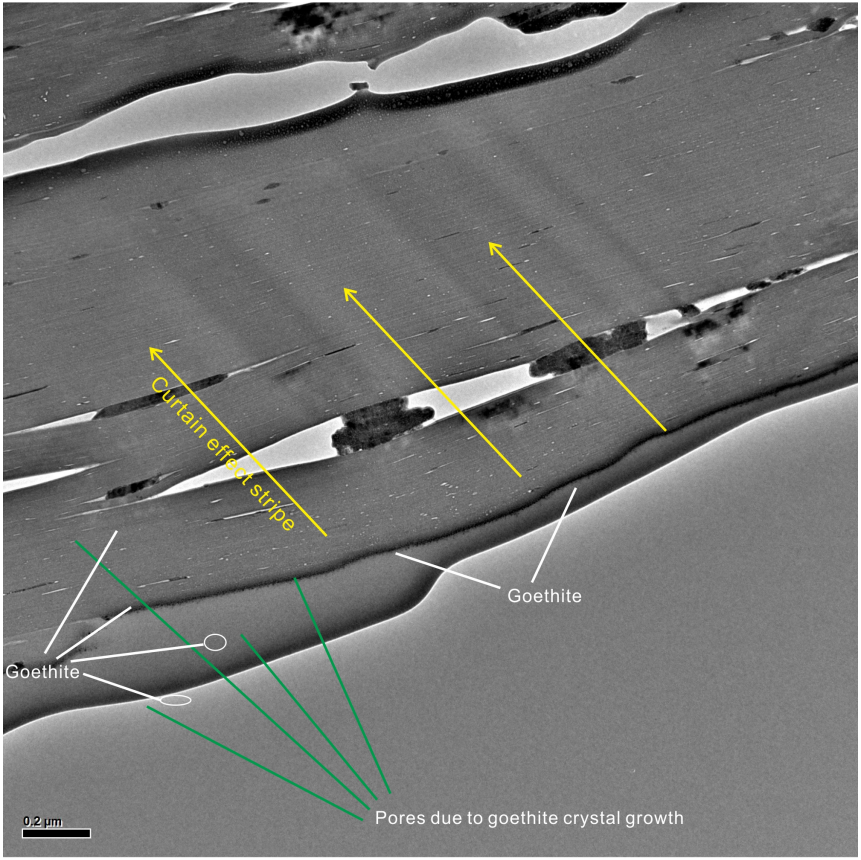

Suppl. Fig. 4. Curtain effect observed in Fig. 11d.

Fig. 4. Suppl. Fig. 4

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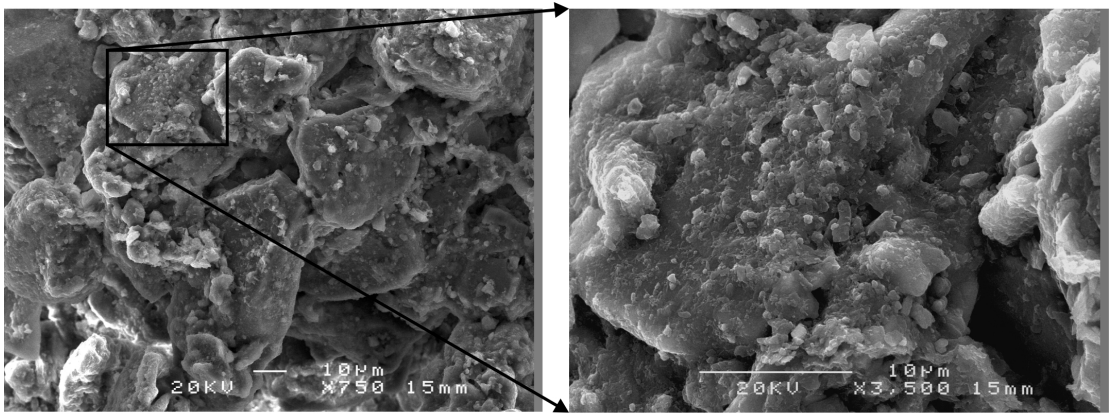

Suppl. Fig. 5. SEM of Gobi desert soil. Coarse grains (several tens micrometer) are coated with fine clay mineral grains <1~2 μm.

Fig. 5. Suppl. Fig. 5

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