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Impact of Cloud Process in the Mixing State and Microphysical Properties of Soot Particles: Implications in Light Absorption Enhancement

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Key Points:

- Cloud processing contributes to the increase of organic coating on soot aggregates, especially for those with fully embedded structure.
- The sulfate coating causes more compaction of soot aggregates than the organic coating upon cloud processing.
- Changes in the microphysical properties of soot particles driven by one cloud event increase their absorption enhancement by 1.29 times.

Abstract

The radiative forcing of soot is dependent on the morphology, mixing state and structure. Cloud processing has been predicted to affect their mixing properties but little is known about the resulting light absorption properties. We collected ambient particles in the pre-cloud period, the cloud residues and interstitials in the in-cloud period at Mt. Tianjing (southern China). The morphology parameters of soot aggregates with varying mixing materials (sulfate (S) and organics (OM)) and mixing structures were investigated by a transmission electron microscope, and their absorption cross section were calculated based on discrete dipole approximation. We found that the number contribution of soot-S decreased from 45% in the pre-cloud period to 32% in the in-cloud period, and that of soot-OM increased from 44% to 60%. Moreover, the number proportion of soot-OM with fully embedded structure increased remarkably in the in-cloud period (29%), compared with that in the pre-cloud period (3%). In addition, the soot-S aggregates became denser after in-cloud aqueous process. However, for soot-OM aggregates, the morphology remained relatively constant. The distinctly different change of soot-S and soot-OM in morphology highlights the chemically resolved reconstruction of soot morphology. Theoretical calculation further shows that the changes of soot particles in the mixing state and morphological characteristics by the cloud process resulted in the light absorption enhancement increase from 1.57 to 2.01. This study highlights that the evolution of microphysical properties upon cloud processing should also be considered in climate models to more accurately evaluate the impacts of soot particles.

Plain Language Summary

While soot particles are the main component of aerosols that produce positive radiative forcing in clouds, the impact of in-cloud processes on key factors (mixing state and microphysical property) for evaluating the optical properties of soot particles is unclear. Here, we report the detailed information on several parameters required to calculate the optical properties of soot particles, throughout the cloud events. And we found that changes in the mixing state, mixing structure, and morphology of soot particles under the influence of in-cloud processes lead to a significant light absorption enhancement. The results also highlight the role of in-cloud aqueous formation of secondary compositions in reshaping the soot particles, which has substantial implications for the climate impact of soot particles. Given that ~70% of the Earth's surface is covered by clouds, taking the mixing state and microphysical properties of soot particles into account in climate models may help constrain the contribution of soot particles to global radiative forcing.

1 Introduction

Soot, also known as black carbon (BC) or elemental carbon (EC) [Buseck et al., 2014], is deeply concerning because it has a multitude of effects on the global atmosphere and Earth's surface. It is the second largest contribution to warm the atmosphere after carbon dioxide [Jacobson, 2001]. Soot particles in the atmosphere exhibit complexity in size, composition, morphology, and mixing structure, which results in the high uncertainties in climate models when predicting their optical properties [Lack and Cappa, 2010; Liu et al., 2017a; Zhang and Mao, 2020] and CCN activity [Li et al., 2018; Liu et al., 2013].

The chemical and physical properties of soot particles are dynamic and vary with aging processes during atmospheric transport. They are sensitive to the formation of secondary components and atmospheric conditions, leading to complex and ever-changing mixing state and mixing structure of soot particles [Liu et al., 2017b; Zelenyuk et al., 2010; Zhang et al., 2018]. Fresh soot particles emitted from biomass burning and fossil fuel combustion are hydrophobic with bare-like structure, which generally shows the chain-like structure composed of several nanospheres with onion-like and graphene-like layers of carbon [Buseck et al., 2014; Li and Shao, 2009]. As the degree of aging increases, the soot aggregates are wrapped thicker and become more compact, resulting in more partly coated and/or fully embedded soot particles [China et al., 2014; China et al., 2015b; Wang et al., 2017; Xu et al., 2020], and higher absorption enhancement [Wu et al., 2018]. The mixing structure and morphology parameters of soot particles are key factors to calculate their optical properties [Adachi

et al., 2010; Cappa et al., 2012; Yu et al., 2019]. From the bare-like structure to being gradually coated by other components, the light absorption of soot particles will be significantly enhanced by factors ranging from 1 to 3.5 [Wu et al., 2018]. And, the optical properties of the bare-like soot aggregates with diverse fractal degrees are also different [Radney et al., 2014; Wang et al., 2021b]. Additionally, soot aggregates coated by various materials may redistribute after liquid-liquid phase separation (LLPS) under high relative humidity, which could lead to an inverted core-shell structure (soot aggregates are distributed in the outer layer of the two-phase particle) [Brunamonti et al., 2015]. Consequently, the core-shell model (concentric spheres composed of soot nuclei and coating) assumed in current climate models results in higher uncertainty of light absorption compared to observations, either overestimation [Cappa et al., 2012; Wu et al., 2018] or underestimation [Kelesidis et al., 2022]. Therefore, an accurate understanding of the mixing structure and morphology parameters of soot particles is crucial for the climate model to evaluate their radiative forcing.

Previous studies have shown that cloud could modify the mixing state and morphology of atmospheric particles [China et al., 2015a; Liu et al., 2018], through collision/coalescence and Brownian capture as well as aqueous reactions. The reconstruction of soot aggregates has been found in high humidity environments such as fog and cloud events [Bhandari et al., 2019; China et al., 2015a], which is affected by the mixing state of soot particles [Khalizov et al., 2009; Qiu et al., 2012; Zhang et al., 2008]. High humidity condition during cloud process can promote the formation of various species including inorganic (such as nitrate, sulfate, and ammonium) and

organic substances (such as oxalic acid, organosulfate) [Kim et al., 2019; Schneider et al., 2017; Zhang et al., 2017b]. While the physical and chemical properties of organic matter have been observed to bring about varying mixing structure and structural reorganization of soot particles [Chen et al., 2020; Chen et al., 2016; Sharma et al., 2018], how the cloud processing driven changes in the mixing state of soot particles affects their microphysical properties is poorly understood yet.

In order to study the effects of cloud processes on mixing state and microphysical properties of soot particles, samples during pre-cloud and in-cloud periods at a remote high-altitude site in southern China were collected and analyzed. We investigated the changes of morphology parameters (i.e., fractal dimension, aspect ratio, roundness, and size) of soot aggregates with different mixing states and mixing structures from pre-cloud to in-cloud periods. The possible influencing factors such as different coating materials and mixing structures were discussed. Finally, the effect of cloud processing on the light absorption of soot particles was evaluated.

2 Methods

2.1 Sampling and Instrumentation

A field observation focused on the cloud events was conducted from May 8 to June 3, 2018 at an atmospheric observation station (112°53′56″ E, 24°41′56″ N; 1690 m above sea level) on the top of Mt. Tianjing. There is a pristine forest covering 273 km^2 and few anthropogenic emissions around the sampling site. Cloud events are prevalent due to the influence of warm and humid air masses from the South China Sea [Lin et al., 2019]. The cloud events investigated in this study were mainly affected by local

biogenic sources and long-range transport from the southwest air masses (**Fig. S1**). Soot particles mainly come from combustion activities in Southeast Asia and industrial emissions in the urban agglomeration of southern China [Zhang et al., 2017a].

A ground-based counterflow virtual impactor (GCVI, model 1205, Brechtel Mfg. Inc., USA) was used to introduce cloud droplets larger than 7.5 μm into the subsequent system [Shingler et al., 2012]. During cloud processes, cloud droplets and unactivated particles are introduced into the inlet of the GCVI, a wind tunnel, which can accelerate droplets or particles to 100 m s^{-1}. The flow rate of the filtered and heated add-flow can be adjusted in the range of 16-23 L min^{-1} to ensure the cut size of 7.5 μm with the transmission efficiency of 50%. The flow rate of sample-flow is kept at a constant 15 L min^{-1} for multiple instruments downstream. The cloud droplets went through an evaporation chamber (40 ℃) to remove the associated water, leaving the cloud residual (RES) particles for the follow-up particle sampling or on-line analysis. The add-flow with high temperature indirectly controls the sample-flow temperature of evaporation chamber. Some semi-volatile organic compounds will be lost under heating, and the loss at 40 ℃ may be less than 1% [Cao et al., 2018]. In addition, a $PM_{2.5}$ cyclone inlet followed by a silica gel diffusion dryer was used for the collection of inactivated interstitial (INT) particles during the cloud events and the ambient particles during free-cloud periods.

A DKL-2 sampler (Genstar Electronic Technology Co., Ltd., China) employing a single-stage cascade impactor with a 0.5 mm diameter jet nozzle was used to collect individual particles on copper grids coated by carbon film (300 mesh, Beijing

Zhongjingkeyi Technology Co., Ltd., China) with the airflow of 1 L min^{-1}. The effective size d_{50} is 0.5 μm for particles with a density of 2 g cm^{-3}. The DKL-2 sampler was described in detail by Li et al. [2011]. The sampling duration varied from 5 to 10 min based on the number concentration of particles. After collecting, samples were stored in a sealed plastic box and placed in a desiccator (RH (relative humidity) < 30%) at 25 ℃ for later analysis.

A transmission electron microscope (TEM, FEI Talos F200S, USA) operated at 200 kV was used to observe the morphology of particles on the copper grids, which was coupled with an energy-dispersive X-ray spectrometer (EDS) to obtain the elemental composition including carbon and heavier elements ($Z \geq 6$). The distribution of particles on the copper grids is not uniform. The diameter of particles distributed in the center is larger than that in the edge. Therefore, in order to ensure that particles analyzed are representative within the entire particle size range, 3-4 areas were selected from the center to the edge on each copper grid. The electron beam of TEM was focused on the particles when the soot aggregates were coated. The components with weak thermal stability were lost under the electron beam, but the refractory components remain unchanged, so the morphology of soot aggregates could be clearly captured (**Fig. S2**). An image analysis software, ImageJ (https://imagej.nih.gov/), was used to obtain the morphology parameters of all particles by analyzing TEM images.

During the observation period, the mass concentrations of $PM_{2.5}$, O_3, SO_2 and NO_X were monitored in real time by tapered element oscillating microbalance (TEOM 1405, Thermo Fisher Scientific Inc., MA, US), O_3 analyzer (Model 49i, Thermo Fischer

Scientific Inc., USA), pulsed UV fluorescence (Model 43i-TLE, Thermo Fischer Scientific Inc., USA), and NO-NO_2-NO_X analyzer (Model 42i-TL, Thermo Fischer Scientific Inc., USA), with details described elsewhere [Gong et al., 2018].

2.2 Division of cloud periods and meteorological characteristics

This field observation spanned two complete non-precipitation cloud processes, which were named as cloud events #1 and #2. Both cloud events formed at night and dissipated at noon of the next day. During the cloud events, prevailing wind direction was from the southwest, and wind speed was in the range of 4.1-9.4 m s^{-1}. The mass concentration of $PM_{2.5}$ was 2-23 μg m^{-3} during cloud event #1 and 4-47 μg m^{-3} during cloud event #2. Two periods were defined according to the visibility (*Vis*) and RH [Lin et al., 2019]: pre-cloud period (*Vis* > 3 km or RH < 95%) and in-cloud period (*Vis* ≤ 3 km and RH ≥ 95%) (**Fig. S3**). Due to rapid development of formation and dissipation of cloud, INT particles were only collected in the stability period with low visibility (*Vis* < 0.1 km) and the mass concentration of $PM_{2.5}$ (< 5 μg m^{-3}) [Yang et al., 2021]. The average visibility and RH during the stability period of cloud processes were 38 ± 13 m and 100 ± 0.2 %, which were 600 ± 890 m and 99 ± 0.7 % in the non-stability (formation and dissipation) period respectively. In the following text, particles in the in-cloud period refer to all the RES particles during cloud processes, except as specifically noted. Overall, 4569 particles were analyzed by TEM/EDS including 1188 particles in the pre-cloud period and 3381 particles in the in-cloud period. Standard errors for the number fraction of particles were estimated assuming Poisson distribution [Pratt et al., 2010].

During two periods of cloud event #1, there was little change for the concentrations of SO_2 and O_3 in the atmosphere. Differently, they changed dramatically during cloud event #2. The average concentrations of SO_2 and O_3 reduced from 3.1 μg m^{-3} and 188.2 μg m^{-3} in the pre-cloud period to 1.5 μg m^{-3} and 82.1 μg m^{-3} in the in-cloud period, respectively. Due to the cloud scavenging of particulate matter, the average concentration of $PM_{2.5}$ was significantly reduced from 20.4 μg m^{-3} in the pre-cloud period and to 5.1 μg m^{-3} during the in-cloud period for cloud event #1 and from 32.7 μg m^{-3} to 12.3 μg m^{-3} for cloud event #2. The average concentration of NO_X was higher during cloud event #2 (10.5 μg m^{-3}) than cloud event #1 (3.8 μg m^{-3}).

2.3 The calculation of morphology parameters of soot aggregates

Fractal dimension (D_f) is a morphology parameter used to characterize the mass-based fractal properties, which can quantify the fractal degree of soot aggregates [Samson et al., 1987]. Brasil et al. [1999] linked the structural properties between computer-simulated three-dimensional aggregates and their two-dimensional projection images, which can be used to infer morphology parameters (such as D_f) of three-dimensional aggregates from analysis of two-dimensional electron microscopy images. This method has been frequently used in the calculation of soot aggregates morphology parameters [Wang et al., 2017; Wentzel et al., 2003]. The D_f follows the statistical scaling law:

$$\mathrm{N} = k_g \left(\frac{2R_g}{d_p}\right)^{D_f} \tag{1}$$

where N and d_p represent the number and average diameter of monomers within a certain soot aggregate, respectively. R_g refers to the gyration radius of the soot aggregate, and k_g is the fractal pre-factor. The calculation method of D_f is described in detail in the supporting information (Text S1). Aspect ratio (AR) and roundness (RN) are also calculated to quantify the morphology of soot aggregates, which can be obtained by equations (2) and (3):

$$\mathrm{AR} = \frac{L_{max}}{W_{max}} \tag{2}$$

$$\mathrm{RN} = \frac{4A_a}{(\pi {L_{max}}^2)} \tag{3}$$

where L_{max} and W_{max} are the maximum length and width of a bounding box. A_a is the projected area of the soot aggregate. For a spherical particle: $D_f = 3$, and AR = RN = 1. For a nonspherical particle: 1 (linear particle) $\leq D_f < 3$, AR > 1, and RN < 1. In addition, the equivalent area diameter (D_{eq}) represents the size of particle, which can be obtained by equation (4).

$$D_{eq} = \sqrt{\frac{4A_a}{\pi}} \tag{4}$$

2.4 The calculation of optical properties of soot particles

The absorption, scattering and extinction cross sections of soot particles at 532 nm were calculated by discrete dipole approximation (DDA) (http://ddscat.wikidot.com/), which has been widely applied to calculate the optical properties of soot particles with different coating materials and mixing structures [Draine and Flatau, 1994]. The input parameters are refractive index of material, the shape and effective radius of particle (D_f, N, d_p). The refractive indices are 1.76+0.63i, 1.53+0i and 1.48+0i for soot

aggregate, sulfate coating and organic coating, respectively [Luo et al., 2019; Nakayama et al., 2010; Worringen et al., 2008]. Shape and effective radius can be obtained based on the images from TEM. Absorption enhancement (E_{abs}) is the ratio of C_{abs} (absorption cross section) of soot particles to soot aggregates, which is described in detail in the supporting information. In this study, the Electron-Microscope-to-BC-Simulation (EMBS) tool, recently developed by Wang et al. [2021b], was applied to build realistic soot shape models with diverse morphology and mixing structures. The average number and diameter of monomers of soot aggregates in the pre-cloud and in-cloud periods are 96, 102 and 45 nm, 44 nm, respectively. So soot aggregate is defined as 100 monomers with the diameter of 44 nm in the theoretical calculation. The variation of E_{abs} with the number of monomers is less than 3% (**Fig. S4**).

3 Results and discussions

3.1 The impact of cloud process on the mixing state and structure of soot particles

Three components were identified within soot particles based on element composition and morphology, including soot, sulfate and organic matter [Li et al., 2016]. Soot was identified by chain-like structure in morphology and abundant carbon in elemental composition. Organic matter exhibited spherical or irregular shape with abundant C and minor O. Sulfate was dominated by S and O, and some were accompanied by a small amount of N, K and Na. It is often bubbly appearance due to the loss of volatile materials (such as ammonium nitrate) by high-energy electron beams during TEM/EDS analysis. Therefore, the inorganic component is identified according to the bubble-shape and S-peak, so sulfate represent inorganic components here. Soot

particles contributed to 12-26% of all analyzed particles by number, which were divided into three classes based on the mixing materials directly contacting with soot aggregates (soot fraction in the whole particle), including bare-like soot aggregate with negligible coating (**Fig. 1a**), soot aggregate coated by sulfate (soot-S) (**Fig. 1b, c, d**), or by organic matter (soot-OM) (**Fig. 1e, f**). Such a classification stresses chemical components in direct contact with soot aggregates, which is slightly different from the classification based on the mixing state of the whole particle [Yuan et al., 2019]. According to various mixing structures between soot aggregates and other materials, soot particles were divided into four classes (**Fig. 1**), including bare-like (**Fig. 1a**), attached (**Fig. 1b**), partly coated (**Fig. 1c**), and fully embedded (**Fig. 1d-f**) [China et al., 2013; Liu et al., 2015]. Attached soot particle was soot aggregate adhering to the surface of the host particle. Partly coated and fully embedded soot particles referred to part and full of soot aggregate wrapped by other materials. Given the limited number of soot particles and similar air mass sources of two cloud events, the following results and discussions are based on a merged dataset from two cloud events.

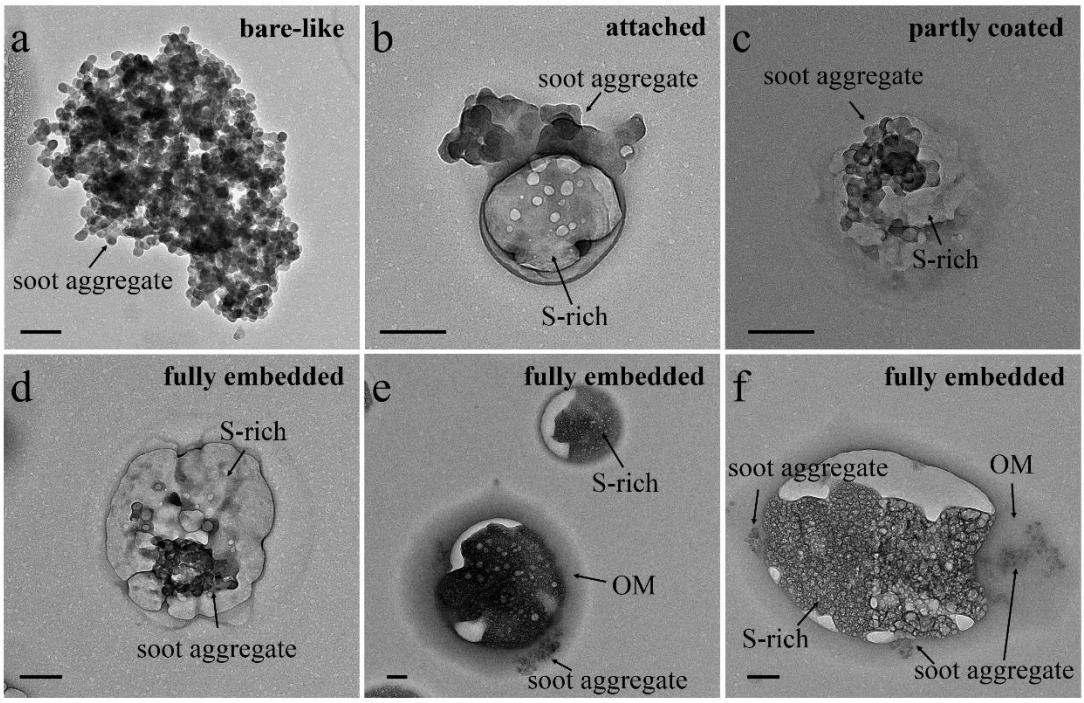

Figure 1. TEM images of soot particles with different mixing structures including bare-like (a), attached (b), partly coated (c) and fully embedded (d-f). The scale in the images is 200 nm.

It can be seen in **Fig. 2** that mixing states and structures of soot particles exhibit distinctly different characteristics between the pre-cloud and in-cloud periods. Soot-OM particles have a higher fraction in the in-cloud period (60 ±2.6%) than that in the pre-cloud period (44 ±5.1%), but soot-S particles account for lower proportion in the in-cloud period (31 ±3.7%) than pre-cloud period (45 ±5.1%). Compared with pre-cloud period, the proportion of soot particles with fully embedded structure in the in-cloud period shows a considerable increase (from 14 ±2.8% to 38 ±2.9%). Specifically, the proportion of soot particles fully embedded in OM, which increase from 3 ±1.3% in the pre-cloud period to 29 ±2.6% in the in-cloud period. Soot particles with partly coated structure reduce from 54 ±5.7% in the pre-cloud period to 37 ±2.9% in the in-

cloud period. The contribution of bare-like and attached soot particles is lower, ranging from 9 ±1.4% to 21 ±3.4%. The proportion of soot particles with LLPS was 2 ±1.0% and 11 ±1.6% in the pre-cloud and in-cloud period respectively, which were mainly completely coated by OM (**Fig. 1e-f**).

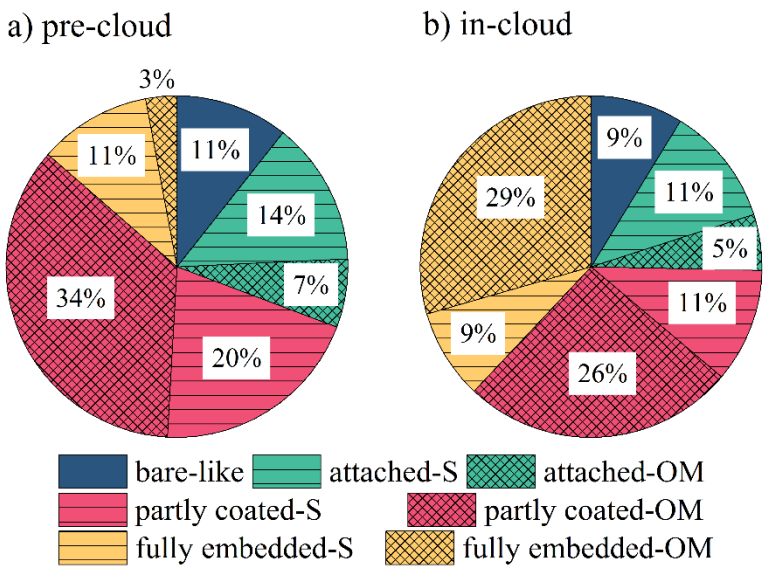

Figure 2. The number fraction of soot particles with different mixing structures coated by sulfate (soot-S) or organics (soot-OM) in the pre-cloud and in-cloud periods.

The increase of soot-OM fraction in the in-cloud period is most likely attributed to the cloud processing involving abundance of ozone and volatile organic compounds (VOCs) [Lv et al., 2019; Wang et al., 2021c], which may also be attributed to the preferential activation of soot-OM particles, but it is unlikely important. As observed by Zhang et al. [2017a] at the same site, soot-OM particles are less activated than soot-S particles. More soot-OM particles than soot-S particles during the in-cloud period may be related to LLPS, in which the soot aggregates are distributed in the organic phase with similar polarity rather than inorganic phase [Brunamonti et al., 2015]. Furthermore, as shown in **Fig. 3**, from the pre-cloud to in-cloud period, the average

coated fraction (F, the area ratio of soot aggregate embedded in host particle to soot aggregate) increased from 46 ± 15% to 67 ± 14% for soot particles with partly coated structure, and average relative coating thickness (D_p/D_c, the diameter ratio between particle and soot aggregate) increased from 2.3 ± 1.2 to 4.4 ± 3.6 for soot particles with fully embedded structure. Consistently, the average D_{eq} of soot particles increased from 845 ± 417 nm to 1214 ± 898 nm after cloud processing. The increase of F, D_p/D_c and D_{eq} indicates that soot aggregates obtain thicker coating due to cloud processing.

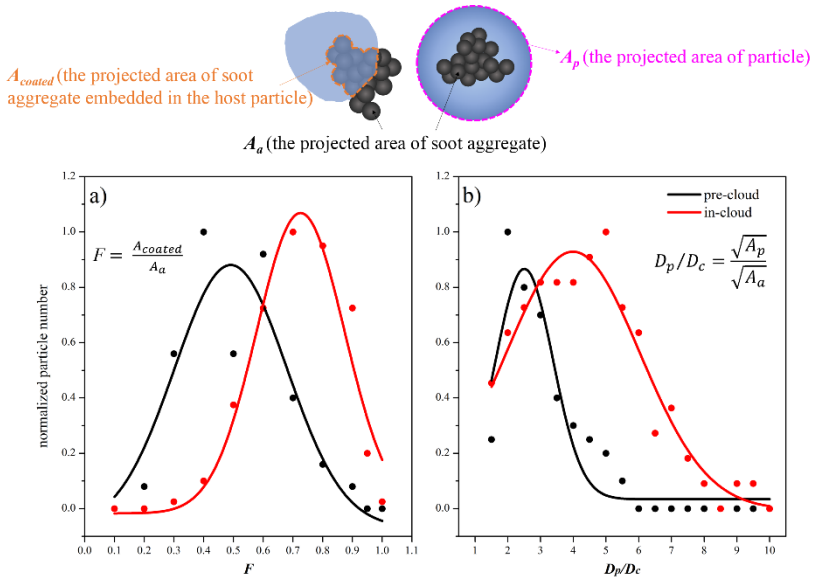

Figure 3. The distribution of F ($0 < F < 1$) for partly coated soot particles (a) and D_p/D_c (> 1) for fully embedded soot particles (b) in the pre-cloud and in-cloud periods. With the increase of F and D_p/D_c, the volume ratio of the coated soot aggregates is higher, and the coating layer is thicker.

3.2 The impact of cloud process on the morphology of soot aggregates

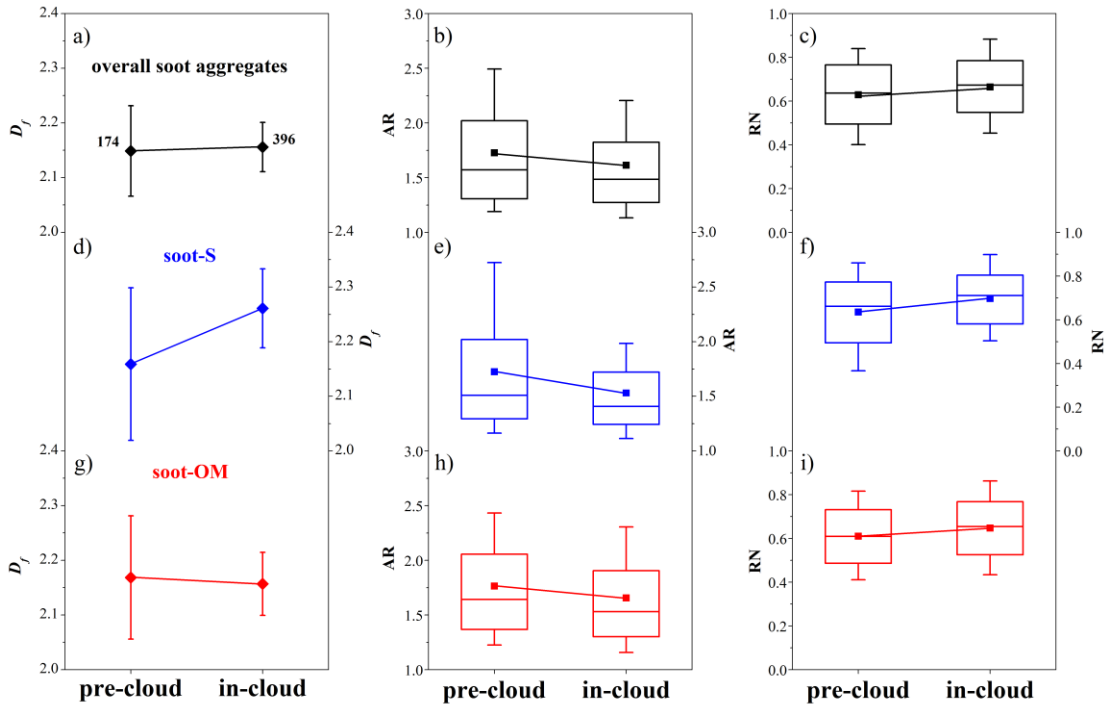

Figure 4. The D_f (a, d, g), AR (b, e, h) and RN (c, f, i) of soot aggregates including overall soot aggregates, soot-S and soot-OM in the pre-cloud and in-cloud period. The number (a) is the amount of soot aggregates used to calculate the morphology parameters. D_f error bars are the error in the fitting of N and $2R_g/d_p$ when calculating D_f. Box and whisker plot shows lower, median, and upper lines, denoting the 25th, 50th, and 75th percentiles, respectively; the lower and upper edges denote the 10th and 90th percentiles, respectively.

The morphology parameters of overall soot aggregates, including D_f, AR and RN, show a limited change from the pre-cloud to in-cloud period (**Fig. 4**). Consistently, the RES and INT soot aggregates during the stability period of cloud process also exhibit similar morphology with similar D_f, AR, and RN (**Fig. S5**). The above result indicates limited restructuring of soot aggregates upon cloud processing, which is inconsistent

with previous studies reporting that high humidity condition facilitates the restructuring of soot aggregates [Qiu et al., 2012; Zhang et al., 2008], leading to larger D_f and RN, and lower AR.

Such inconsistency might be attributed to the chemically resolved reconstruction of soot aggregates due to cloud processing. As shown in **Fig. 4**, the D_f of soot-S aggregates was 2.16 ± 0.14 in the pre-cloud period, and increased to 2.26 ± 0.07 in the in-cloud period. Differently, the D_f of soot-OM aggregates between the pre-cloud and in-cloud periods were quite similar (2.17 ± 0.11 and 2.16 ± 0.06). Similar trend was also observed for the AR and RN of soot aggregates (**Fig. 4**), with larger changes of AR and RN for soot-S aggregates from the pre-cloud to in-cloud periods. Such difference indicates that organics lead to less compaction of soot aggregates, rather than sulfate. The restructure of soot aggregates depends on the uptake of water by the coating materials [Guo et al., 2016], and the following evaporation of water [Enekwizu et al., 2021; Ma et al., 2013]. Complete encapsulation of organic coating produces lower surface tension than partly coated structure and sulfate coating during water evaporation [Schnitzler et al., 2017], resulting in less degree of reconstruction between monomers of soot aggregates fully embedded in organics. Such phenomenon is similar to that reported by Cross et al. [2010], who found that sulfuric acid coating caused a more compact shape of soot aggregates than DOS (dioctyl sebacate) coating in laboratory experiments. Therefore, with the increase contribution of soot-OM in the in-cloud period, in particular the fully embedded structure (> 50%) (**Fig. 2**), the overall soot aggregates show similar morphology parameters between pre-cloud and in-cloud

period.

The differences in morphology, mixing state and mixing structure from the inactivated INT to activated RES particles during the stability period of cloud events can also support the above hypothesis. The proportion of soot-OM in the RES particles (68 ± 4.6%) was higher than that in the INT particles (48 ± 7.1%), and the proportion of soot-OM particles with fully embedded structure in the RES particles (37 ± 3.4%) was about 4 times that in the INT particles (9 ± 3.5%) (**Fig. S6**). Furthermore, the D_f of soot-OM aggregates in the in-cloud period was smaller than that of the soot-S aggregates for the RES particles. Higher proportions and lower D_f value of soot-OM aggregates lead to the limited change in the morphology of overall soot aggregates between the RES and INT particles. Our previous study also found a phenomenon inconsistent with the general concept that lower D_f of soot aggregates in the RES particles than that in the INT particles at the same site [Fu et al., 2020], which is most likely due to the higher fraction of soot-OM in the RES particles (58 ± 6.2%) than that in the INT particles (28 ± 5.0%).

3.3 Effect of cloud processing in light absorption of soot particles

Fig. 5 shows the E_{abs} of soot particles in the pre-cloud and in-cloud periods, based on the observed morphology, mixing state, and mixing structure. In order to illustrate the changes in the light absorption of soot particles within a representative size range upon cloud processing, five groups of D_p/D_c were selected, ranging from 1.5 to 3.9 in the pre-cloud period and from 3.1 to 5.5 in the in-cloud period (**Table S1**). The selection of the D_p/D_c range is based on the observed particles, as detailed in the supporting

information (Text S3). For bare-like soot particles, the D_f of soot-S aggregates increases from 2.16 ±0.14 in the pre-cloud period to 2.26 ±0.07 in the in-cloud period, resulting in a limited absorption enhancement with the E_{abs} of 1.02. As reported elsewhere, the enhancement of light absorption of soot particles with attached structures is limited (E_{abs} < 1.1) [Adachi and Buseck, 2013; Schnaiter et al., 2003; Wang et al., 2021b]. Differently, the light absorption increased significantly for soot particles with partly coated and fully embedded structures (**Fig. 5a, b**), associated with the increase of coating degree including coated fraction and thickness [Adachi et al., 2010; Guo et al., 2016]. With the increase of F and D_p/D_c after cloud processing, E_{abs} are 1.76 ±0.29 in the pre-cloud period and 2.36 ±0.38 in the in-cloud period for soot particles with partly coated structure. For soot particles with fully embedded structure, E_{abs} are 2.35 ±0.28 in the pre-cloud period and 2.63 ±0.08 in the in-cloud period. The E_{abs} of soot particles with LLPS was 1.78 ± 0.14 and 1.93 ± 0.07 in the pre-cloud and in-cloud period respectively, which was smaller than that of soot particles without LLPS, with an average of 26% over different D_p/D_c (**Fig. S8**). The E_{abs} of soot particles with different mixing structures vary greatly, which may be one of the reasons for the lower E_{abs} of soot particles in some field investigation cases [Cappa et al., 2012; Fu et al., 2021], that is, the attached and partly coated structures soot particles may account for the main proportion. In the pre-cloud period, the average E_{abs} of partly coated soot particles (1.76 ±0.29) and the average E_{abs} of fully embedded soot particles (2.35 ±0.28) were both within the range reported by current laboratory studies (1-1.9 for partly coated structure and 2.2-2.5 for fully embedded structure) [Chakrabarty and Heinson, 2018; Scarnato et

al., 2013], which were lower than the average E_{abs} of soot particles with partly coated (2.36 ± 0.38) and fully embedded (2.63 ± 0.08) structure in the in-cloud period. Additionally, the E_{abs} of soot-S and soot-OM particles with different mixing structures, F and D_p/D_c is in the range of 1.0-2.7 and 1.0-3.0 respectively, which is consistent with previous studies [Peng et al., 2016; Schnaiter et al., 2003; Schnaiter et al., 2005].

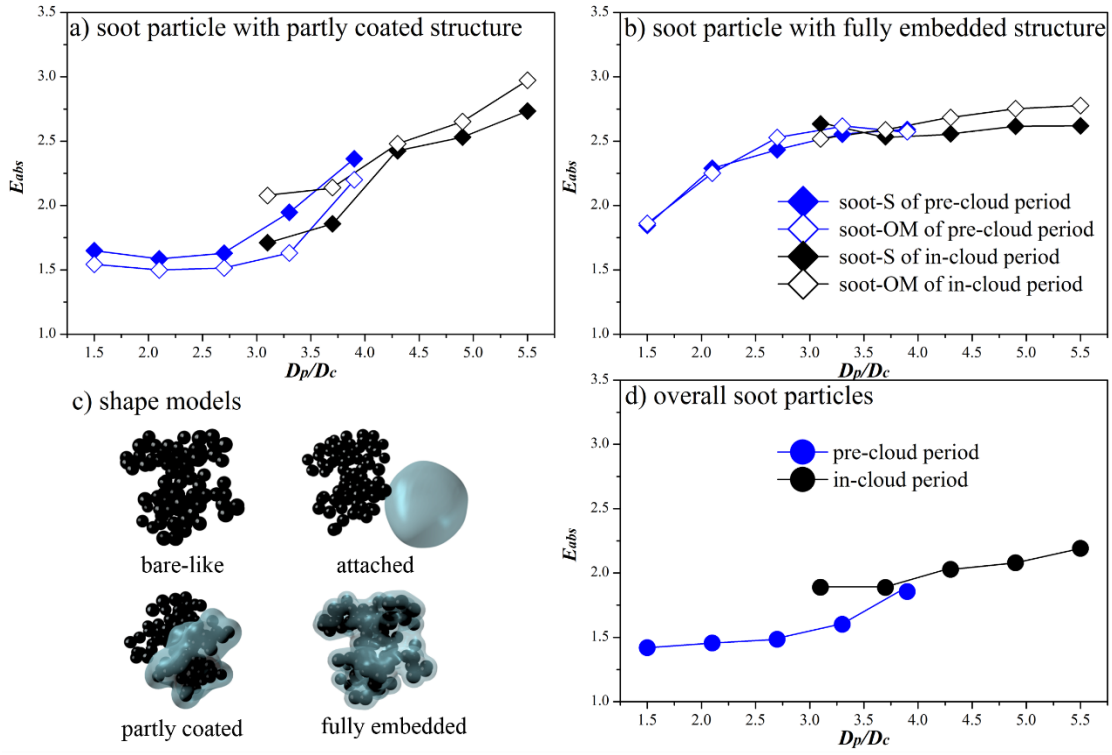

Figure 5. Shape models of soot particles with different mixing structures, and E_{abs} of soot particles in the pre-cloud and in-cloud periods.

For the overall soot particles, the cloud process likely induces a pronounced increase of light absorption based on theoretical calculations. Corresponding to the changes in the proportion of soot particles with various mixing states and structures upon cloud processing, the E_{abs} of all soot particles increased from 1.57 ± 0.16 in the pre-cloud period to 2.01 ± 0.12 in the in-cloud period (**Fig. 5d**), and the cloud process

resulted in a factor of 1.29 ± 0.06 increase in E_{abs}. Our calculated E_{abs} of soot particles in the pre-cloud period is higher than that in urban areas [Healy et al., 2015; Lan et al., 2013; Nakayama et al., 2014], which may be due to the higher degree of aging of the soot particles at this remote site. Higher E_{abs} of soot particles (2.1) has also been observed at the cloudy Mt. Tai in northern China [Wang et al., 2021a]. As indicated by Peng et al. [2016], the E_{abs} of soot particles could increase by a factor of 2.4 after several hour's aging in polluted urban air. Our study indicates that cloud processing during one event could increase the E_{abs} of soot particles by 1.29 times, which underlines the potential effect of cloud on rapid aging of soot particles.

3.4 A conceptual model for the impact on the mixing state and microphysical properties of soot particles of cloud process

We came up with a conceptual model, as illustrated in **Fig. 6**, to reflect the changes of mixing state and microphysical properties of soot particles from the pre-cloud to in-cloud period. In the pre-cloud period, soot particles come from long-range transport and are mainly partly coated. Aged soot particles would be activated and grow into cloud droplets during cloud events. The mixing structure of soot particles is expected to change since the water-soluble components mixed with the soot aggregates will be dissolved in the cloud droplets. In addition, secondary organic compositions could also be formed through uptake and aqueous processing of VOCs [Fu et al., 2020; Zhang et al., 2017a]. After the evaporation of cloud droplets, LLPS occurs and would lead to two-phase solid particles composed of outer organic phase and inner inorganic phase [Shiraiwa et al., 2013], and soot aggregates will redistribute in organic phase with

similar polarity. Although not emphasized, the soot aggregates have been found to be dominantly embedded in the organic phase in the remote region [Yu et al., 2019], with a large fraction (61%) of soot-OM aggregates distributed in outer organic phase likely due to cloud processing. The production of organic matter in cloud and the occurrence of LLPS correspond to the significant increase of soot-OM particles with fully embedded structure, which would significantly enhance the light absorption of soot particles.

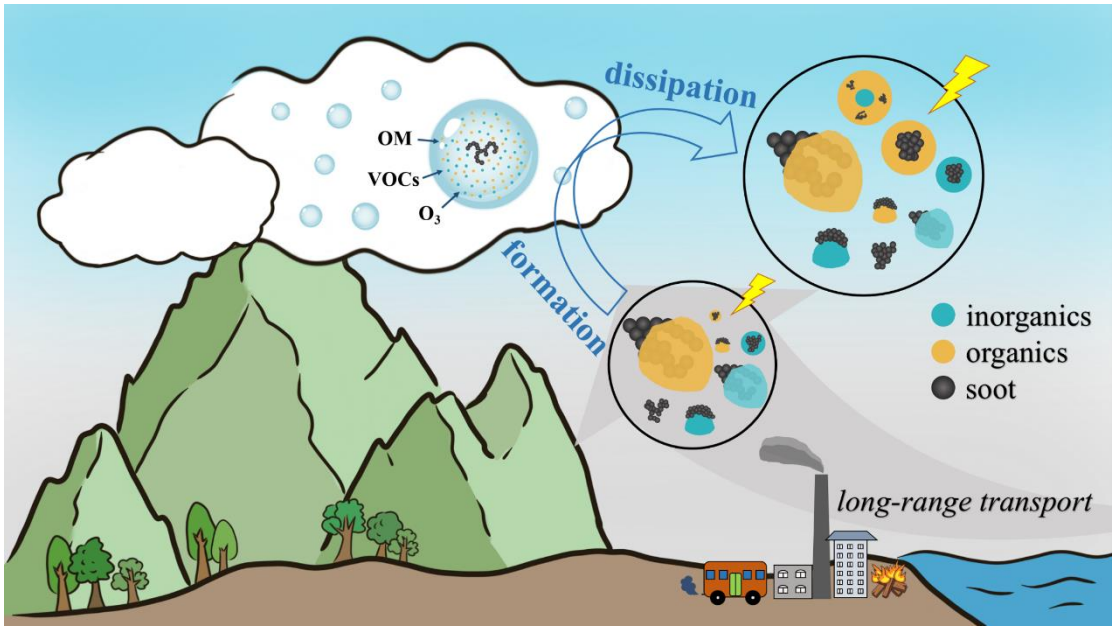

Figure 6. Schematic diagram showing the change in morphology, mixing state, and mixing structure of soot particles throughout cloud processing.

4 Atmospheric implications and conclusions

This study emphasizes that it is necessary to consider the encapsulating materials and mixing structures for better understanding of the impact of cloud on soot particles. Attributed to cloud processing, the soot-S aggregates become more compact, while the soot-OM aggregates do not. Meanwhile, the changes in morphology of soot aggregates,

mixing state and mixing structure of soot particles driven by cloud processing would have substantial implications for the optical properties of soot particles. Theoretical calculation shows that the E_{abs} of soot-particles processed by cloud is as high as 2.01 ± 0.12, which is 1.29 ± 0.06 times that of the pre-cloud period. Given that clouds cover nearly 70% of the Earth [King et al., 2013], such a significant increase in E_{abs} indicates that cloud processing may represent a critical factor, which has not been revealed in the evolution of light absorption of soot. The results also support the significance of morphology, mixing state and mixing structure of soot particles in model calculations to evaluate the climate impact of soot particles [Penner et al., 2006; Zhuang et al., 2010]. While such information is accounted for in particle-resolved aerosol model [Fierce et al., 2020], it is still not considered in most climate models [Cooke and Wilson, 1996; Park et al., 2011; Zhang et al., 2019]. In addition, field observations found high uncertainty in the abundance of soot particles in ice clouds [Cozic et al., 2008; Kupiszewski et al., 2016]. Our observations indicate that the morphological evolution of soot aggregates due to warm cloud processing was mainly driven by the coating of organic compounds, which may have potential influence on the ice nucleation activities [Nichman et al., 2019]. Laboratory simulation experiments have shown a significant enhancement of ice nucleation activity of soot particles processed by cloud, most likely attributed to the modification of morphology by cloud processing [Mahrt et al., 2020]. Our results at the remote site surrounded by a large area of forest may represent the mixing state and morphological characteristics of soot particles in the area with significant biogenic VOCs precursors, and thus can be used as a reference for the

climate model to access the climatic impact of soot particles in similar regions.

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Conflict of Interest

There are no conflicts of interest in the article.

Data Availability Statement

Data supporting the results are available in the supporting information. The processed data presented in this paper are available on Zenodo (https://doi.org/10.5281/zenodo.7073072) [Fu et al., 2022], including the number fraction of soot particles with different mixing states and structures, the distribution of F and D_p/D_c, morphology parameters of soot aggregates, and E_{abs} of soot particles in the pre-cloud and in-cloud periods. The back trajectories data are calculated with hybrid single-particle Lagrangian integrated trajectory model (https://www.ready.noaa.gov/HYSPLIT_hytrial.php) [NOAA, 2022]. The source code of EMBS is from Wang et al. [2021b]. The source code of DDA developed by Bruce T. Draine and Piotr J. Flatau, and the version used in this study is DDSCAT 7.3.3, which can be obtained online (http://ddscat.wikidot.com/) [Draine and Flatau, 2019].

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Figure1.

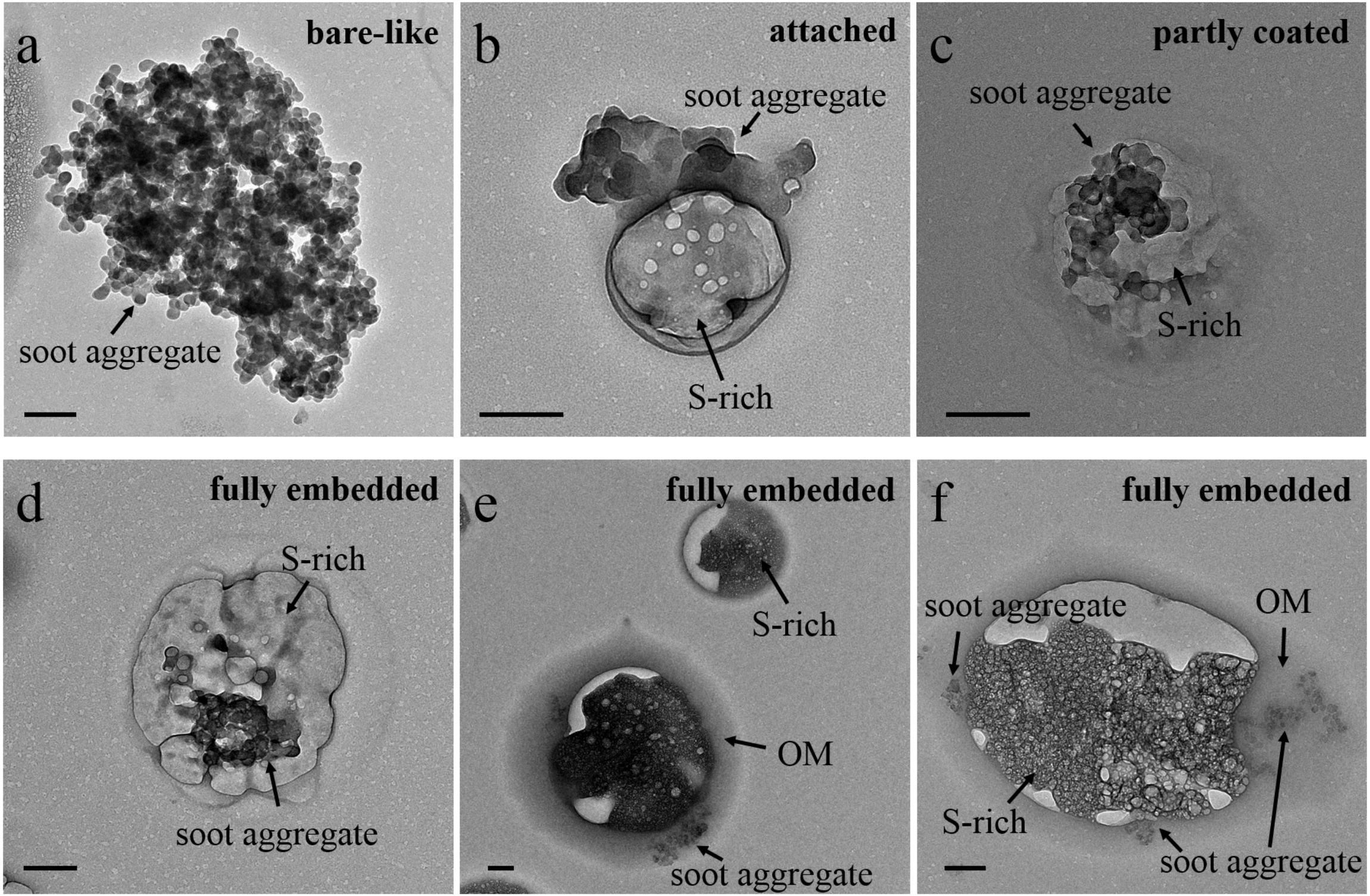

a
bare-like
soot aggregate
b
attached
soot aggregate
S-rich
c
partly coated
soot aggregate
S-rich
d
fully embedded
S-rich
soot aggregate
e
fully embedded
S-rich
OM
soot aggregate
f
fully embedded
soot aggregate
OM
S-rich
soot aggregate

Figure2.

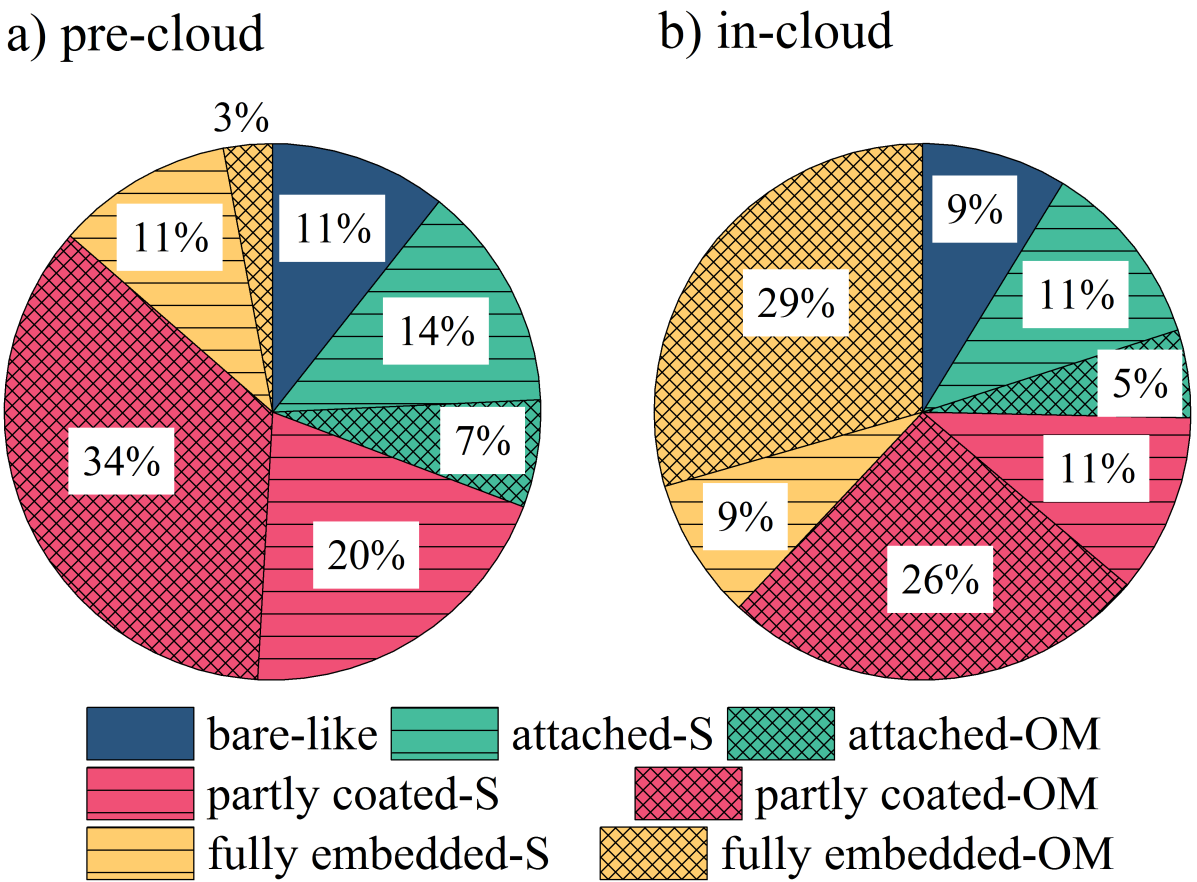

a) pre-cloud
3%
11%
11%
14%
7%
34%
20%
b) in-cloud
9%
11%
5%
29%
11%
9%
26%
bare-like
attached-S
attached-OM
partly coated-S
partly coated-OM
fully embedded-S
fully embedded-OM

Figure3.

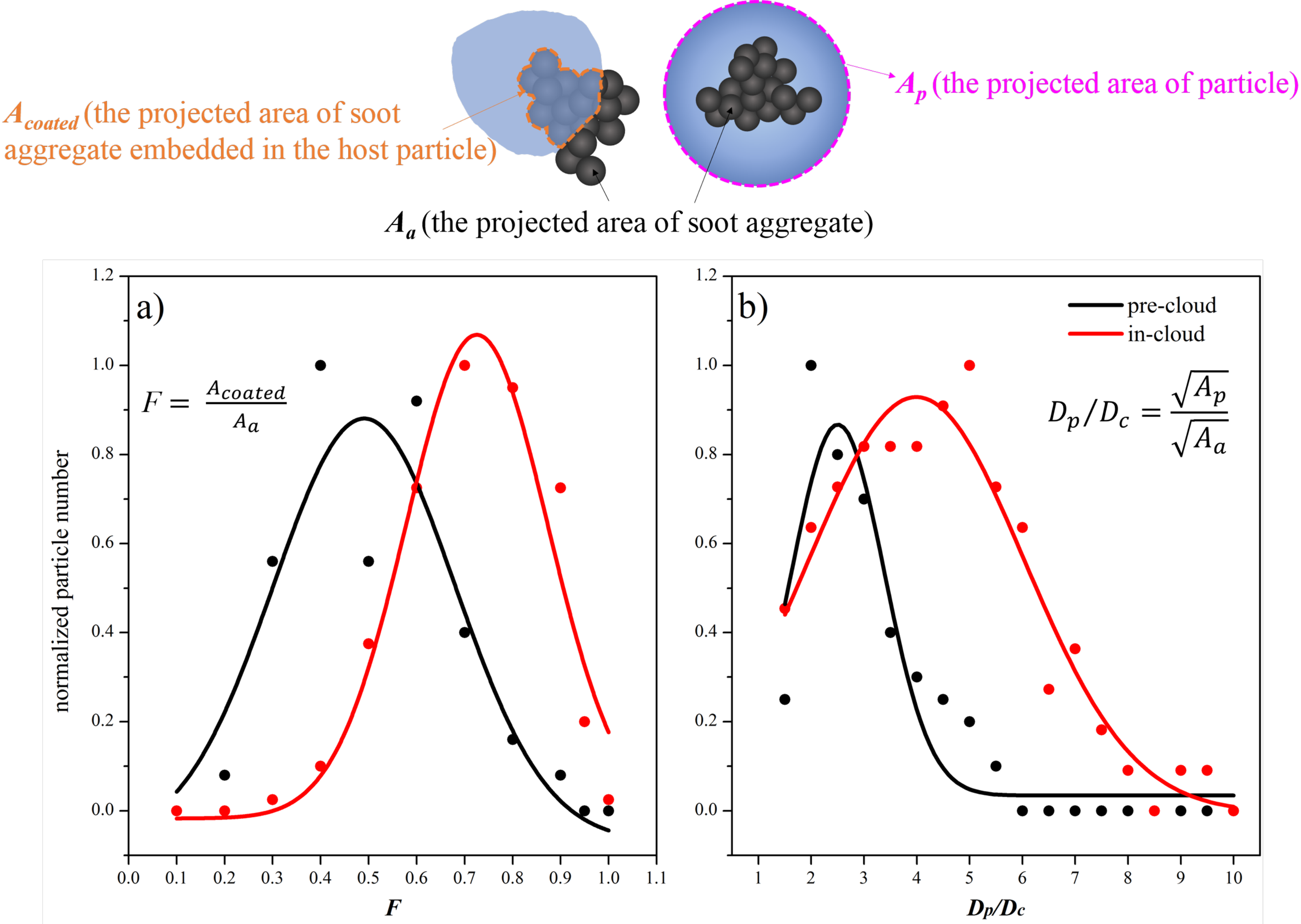

A_{coated} (the projected area of soot aggregate embedded in the host particle)
A_p (the projected area of particle)
A_a (the projected area of soot aggregate)
a)
$F = \frac{A_{coated}}{A_a}$
normalized particle number
F
b)
pre-cloud
in-cloud
$D_p/D_c = \frac{\sqrt{A_p}}{\sqrt{A_a}}$
Dp/Dc

Figure4.

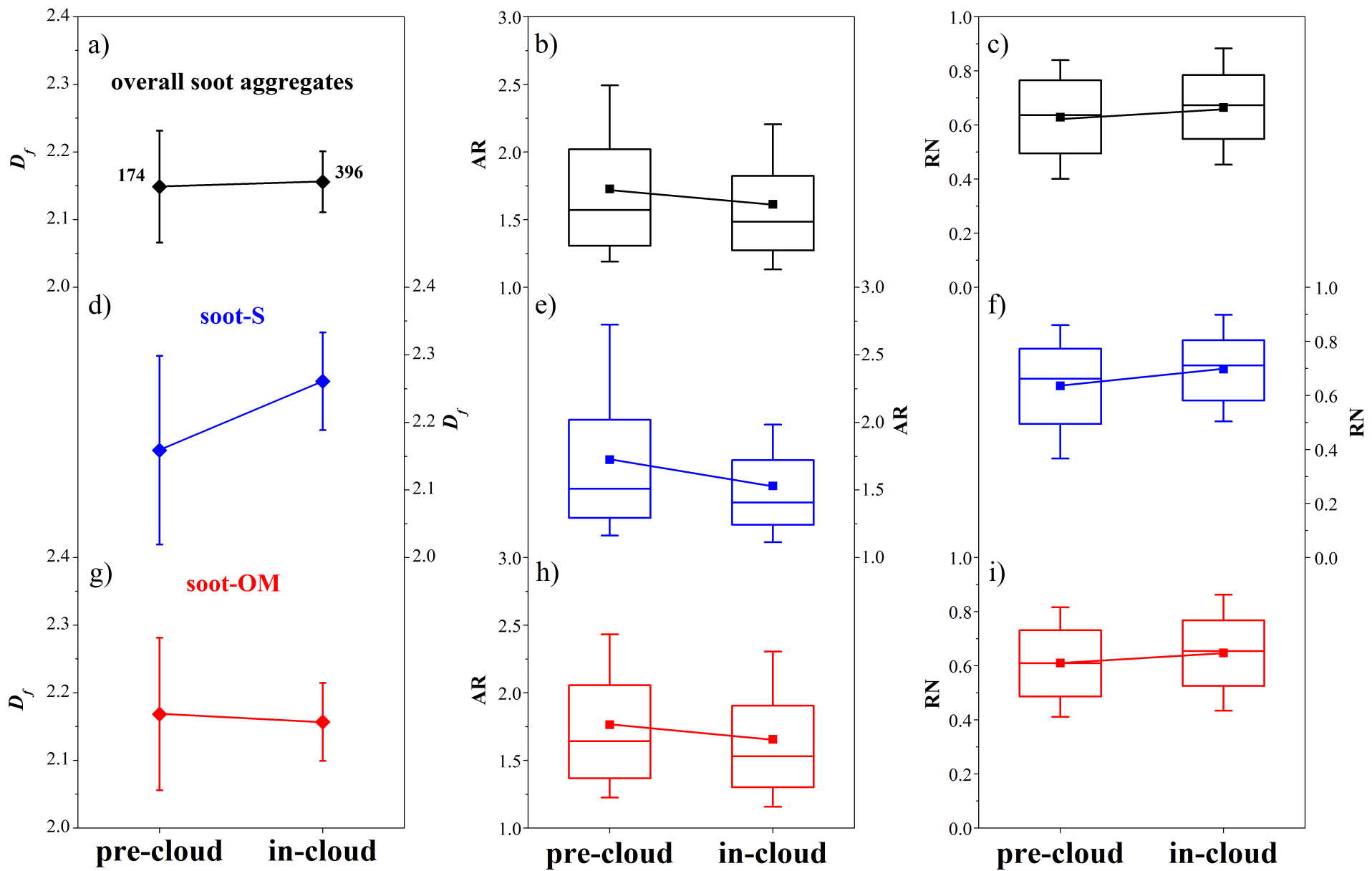

a)
overall soot aggregates
174
396
d)
soot-S
g)
soot-OM
b)
e)
h)
c)
f)
i)
D_f
AR
RN
pre-cloud
in-cloud

Figure5.

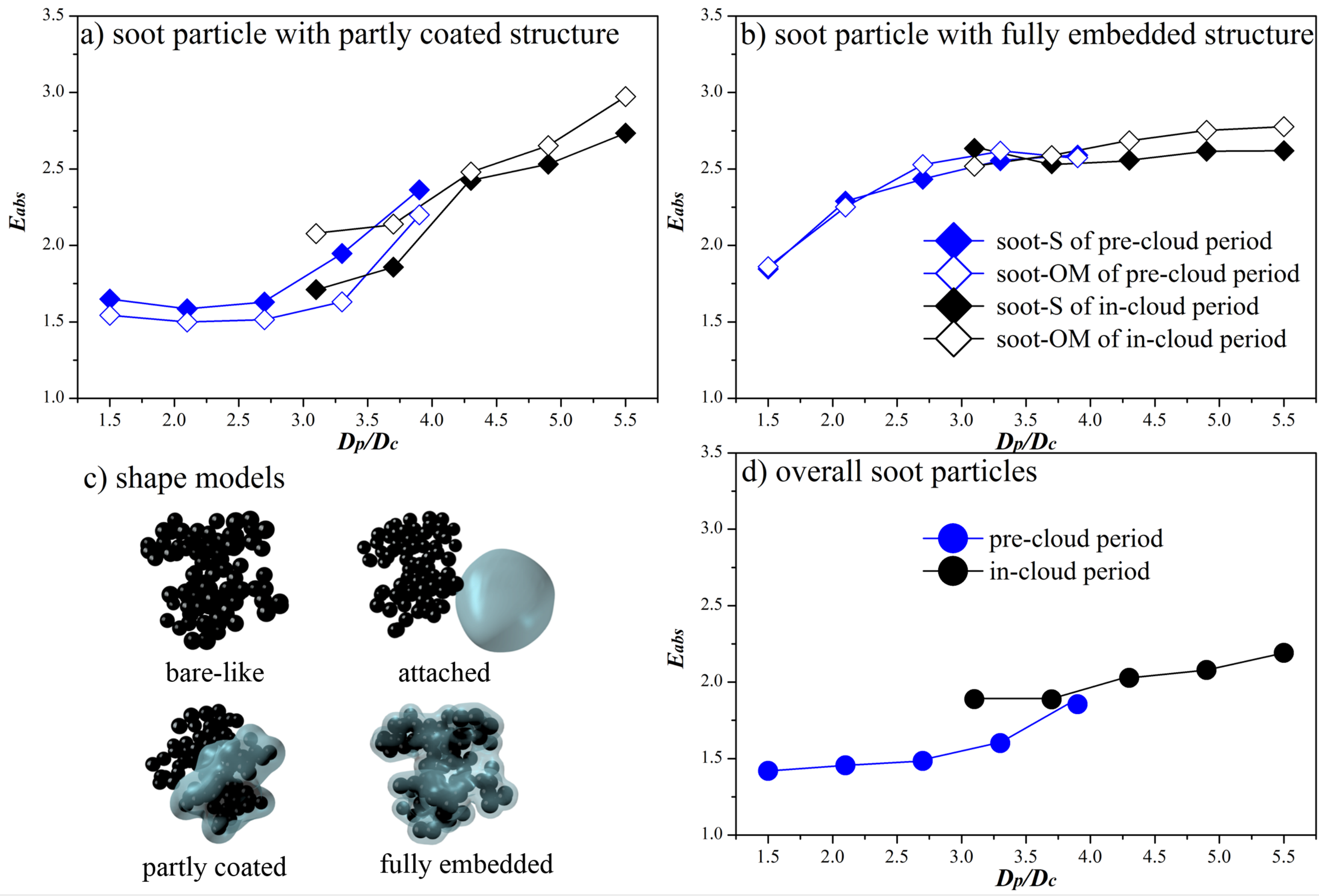
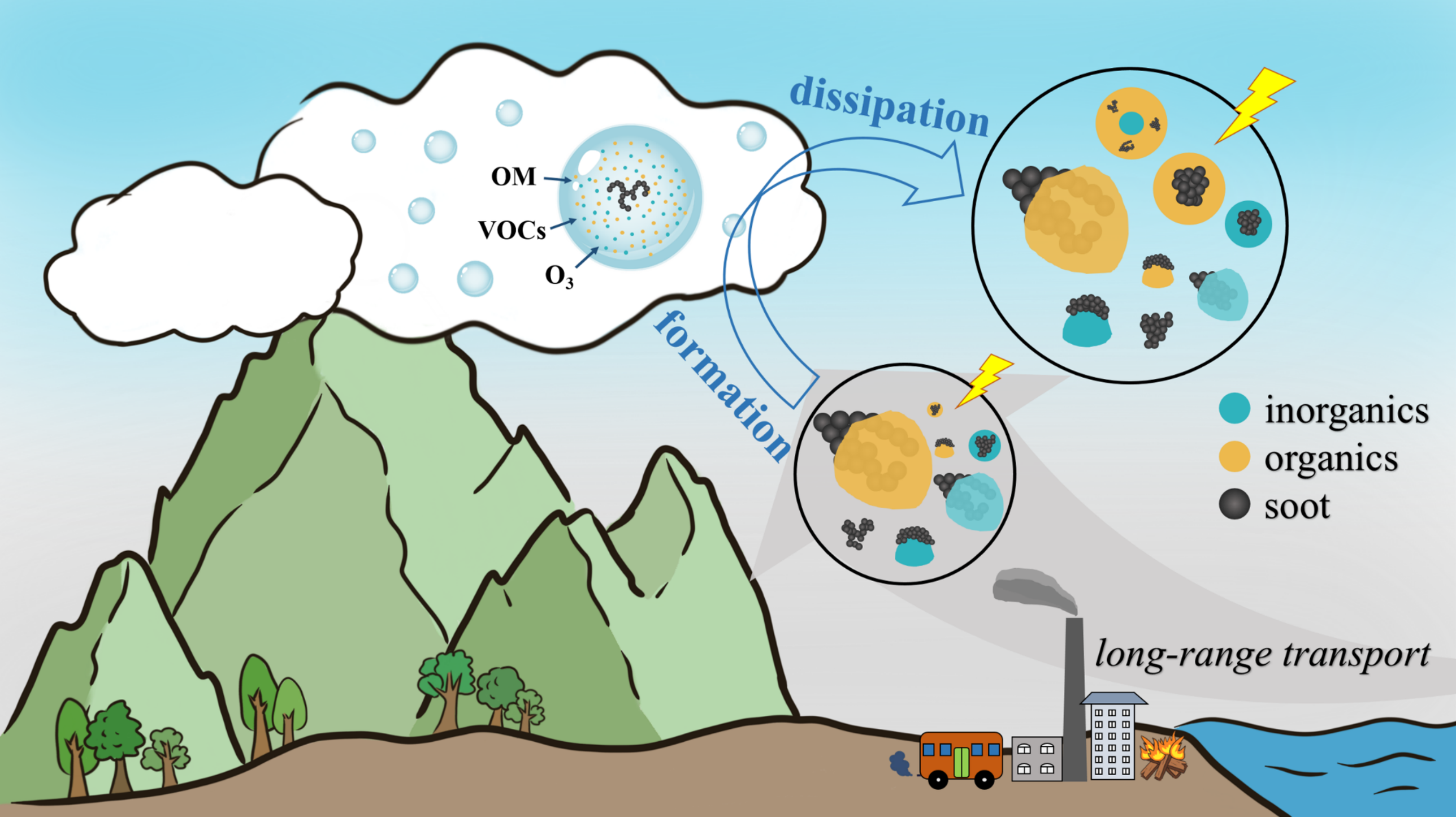

a) soot particle with partly coated structure
b) soot particle with fully embedded structure
c) shape models
d) overall soot particles
Eabs
Dp/Dc
soot-S of pre-cloud period
soot-OM of pre-cloud period
soot-S of in-cloud period
soot-OM of in-cloud period
pre-cloud period
in-cloud period
bare-like
attached
partly coated
fully embedded

Figure6.


OM
VOCs
O_3
dissipation
formation
inorganics
organics
soot
long-range transport