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Observation of nitrate coatings on atmospheric mineral dust particles

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Abstract

Nitrate compounds have recently received much attention because of their ability to alter the hygroscopic properties and cloud condensation nuclei (CCN) activity of mineral dust particles in the atmosphere. However, very little is known about specific characteristics of nitrate-coated mineral particles in an individual particle scale in field study. The sample collection was conducted during brown haze and dust episodes occurred between 24 May and 21 June 2007 in Beijing, northern China. The sizes, morphologies, and compositions of mineral dust particles together with their coatings were analyzed using transmission electron microscopy (TEM). 92% of the internally mixed mineral particles analyzed are covered with Ca-, Mg-, and Na-rich coatings, and 8% are associated with K- and S-rich coatings. The major coatings contain Ca, Mg, O, and N with minor amounts of S and Cl, suggesting that they are possibly nitrates mixed with less sulfates and chlorides. These nitrate coatings strongly relate with the presence of alkaline mineral components (e.g., calcite and dolomite) within individual mineral particles. Calcium sulfate particles with the diameter from 10 to 500 nm were also detected within $Ca(NO_3)_2$ and $Mg(NO_3)_2$ coatings. Our results indicate that mineral particles in brown haze episodes were involved in atmospheric heterogeneous reactions with two or more acidic gases (e.g., SO_2, NO_2, HCl, and HNO_3). Mineral particles that acquire hygroscopic coatings tend to be more spherical and larger. Such changes enhance their light scattering and CCN activity, both of which have cooling effects on the climate.

1 Introduction

A significant amount of mineral dust particles (1000–3000 Tg) are annually injected into the troposphere (Andreae, 1995). Mineral dust particles are lifted into the atmosphere by strong surface winds and can be transported long distances (Husar et al., 2001; Fairlie et al., 2007), influencing climate, and enhancing heterogeneous chemistry of the atmosphere on regional and global scales (Ravishankara, 1997; Buseck and Posfai, 1999; Tegen et al., 2000; Xu et al., 2004;). Mineral dust particles scatter and absorb incoming solar radiation (Sokolik and Toon, 1996; Haywood and Boucher, 2000; Seinfeld et al., 2004;) and can act as cloud condensation nuclei (CCN) (DeMott et al., 2003; Knopf and Koop, 2006). Heterogeneous chemistry of mineral dust with HNO_3 and NO_2 can influence photochemical cycles in the troposphere (Dentener et al., 1996; Jacob, 2000).

Fresh mineral dust particles in the troposphere are far more inert than chlorides, sulfates, and nitrates, when aged by soluble aerosol components, these mineral dust particles will have enhanced their hygroscopicity and altered their sizes and shapes (Krueger et al., 2003; Krueger et al., 2004; Laskin et al., 2005b). As a result, the coated dust particles become more efficient CCN (Kelly et al., 2007). Therefore, knowledge about the soluble components coated on mineral particles is important for evaluating their impact on climate in global and regional scales.

Laboratory experiments and modeling work suggest that climate forcing and heterogeneous atmospheric chemistry of individual mineral dust particles strongly depend on their alkaline mineral components (e.g., calcite, dolomite, and halite) (Krueger et al.,Borensen et al., 2000; 2004; Kelly and Wexler, 2005). Several field studies have indicated that mineral dust particles, through heterogeneous uptake of acidic gases, acquired coatings of sulfates (Kojima et al., 2006; Sullivan et al., 2007), nitrates (Laskin et al., 2005a; Matsuki et al., 2005), or their mixtures (Zhang et al., 2000; Hwang and Ro, 2006;). Although laboratory studies provided detailed information regarding nitrate coatings formed through heterogeneous reactions (Krueger et al., 2003, 2004; Laskin et al., 2005b), few studies presented data about nitrate coatings on ambient particles.

With the rapid urbanization of cities in China, huge amounts of emissions from urban cities frequently extend to regional pollution episodes (Li et al., 2007; Chan and Yao, 2008). SO_2 emissions declined from 1996, but NO_x emissions increased by 70% (Streets et al., 2003; Zhang et al., 2007). The increase in NO_x significantly affects atmospheric interactions and chemistry in these areas (Guinot et al., 2007). In particular, the regional haze episodes that commonly occur over northern China in spring and winter include high concentrations of mineral dust particles, SO_2, and NO_2 (Wang et al., 2006). Mineral particles collected in the polluted hazes from northern China provide a good opportunity to study the heterogeneous reactions that occur in such ambient environments.

The goal of this study is to understand the properties of nitrate-coated mineral particles collected in regional polluted haze episodes over northern China. We used transmission electron microscopy (TEM) to observe mineral particles with visible coatings. Because of TEM resolution down to fractions of a nanometer, it can provide detailed information on sizes, compositions, morphologies, structures, and mixing states of individual aerosol particles (Posfai et al., 1995; Buseck et al., 2000; Middlebrook et al., 2003; Johnson et al., 2005 Niemi et al., 2006). Characterization of calcium nitrate and magnesium nitrate coatings on mineral particles were investigated in detail.

2 Sampling and experiments

2.1 Haze and dust episodes over northern China

Thirty-seven aerosol samples were collected in ten severe pollution brown haze episodes between 31 May and 21 June 2007 in Beijing, northern China. Temperature and relative humidity (RH) ranged from 21 to 36 °C and 30 to 80%, respectively, and visibility was between 1 and 6 km. Low wind speeds ($1–3\,m\,s^{-1}$) from a southwesterly or southerly direction dominated during the haze periods. High concentrations of PM_{10} ($200–370\,\mu g\,m^{-3}$), SO_2 ($21–51\,\mu g\,m^{-3}$), and NO_2 ($51–88\,\mu g\,m^{-3}$) were monitored in the brown haze days in Beijing (http://www.bjee.org.cn/api/index.php). In addition, four dust samples were also collected in one dust episode on 24 May after precipitation from 21 May to 23 May 2007. The dust episode was a severe pollution episode with high concentration of PM_{10} ($288\,\mu g\,m^{-3}$) and low concentrations of anthropogenic pollutants (SO_2, $9\,\mu g\,m^{-3}$ and NO_2, $46.4\,\mu g\,m^{-3}$). During the dust period, temperature and RH were 31°C and 21%, respectively, and visibility was about 1 km. The wind was westerly with speeds varying from 7 to 1 m s^{-1}.

Backward trajectory analysis determines the transport paths of air masses arriving at a sampling site. NOAA/ARL Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) (Draxler and Rolph, 2003) was employed to calculate 10 24-h backward trajectories of air masses arriving at Beijing at 500 m between 24 May to 21 June 2007 (Fig. 1). Dust air mass from northwest of Beijing had low humidity and passed over desert and loess plateau of northern China. Haze air masses from southeast of Beijing had high humidity and passed over the industrial Hebei, Shanxi, and Shandong provinces. The backward trajectories shown in Fig. 1 are consistent with the observations of meteorological parameters and mass concentrations of pollutants on the ground.

2.2 Aerosol sampling

The collection site (39°59′ N, 116°20′ E) was located in the northwest of Beijing. Samplers were mounted on the top of a building located at the China University of Mining and Technology, 18 m above ground. Aerosol particles were deposited onto copper TEM grids coated by carbon film using a single-stage cascade impactor with a 0.5-mm-diameter jet nozzle. An air flow rate is 1.0 l min^{-1}. The collection efficiency of the impactor is 50% cutoff aerodynamic diameter at 0.3 μm and almost 100% at 0.5 μm if the density of particles is 2 g cm^{-3}. The sampler was described in more detail by Okada and Hitzenberger (2001). The sampling time ranged from 30 to 120 s, depending on the visibility. After sampling, the samples were sealed in dry plastic capsules, preventing contamination of the particles on the TEM grids from ambient air pollutants.

2.3 Analytical methods

Aerosol samples were analyzed using a 200 kV Philips CM200 TEM. TEM images were used to determine particle sizes, morphologies, and mixing states. Compositions were determined using energy-dispersive X-ray spectrometry (EDS). Combining EDS and selected-area electron diffraction (SAED), we were able to verify the identities of some mineral particles.

All samples were first observed in magnification ×500–800 using TEM. The distributions of particles on the TEM grids were not uniform. Coarser particles were deposited near the center of each grid, and finer particles deposited at the periphery. Therefore to ensure that the analyzed particles were representative of the collected size distribution, three to four areas were chosen from the center and periphery. Abundant mineral particles from haze samples show visible coatings whereas few mineral particles from dust samples show visible coatings. The primary observations help us to choose 20 typical samples collected in ten brown haze episodes and one sample collected in one dust episode in our study. Mineral particles in the chosen samples were observed in magnification of more than ×2550 using TEM. TEM/EDS obtained detailed compositions and morphologies of individual mineral particles with visible coatings. The diameters of mineral particles analyzed were also measured. We used the best fitting ellipse to a particle outline, and the diameter of each particle was calculated as the arithmetic mean of the short and long axes of the ellipse.

3 Results

3.1 Coated mineral particles

Mineral dust particles from the haze samples make up 1/3 (by number) of all collected aerosol particles with diameter more than 0.1 μm. Other studies using bulk composition analysis indicated that mineral dust, which originated from natural soil, construction dust and re-suspended road dust, made up about 39–67% (by mass) in PM_{10} collected in Beijing haze episodes (Sun et al., 2006). Almost all the particles collected in the dust episode are mineral dust. These dust particles were transported mainly from desert and loess soil in northwestern China (Zhang et al., 2003; Shao et al., 2008).

TEM observations indicate that approximate 90% of the mineral dust particles are covered by visible coatings in the haze samples, whereas only 5% are in the dust sample. We will refer to mineral dust particles associated with visible coatings as coated mineral particles (Fig. 2). Size distributions of the coated mineral particles show a wide size range from 0.4 to 16 μm with median size 3.1 μm in diameter (Fig. 3).

Based on morphological features, we can distinguish two parts of each coated mineral particle: core and coating (Fig. 2). One or more mineral particles may act as cores that are enclosed within coatings. In our samples, the main core minerals are clay, feldspar, quartz, dolomite, calcite, hornblende, and hematite. Cores show 0.2 to 13 μm with median size 2.1 μm in diameter (Fig. 3). Coatings usually cover the entire or partial surfaces of mineral particles (Fig. 2). Most coatings are transparent in TEM images and sensitive to the strong electron beam.

3.2 Coatings on mineral particles

EDS analysis shows that coatings mainly include N, O, S, Ca, Mg, Na, K, and Cl. Although some mineral particles covered two or more coatings, we always can identify one dominant component through their EDS spectra. Based on the major compositions, the coatings were classified into five categories (Fig. 4). They include mainly Ca-rich (71%), Mg-rich (12%), and Na-rich (9%) as well as less K-rich (4%) and S-rich (4%).

Most of mineral particles associated with Ca-rich coatings are the mixtures of silicates and calcite (or dolomite) (Fig. 5). EDS analysis shows that Ca-rich coatings also contain O and N with minor amounts of S, Cl, and Mg. Calcium sulfate particles with the diameter from 10 to 500 nm were detected in these coatings (Fig. 5b). The coatings show an amorphous pattern using SAED. The ternary diagram of Ca-O-N shows that 94% of Ca-rich coatings are distributed between $CaCO_3$ and $Ca(NO_3)_2$ (Fig. 6). In our study, the oxygen intensities from EDS spectra are also larger in the coatings than in the corresponding cores. The coating of the similar properties was described as $Ca(NO_3)_2$ by Laskin et al. (2005b). Most of Ca-rich coatings also examined by EDS include the minor chlorine. Murphy et al. (2006) measured chlorides at the surfaces of most nitrate coatings on dust particles in the troposphere. Scavenging of HCl and HNO_3 from the gas phase by mineral particles is also thermodynamically favorable (Kelly and Wexler, 2005). According to the compositions of the coatings, the minor Cl in Ca-rich coatings is inferred from $CaCl_2$ and $MgCl_2$ internally mixed with $Ca(NO_3)_2$.

Mineral particles associated with Mg-rich coatings are the mixtures of silicates and dolomite. Mg-rich coatings also contain O and N with minor amounts of Ca and Cl. Some of them also include tiny calcium sulfate particles (Fig. 7a, b). The coatings give amorphous patterns in SAED. Mg-rich coatings show properties in TEM similar to Ca-rich coatings. Although characteristics of Mg-rich components (e.g., $Mg(NO_3)_2$, $MgSO_4$, and $MgCl_2$) were paid attention in laboratory experiments (Ha and Chan, 1999; Li et al., 2008), the study of the association of Mg-rich coatings with mineral particles is very limited in field study. We believe that Mg-rich coatings are possibly mixtures of $Mg(NO_3)_2$ and Mg-bearing sulfates as well as minor chlorides (i.e., $MgCl_2$ and $CaCl_2$). In addition, we measured that most of Mg-rich coatings internally mixed with $Ca(NO_3)_2$ (Fig. 7f). The mixture was also described in the laboratory study of China loess reacted with nitric acid (Laskin et al., 2005b).

Most of Na-rich coatings on TEM grids are amorphous, and few also show crystal structure of Na_2SO_4 (Fig. 7c). EDS analysis shows that Na-rich coatings also consist of O, S, and N with minor amounts of Ca and Mg. Their compositions indicate that they possibly include $NaNO_3$ and Na_2SO_4 as well as minor $Ca(NO_3)_2$ and $Mg(NO_3)_2$.

K- and S-rich coatings usually enclose or coagulate with mineral particles (Fig. 7d, e). We also found many K- and S-rich particles without mineral particles in our samples. K-rich coatings also consist of O, S, and N, suggesting that they are a mixture of K-bearing sulfates and KNO_3 (Fig. 7e). S-rich particles are sensitive to the electron beam, and also consist of N and O (Fig. 7d). The particles are likely ammonium sulfate.

4 Discussion

4.1 Comparisons of coatings on mineral particles

Numerous studies have shown that nitrate coatings are atmospheric mineral particles through heterogeneous reactions with gaseous nitric acid (Zhang and Iwasaka, 1999; Laskin et al., 2005a; Matsuki et al., 2005 Sullivan et al., 2007). Our results show that nitrate coatings on mineral particles mainly formed in the brown haze episodes, whereas minor occurred in the dust episode. Higher concentrations of SO_2 and NO_x as well as higher RH shown in Fig. 1 occurred in brown haze than in dust episodes. These comparisons indicate that high concentrations of anthropogenic acidic gases and high RH can enhance heterogeneous reactions on mineral dust and form coatings. Our results also show that $Ca(NO_3)_2$ and $Mg(NO_3)_2$ coatings formed on mineral particles which contain calcite and dolomite components. It is in agreement with previous studies (Zhang and Iwasaka, 1999; Matsuki et al., 2005; Laskin et al., 2005a; Hwang and Ro, 2006). On the other hand, only a small number of K- and S-rich coatings on mineral particles occurred in brown haze episodes. Ammonium sulfate and K-bearing salts tend to accumulate in submicron dust particles because the fine dust particles in the atmosphere are easily transported and have a long lifetime (Sullivan et al., 2007).

4.2 Reactions on mineral particles

Mineral particles containing alkaline mineral components with hygroscopic coatings are more reactive with acidic gases than those without coatings in the atmosphere (Usher et al., 2003). In our samples, most of nitrate coatings include minor amounts of sulfates and chlorides, likely as a result of heterogeneous reactions. The reactions of alkaline mineral dust with HNO_3 are several orders of magnitude higher than with HCl, NO_2, or SO_2 (Ullerstam et al., 2003; Ooki and Uematsu, 2005; Vlasenko et al., 2006). In the polluted air of Beijing including abundant HNO_3, SO_2, and NO_2 (Bergin et al., 2001), alkaline mineral particles should first react with HNO_3 and form nitrate coatings on mineral particles. The hydrophilic coatings significantly enhance the uptake capacity of water and some gases (e.g., NO_x, SO_2, HCl, and O_3) on mineral particles in the atmosphere (Usher et al., 2003; Fountoukis and Nenes, 2007).

Our studies clearly show that calcium sulfate particles occurred in $Ca(NO_3)_2$ and $Mg(NO_3)_2$ coatings, although calcium sulfate associated with $Ca(NO_3)_2$ was previously detected by Zhang et al. (2000) and Hwang and Ro (2006). Pandis and Seinfeld (1989) showed that conversion of S (IV) to S (VI) in the atmosphere is in aqueous chemistry through oxidation by H_2O_2, O_3, and/or O_2 (catalyzed by Fe^{3+} and Mn^{2+}). Therefore, the possibly explain of the presence of calcium sulfate particles is that SO_2 absorbed in aqueous nitrate coatings was converted into calcium sulfate particles through aqueous chemical reactions. Calcium sulfate and nitrate coatings together forming on mineral dust particles is consistent with previous laboratory simulation that calcite can react with SO_2 and HNO_3 to form sulfate crystalline particles and nitrate deliquescent layer (Al-Hosney and Grassian, 2005).

4.3 Atmospheric implications

Mineral dust particles with nitrate coatings are hydrophilic, and those without coating are commonly hydrophobic (Kelly et al., 2007). The deliquescence relative humidities (DRHs) of hydrated $Ca(NO_3)_2$ and $Mg(NO_3)_2$ are ~12% and ~11%, respectively (Tang and Fung, 1997; Li et al., 2008). The DRHs are lower than the RH measured in every brown haze day. The results indicate that mineral dust particles with the nitrate coatings should be larger and more spherical in moist air (Fig. 2). The coated mineral particles can act as CCN and enhance scattering when they are entrained and transported in the troposphere (Gibson et al., 2006a; Kelly et al., 2007).

HNO_3 in the atmosphere is taken up by mineral dust particles as nitrates, reducing photochemically active NO_x (Underwood et al., 2001; Hanisch and Crowley, 2001; Gibson et al., 2006b). As a result, mineral dust particles in northern China should affect photochemical oxidation in the regional atmosphere.

5 Conclusions

Individual particle analysis by TEM provides detailed information regarding the coated mineral particles collected during dust and brown haze episodes between 24 May and 21 June 2007 in Beijing, northern China. TEM observations of mineral particles show that about 90% of mineral particles have coatings in the haze samples and 5% are in the dust sample. Mineral particles are mainly covered with $Ca(NO_3)_2$, $Mg(NO_3)_2$, and $NaNO_3$ coatings. High concentrations of SO_2 and NO_x as well as high RH occurred in brown haze can enhance heterogeneous reactions on alkaline mineral dust and form nitrate coatings. Once mineral particles coated with these hygroscopic coatings, they are more spherical and larger. Such changes enhance cooling contributions in the study region. Based on the compositions of coatings on mineral particles, calcium nitrate and magnesium nitrate coatings internally mix minor sulfates and chlorides. Many calcium sulfate particles with the diameter from 10 to 500 nm are enclosed within these coatings. Calcium sulfate particles likely formed in aqueous nitrate coatings in the atmosphere. The results show that mineral particles including alkaline components can be involved in atmospheric heterogeneous reactions with two or more acidic gases.

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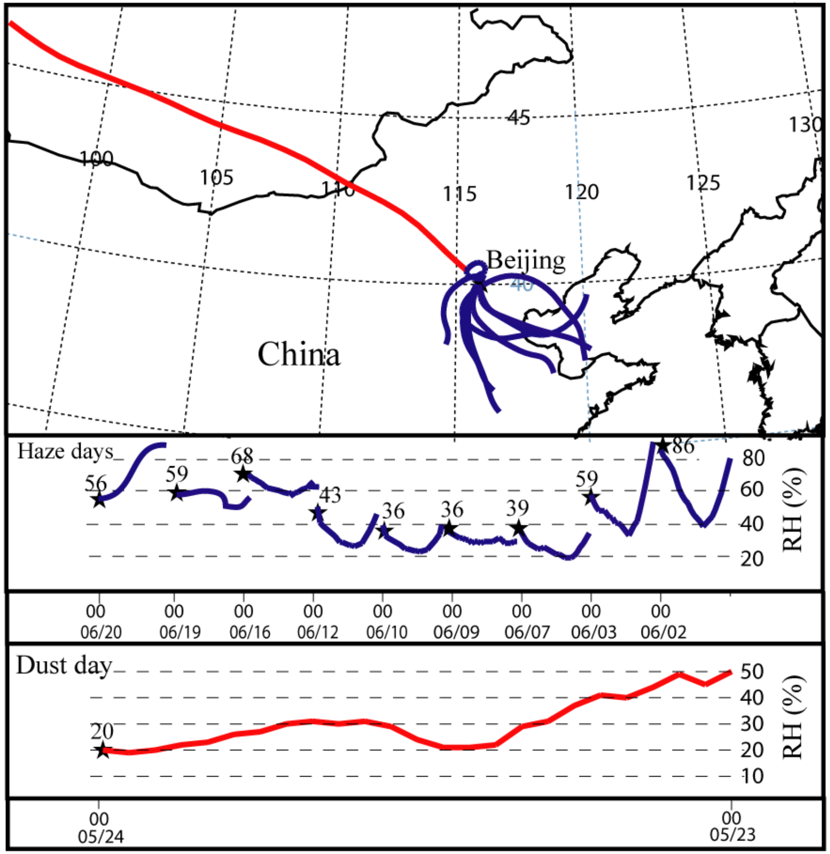

Fig. 1. Ten 24-h backward trajectories of air masses arriving at Beijing at 500 m and their relative humidities between 24 May and 21 June 2007. Dust air mass with relative humidity at 20% was transported from northwest of Beijing; Haze air masses with relative humidities from 36 to 86% were transported from southeast of Beijing.

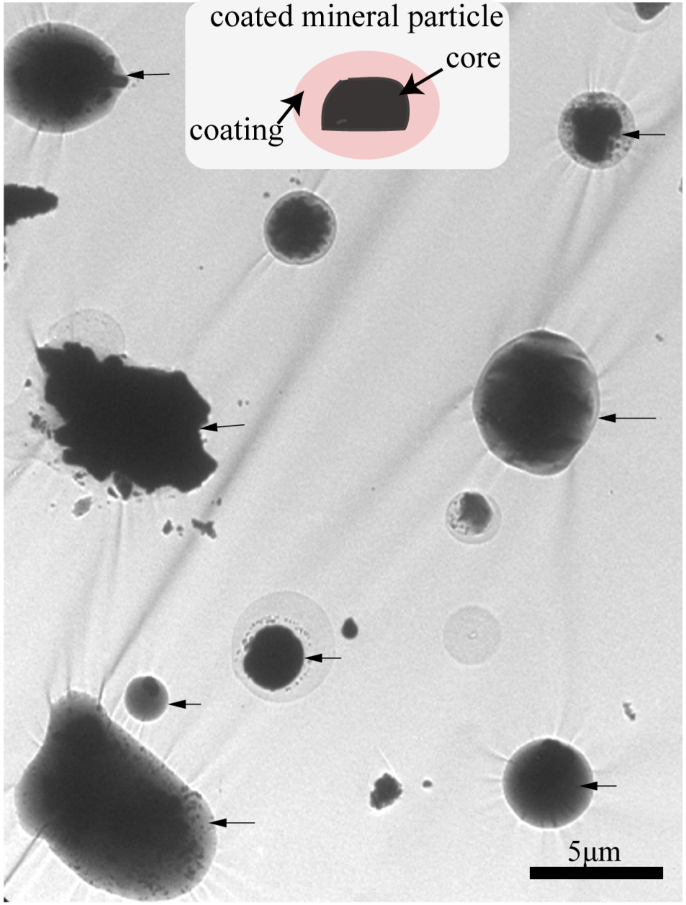

Fig. 2. TEM image of the coated mineral particles. Coated mineral particles include two parts: core and coating. Arrows indicate coated mineral particles.

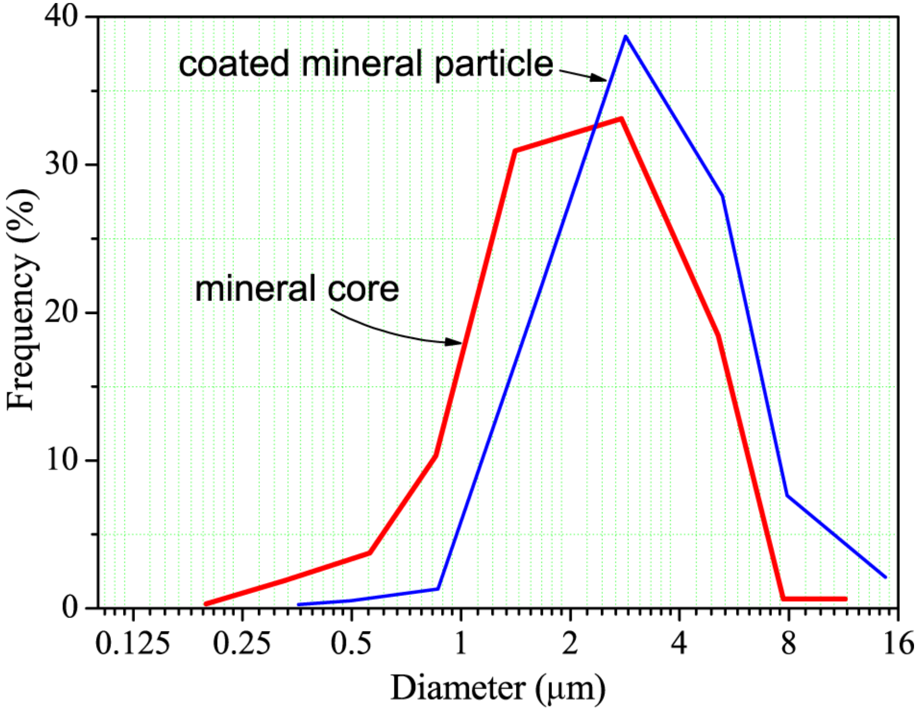

Fig. 3. Size distributions of 332 coated mineral particles and their mineral cores.

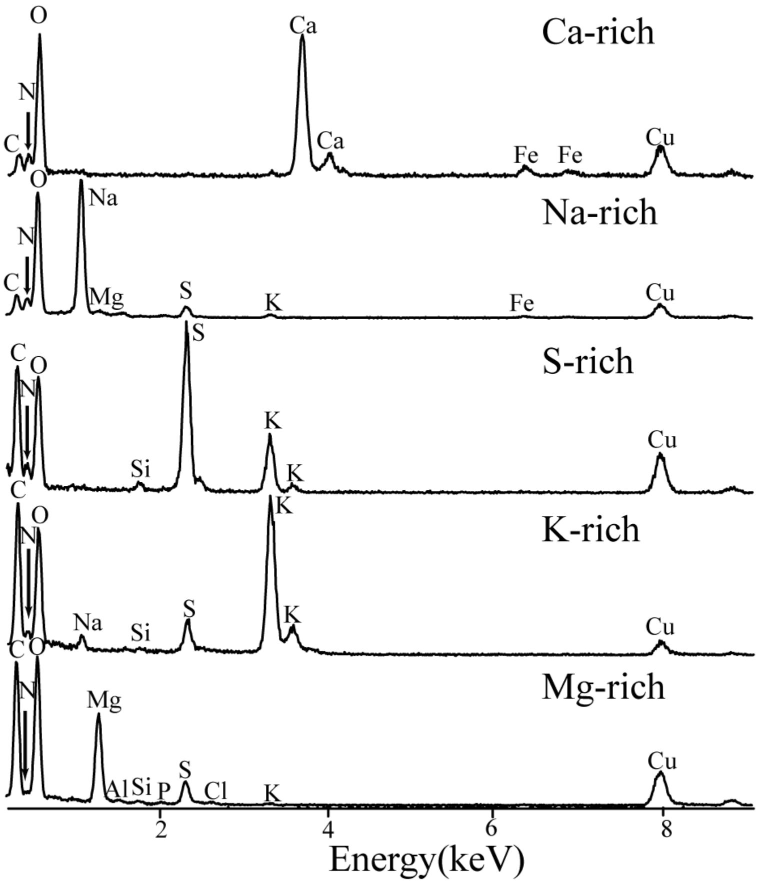

Fig. 4. Typical EDS spectra of Ca-, Na-, S-, K-, and Mg-rich coatings. C and Cu in spectra were not considered because of copper TEM grids and the carbon film.

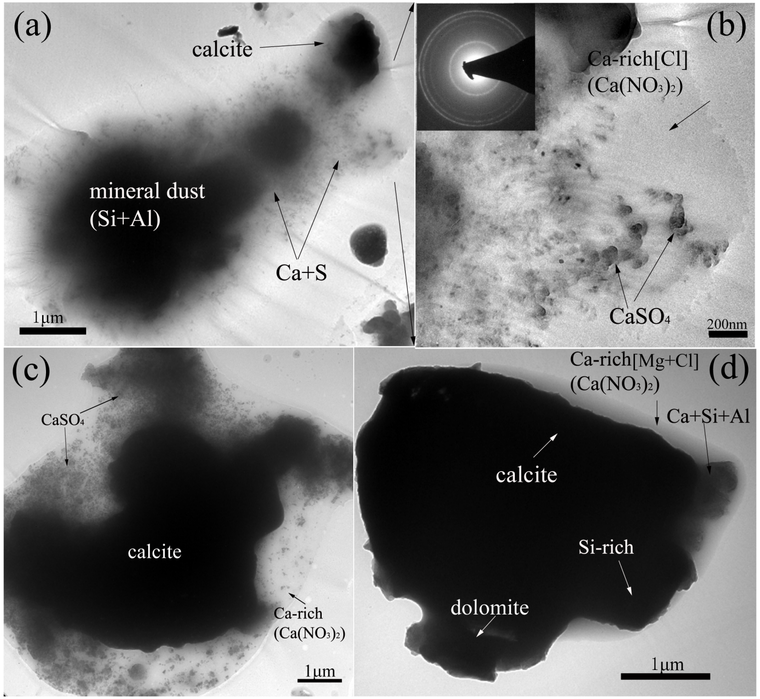

Fig. 5. TEM images of mineral dust particles covered by Ca-rich coatings. **(a)** A mineral particle that includes different minerals (aluminosilicate and calcite) is covered by Ca-rich coatings. **(b)** Ca-rich coatings include tiny particles. SAED diffraction pattern indicates that these particles are calcium sulfate. **(c)** Calcite particle is covered by Ca-rich coatings with calcium sulfate particles. **(d)** Mineral aggregates with different mineral components are covered partially by calcium nitrate; Major compositions are shown in parentheses, and minor elements are mentioned in square brackets.

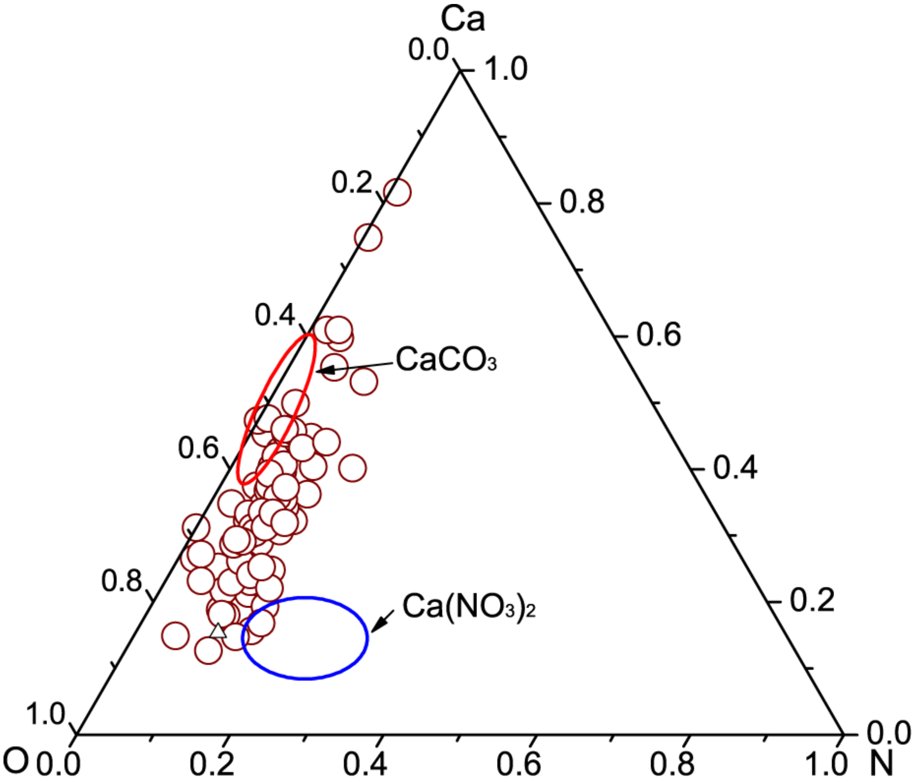

Fig. 6. Ternary diagrams showing EDS data of elemental compositions of Ca-rich coatings. Reference areas of $CaCO_3$ (red ellipse) and $Ca(NO_3)_2$ (blue ellipse) were described by Laskin et al. (2005b) in laboratory.

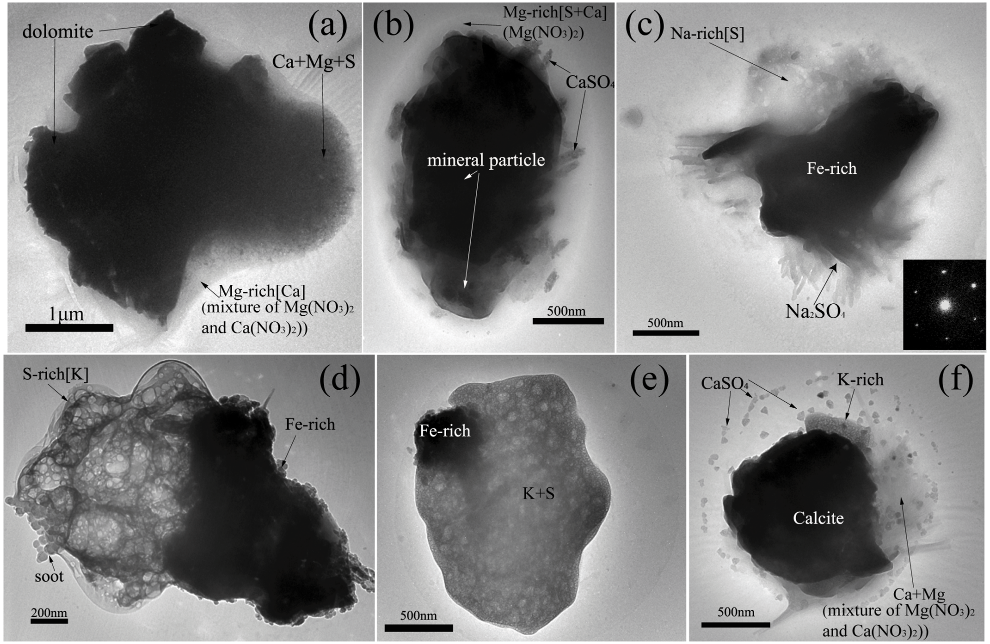

Fig. 7. TEM images of mineral particles with coatings. **(a)** Dolomite particle is covered by Mg-rich coatings including calcium sulfate and magnesium sulfate particles. **(b)** Mineral particle is covered by Mg-rich coatings including calcium sulfate particles. **(c)** Fe-rich mineral particle is coated by $NaNO_3$ and Na_2SO_4, confirmed by SAED. **(d)** Fe-rich mineral particle coagulate with soot and S-rich particle with minor K. **(e)** Fe-rich mineral particle coagulate with “K+S” particle. **(f)** Calcite particle is coated by a mixture of K-rich, $Ca(NO_3)_2$, $Mg(NO_3)_2$, and calcium sulfate.