

Observation of nitrate coatings on atmospheric mineral dust particles

W. J. Li^{1,2} and L. Y. Shao¹

¹State Key Laboratory of Coal Resources and Safe Mining & Department of Resources and Earth Science, China University of Mining and Technology, Beijing, China

²School of Earth and Space Exploration & Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, USA

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Abstract. Nitrate compounds have 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 ambient nitrate-coated mineral particles on an individual particle scale. In this study, sample collection was conducted during brown haze and dust episodes between 24 May and 21 June 2007 in Beijing, northern China. Sizes, morphologies, and compositions of 332 mineral dust particles together with their coatings were analyzed using transmission electron microscopy (TEM) coupled with energy-dispersive X-ray (EDX) microanalyses. Structures of some mineral particles were verified using selected-area electron diffraction (SAED). TEM observation indicates that approximately 90% of the collected mineral particles are covered by visible coatings in haze samples whereas only 5% are coated in the dust sample. 92% of the analyzed mineral particles are covered with Ca-, Mg-, and Na-rich coatings, and 8% are associated with K- and S-rich coatings. The majority of coatings contain Ca, Mg, O, and N with minor amounts of S and Cl, suggesting that they are possibly nitrates mixed with small amounts of sulfates and chlorides. These nitrate coatings are strongly correlated with the presence of alkaline mineral components (e.g., calcite and dolomite). CaSO₄ particles with diameters from 10 to 500 nm were also detected in the coatings including Ca(NO₃)₂ and Mg(NO₃)₂. Our results indicate that mineral particles in brown haze episodes were involved in atmospheric hetero-

geneous reactions with two or more acidic gases (e.g., SO₂, NO₂, HCl, and HNO₃). Mineral particles that acquire hygroscopic nitrate coatings tend to be more spherical and larger, enhancing 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 injected into the troposphere annually (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; Bauer et al., 2007). 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) (Levin et al., 1996; Yin et al., 2002). Heterogeneous chemical reactions of mineral dust with HNO₃ and NO₂ 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 particles will have enhanced hygroscopicity and altered sizes and shapes (Krueger et al., 2003, 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



Correspondence to: L. Y. Shao
(shaol@cumt.edu.cn)

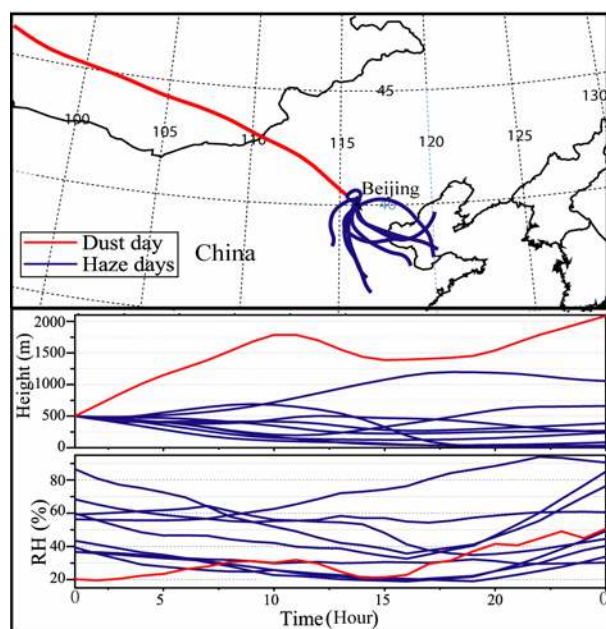


Fig. 1. Ten 24-h backward trajectories of air masses arriving at Beijing at 500 m and their relative humidities between 24 May and 21 June 2007. Humidities from 20 to 50% along with heights from 500 to 2200 m were shown in one dust air mass (red lines) from northwest of Beijing; Humidities from 20 to 92% along with heights from 20 to 1000 m were shown in nine haze air masses (blue lines) from southeast of Beijing.

components coated on mineral particles is important for evaluating their impact on both global and regional climates.

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) (Borensen et al., 2000; Krueger et al., 2004; Kelly and Wexler, 2005). Several field studies have indicated that mineral dust particles, through heterogeneous uptake of acidic gases, acquire coatings of sulfates (Kojima et al., 2006; Sullivan et al., 2007), and/or nitrates (Zhang et al., 2000; Laskin et al., 2005a; Matsuki et al., 2005; 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 present data on nitrate coatings detected in ambient particles.

With the rapid urbanization in China, huge amounts of emissions from cities frequently extend to regional pollution episodes (Li et al., 2007; Chan and Yao, 2008). SO_2 emissions declined from 1996 to present, 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 Beijing (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. Resolution down to fractions of a nanometer 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). $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ coatings on mineral particles are studied 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. Visibility varied between 1 and 6 km. Low wind speeds ($1\text{--}3\text{ m s}^{-1}$) from a southwesterly or southerly direction dominated during the haze periods. High concentrations of PM_{10} ($200\text{--}370\text{ }\mu\text{g m}^{-3}$), SO_2 ($21\text{--}51\text{ }\mu\text{g m}^{-3}$), and NO_2 ($51\text{--}88\text{ }\mu\text{g m}^{-3}$) were monitored in the brown haze days in Beijing (<http://www.bjee.org.cn/api/index.php>). In addition, four samples were collected in one dust episode on 24 May after precipitation from 21 to 23 May 2007. The dust episode was severe with a high PM_{10} concentration ($288\text{ }\mu\text{g m}^{-3}$) and low concentrations of anthropogenic pollutants (SO_2 , $9\text{ }\mu\text{g m}^{-3}$ and NO_2 , $46.4\text{ }\mu\text{g m}^{-3}$). During the dust period, temperature and RH were 31°C and 21%, respectively, and visibility was about 1 km. Wind was from a westerly direction with speeds varying from 1 to 7 m s^{-1} .

Backward trajectory analysis can determine transport paths of air masses arriving at a sampling site. The NOAA/ARL Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) (Draxler and Rolph, 2003) was employed to calculate ten 24-h backward trajectories of air masses arriving at Beijing between 24 May to 21 June 2007 at 500 m elevation (Fig. 1). One air mass from the northwest of Beijing with low humidity passed over the desert and loess plateau of northern China, carrying a high concentration of dust particles. From southeast of Beijing, air masses with high humidity passed over the industrial Hebei, Shanxi, and Shandong provinces, bringing haze particles. The backward trajectories shown in Fig. 1 are consistent with observations

of the 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 around 1 km from the fourth ring road of Beijing city. The height of the collection site was 60 m above sea level. Samplers were mounted on the top of a building located at the China University of Mining and Technology, 18 m above ground. The campus is surrounded by residential houses and a shopping center. The 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, and an air flow rate is 1.01 min^{-1} . The collection efficiency of the impactor is 50% for particles with an aerodynamic diameter of $0.3 \mu\text{m}$ and almost 100% at $0.5 \mu\text{m}$ if the density of particles is 2 g cm^{-3} . The sampler is described in more detail by Okada and Hitzenberger (2001). Sampling time ranged from 30 to 120 s, depending on the visibility. After sampling, the TEM grids were sealed in dry plastic capsules to prevent contamination.

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. Elemental compositions were determined using energy-dispersive X-ray spectrometry (EDX). A beryllium tip holder was used to obtain elemental compositions of individual particles to decrease X-rays sourced from the holder. Combining EDX and selected-area electron diffraction (SAED), we were able to verify the identity of some mineral particles.

All samples were primarily observed at $\times 500$ to 800 magnification 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 on 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. Many mineral particles from haze samples show visible coatings whereas few mineral particles from dust samples show visible coatings. The primary observations allowed us to choose 20 TEM grids collected in ten brown haze episodes and one sample collected in a single dust episode in our study. Mineral particles with various sizes in the chosen samples were observed at different magnifications ($\times 2550$ to $40\,000$) using TEM. There were between 10 and 40 mineral particles measured in each haze sample. We used TEM/EDX to obtain elemental compositions of different parts of individual particles. The EDX results are semi-quantitative, especially for light elements, such as C, N, and O. Because EDX spectra were affected by carbon film and copper grids, C and Cu were not calculated in

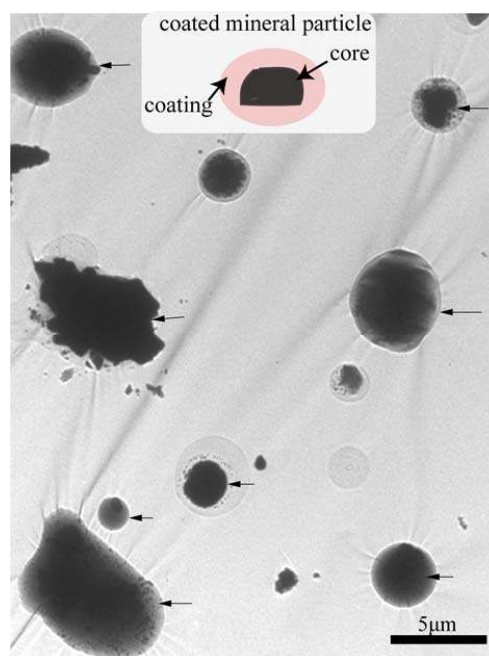


Fig. 2. TEM image of the coated mineral particles. Coated mineral particles include two parts: core and coating. Arrows indicate coated mineral particles.

our study. Therefore, inorganic components internally mixed in mineral dust particles were considered. Size of each particle was calculated using 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 (Kojima et al., 2005).

3 Results

3.1 Coated mineral particles

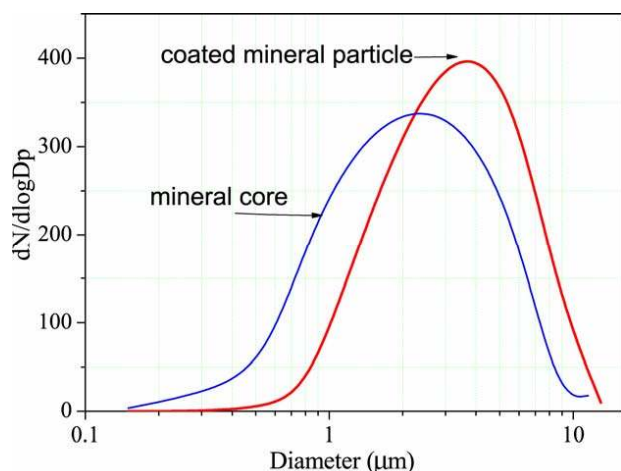
Mineral dust particles from the haze samples make up 1/3 (by number) of all collected aerosol particles with diameters greater than $0.1 \mu\text{m}$. Other studies using bulk composition analysis indicated that mineral dust, which originated from natural soil, construction dust, and re-suspended road dust, made up about 39–67% (by mass) in PM_{10} collected during 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 approximately 90% of mineral dust particles are covered by visible coatings in 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

Table 1. Relationships of cores and coatings of 332 mineral dust particles.

	Si-rich core (%)	Si-Al core (%)	Ca-Mg core (%)	Ca-rich core (%)	Fe-rich core (%)	Na-rich core (%)	number of particles
Ca-rich coating	6	13	10	63	7	0	236
Mg-rich coating	6	13	66	15	0	0	40
Na-rich coating	0	13	20	27	0	40	30
K-rich coating	30	40	10	10	10	0	13
S-rich coating	18	36	0	18	18	9	13

Si-rich (Si, [Ca]): quartz; Si-Al (Si, Al, [Ca]): clay, feldspar, and hornblende; Ca-Mg (Ca, Mg, [Si, Al]): dolomite; Ca-rich (Ca, [Si, Mg, Al]): calcite; Fe-rich (Fe, [Ca, Si, Al]): hematite; Na-rich (Na, [Si, Al]): halite.

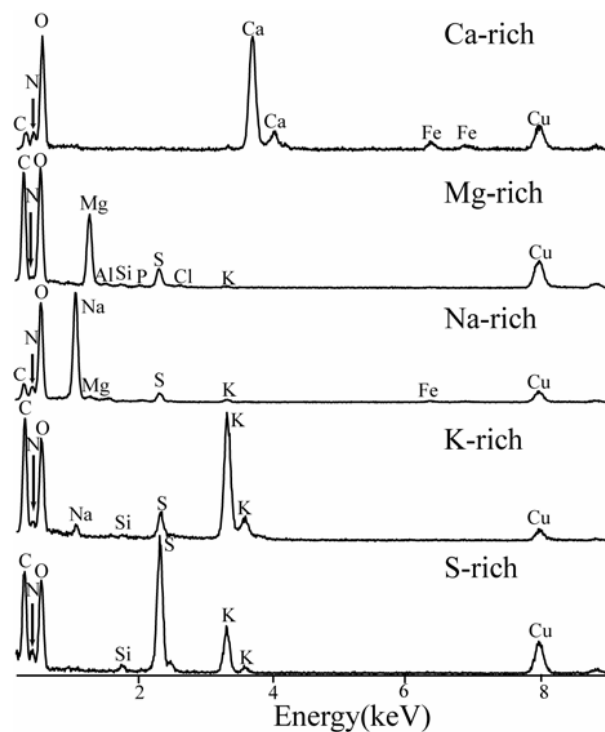
**Fig. 3.** Size distributions of 332 coated mineral particles and their cores.

332 coated mineral particles range from 0.4 to 16 μm with a median diameter of 3.1 μm (Fig. 3).

Based on morphological features, we can distinguish two parts of each coated mineral particle: core and coating (Fig. 2). In our samples, the cores are composed of Si-rich (e.g., quartz), Si-Al (e.g., clay, feldspar, and hornblende), Mg-Ca (e.g., dolomite), Ca-rich (e.g., calcite), and Fe-rich (e.g., hematite) (Table 1). One or more mineral components may act as cores that are enclosed within a single coating. Cores have diameters from 0.2 to 13 μm with median size 2.1 μm (Fig. 3). Most coatings are transparent in TEM images and sensitive to the strong electron beam.

3.2 Coatings on mineral particles

A total of 330 coated mineral particles in ten haze samples and two coated mineral particles in one dust sample were investigated using TEM/EDX. EDX analysis shows that coatings mainly include N, O, Na, Mg, S, Cl, K, and Ca. Although some mineral particles were covered with two or more components, one dominant component could be identified

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

using EDX spectra. Based on the major compositions, the coatings were classified into five categories (Fig. 4). They include Ca-rich (71%), Mg-rich (12%), and Na-rich (9%) as well as small amounts of K-rich (4%) and S-rich coatings (4%).

Ca-rich coating: Most of mineral particles associated with Ca-rich coatings are mixtures of silicates and calcite (or dolomite) (Table 1 and Fig. 5). EDX analysis shows that Ca-rich coatings also contain O and N with minor amounts of S, Cl, and Mg. CaSO_4 particles with the diameter from 10 to 500 nm were detected in these amorphous coatings

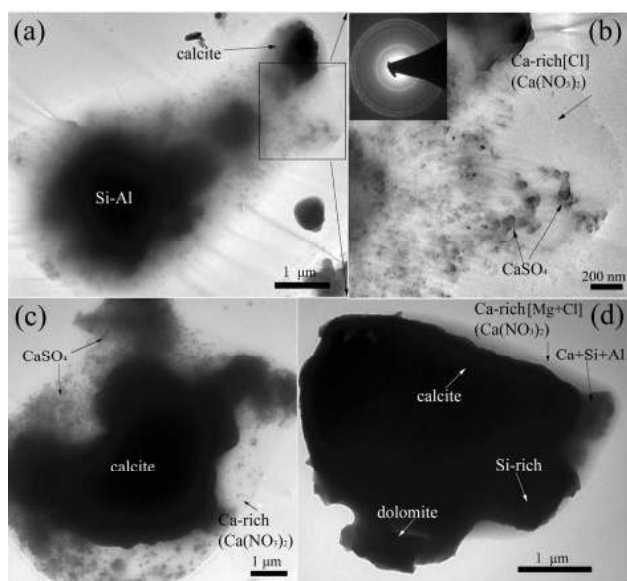


Fig. 5. TEM images of mineral dust particles covered by Ca-rich coatings. Major compositions are shown in parentheses, and minor elements are mentioned in square brackets. **(a)** A mineral particle that includes different mineral components (aluminosilicate and calcite (CaCO_3)) is covered by Ca-rich coatings. **(b)** High-resolution TEM image of the partial mineral particle in image (a). Amorphous Ca-rich coatings including the crystal particles with the diameter at 20–50 nm. SAED diffraction indicates that these particles are CaSO_4 . **(c)** Calcite particle is covered by Ca-rich coatings with CaSO_4 particles. **(d)** Mineral aggregates with different mineral components are covered partially by Ca-rich coatings.

(Fig. 5b). The ternary diagram of Ca–O–N shows that most Ca-rich coatings are closely distributed around the standard $\text{Ca}(\text{NO}_3)_2$ generated in laboratory (Fig. 6). In our study, the oxygen intensities from EDX spectra are also larger in the coatings than in the corresponding cores. The properties of coatings are similar to that of $\text{Ca}(\text{NO}_3)_2$ described by Laskin et al. (2005b). Most Ca-rich coatings examined by EDX analysis also include minor chlorine. Murphy et al. (2006) measured chlorides at the surface of most nitrate coatings on dust particles in the troposphere using laser mass spectrometry. Scavenging of HCl and HNO_3 from the gas phase by mineral particles is also thermodynamically favorable (Kelly and Wexler, 2005). Minor Cl in Ca-rich coatings is inferred from CaCl_2 and MgCl_2 internally mixed with $\text{Ca}(\text{NO}_3)_2$.

Mg-rich coating: Mineral particles associated with Mg-rich coatings are mixtures of silicates and dolomite (Table 1). Mg-rich coatings also contain N and O with minor amounts of Cl and Ca. CaSO_4 inclusions are also detected in some coatings (Fig. 7a, b). Mg-rich coatings are amorphous. Although characteristics of Mg-rich components (e.g., $\text{Mg}(\text{NO}_3)_2$, MgSO_4 , and MgCl_2) were studied in laboratory experiments (Ha and Chan, 1999; Li et al., 2008), the association of Mg-rich coatings with mineral particles is very

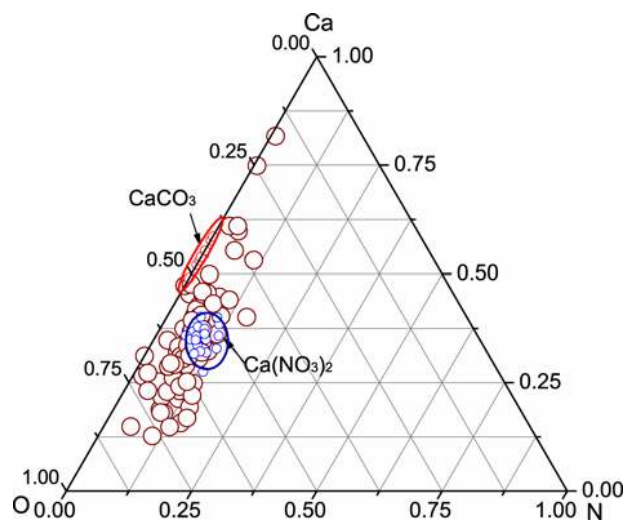


Fig. 6. Ternary diagrams showing EDX data of elemental compositions of Ca-rich coatings of 236 mineral particles. Reference areas represent the elemental compositions of laboratory generated CaCO_3 (red ellipse) and $\text{Ca}(\text{NO}_3)_2$ (blue ellipse) particles. All the particles were analyzed in the same TEM system with very close conditions.

limited in field studies. We believe that Mg-rich coatings are possibly mixtures of $\text{Mg}(\text{NO}_3)_2$ and Mg-bearing sulfates as well as minor chlorides (i.e., MgCl_2 and CaCl_2). In addition, measurements show that most Mg-rich coatings were internally mixed with $\text{Ca}(\text{NO}_3)_2$ (Fig. 7f). Similar mixtures were described in a laboratory study of China loess reacted with HNO_3 (Laskin et al., 2005b).

Na-rich coating: Some Na-rich coatings yield SAED patterns of Na_2SO_4 but the majority of coatings are amorphous (Fig. 7c). EDX analysis shows that Na-rich coatings also consist of N, O, and S with minor amounts of Mg and Ca. Their compositions indicate that they possibly include NaNO_3 and Na_2SO_4 as well as minor $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$.

K- and S-rich coating: K- and S-rich coatings usually enclose or coagulate with the submicron mineral particles (Fig. 7d, e). We also found many K- and S-rich particles without mineral particles in our samples. K-rich coatings consist of N, O, and S, 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 $(\text{NH}_4)_2\text{SO}_4$.

4 Discussion

4.1 Comparisons of coatings on mineral particles

Numerous studies have shown that nitrate coatings form on atmospheric mineral particles through heterogeneous

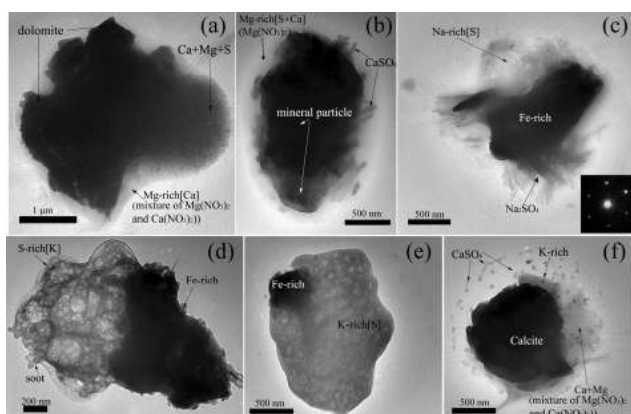


Fig. 7. TEM images of mineral particles with coatings. Major compositions are shown in parentheses, and minor elements are mentioned in square brackets. (a) Dolomite particle ($\text{CaMg}(\text{CO}_3)_2$) is covered by Mg-rich coatings with CaSO_4 and MgSO_4 particles. (b) Mineral particle is covered by Mg-rich coatings including CaSO_4 particles. (c) Fe-rich mineral particle is coated by NaNO_3 and Na_2SO_4 , Na_2SO_4 was 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-rich particle. (f) Calcite particle is enclosed by a mixed coating which likely includes K-rich, $\text{Ca}(\text{NO}_3)_2$, and $\text{Mg}(\text{NO}_3)_2$ with CaSO_4 particles.

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 abundant nitrate coatings formed on mineral particles during brown haze episodes, whereas few coatings occurred in the dust episode. Higher concentrations of SO_2 and NO_2 as well as higher RH shown in Fig. 1 occurred during brown haze episodes than during dust episode. These comparisons indicate that high concentrations of anthropogenic acidic gases and high RH can enhance heterogeneous reactions on mineral dust and form coatings. Consistent with this conclusion, abundant mineral dust particles containing calcite or dolomite without coatings were detected in the dust sample. Our results also show that $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ coatings preferentially formed on mineral particles which contain calcite and dolomite components (Table 1). This 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, a small number of K- and S-rich coatings on mineral particles occurred in brown haze episodes (Table 1). Ammonium sulfate and K-rich particles tend to accumulate in submicron clay mineral particles through their coagulations in air (Sullivan et al., 2007).

4.2 Reactions on mineral particles

Mineral particles with hygroscopic coatings are more reactive with acidic gases than those without coatings (Usher et al., 2003). In our samples, most nitrate coatings include mi-

nor 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 faster than with HCl , NO_2 , or SO_2 (Ullerstam et al., 2003; Oooki and Uematsu, 2005; Vlasenko et al., 2006). The polluted air of Beijing contains abundant HNO_3 , SO_2 , and NO_2 (Bergin et al., 2001), alkaline mineral particles may first react with HNO_3 and form nitrate coatings on mineral particles. The hydrophilic nitrate 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 study clearly shows that CaSO_4 particles occurred in $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ coatings, although CaSO_4 associated with $\text{Ca}(\text{NO}_3)_2$ 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 occurs during aqueous chemistry through the oxidation of S(IV) by H_2O_2 , O_3 , and/or O_2 (catalyzed by Fe^{3+} and Mn^{2+}). The presence of CaSO_4 particles in coatings is likely to be the result of SO_2 absorbed on aqueous nitrate coatings and then converted into CaSO_4 particles through aqueous chemical reactions. CaSO_4 and nitrate coatings together forming on mineral dust particles are 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; Shi et al., 2008). The deliquescence relative humidities (DRHs) of hydrated $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ are $\sim 12\%$ and $\sim 11\%$, 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 during the polluted days of high RH. 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). In the global scale, the coating processes can change the distributions of sulfate, nitrate, and mineral particle in atmosphere, and therefore change their impact on earth radiation (Bauer et al., 2007).

HNO_3 in the atmosphere is taken up by mineral dust particles as nitrates, reducing photochemically active NO_x (Hanisch and Crowley, 2001; Underwood et al., 2001; Liao et al., 2003; Gibson et al., 2006b). As a result, mineral dust particles in northern China can affect photochemical oxidation in the regional atmosphere.

5 Conclusions

TEM analysis provides detailed information regarding the coated mineral particles collected during brown haze and dust 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% in the dust sample. Mineral particles are mainly covered with coating including $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, and NaNO_3 . High concentrations of NO_2 and high humidity during the brown haze days can enhance heterogeneous reactions on alkaline mineral dust and form nitrate coatings. These coatings enhance both the size and hygroscopic properties of mineral particles. These large particles will contribute to cooling in the study region. Ca- and Mg-rich coatings also contained minor sulfates and chlorides. Many CaSO_4 particles with diameters from 10 to 500 nm are enclosed within these coatings. These tiny CaSO_4 particles likely formed in aqueous nitrate coatings in polluted air. 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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