Physicochemical Properties of Individual Airborne Particles in Beijing during Pollution Periods

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ABSTRACT

Particulate pollution is a serious environmental problem in China and has received much attention from the public. Airborne particles were collected during haze days in Beijing from June 2013 to May 2014. The morphology and elemental composition were investigated with transmission electron microscopy coupled with energy dispersive X-ray spectrometry (TEM-EDX). Six types of individual particles were identified, including sulfate particles (35.1%), mineral particles (26.0%), metal particles (13.5%), fly ash (13.2%), organic particles (5.9%), and soot aggregates (5.7%). Non-carbonaceous particles are mainly "S-rich", ranging from 37.4% in spring to 56.7% in summer, with certain amount of "Si-rich", "Ca-rich", "Fe-rich", and "K-rich" particles. The relative number percentage of sulfate particles shows a positive correlation with relative humidity (RH), suggesting that high RH might accelerate the sulfation of individual particles. Based on air mass backward trajectories, the high pollution in Beijing might be influenced by local emissions and air masses from adjacent areas south of Beijing. Air masses from Inner Mongolia carry higher concentrations of mineral particles and alleviate the abundance of "S-rich" and other particles.

Keywords: Pollution period; Individual particle; TEM-EDX; Sulfate particles.

INTRODUCTION

Atmospheric particles, which are typically composed of a complex constituent of organic and inorganic species, receive much attention because they are responsible for a multitude of climate and environmental issues in megacities in China (Huang et al., 2014). Depending on their composition, they directly and indirectly affect the climate by scattering or absorbing solar radiation (Griessbach et al., 2013; Rozanov et al., 2014). Atmospheric particles can act as cloud condensation nuclei (CCN), which have an impact on the formation, lifetime, and radiation properties of clouds (DeMott et al., 2003; Dusek et al., 2006; Lohmann, 2008). They can also change the precipitation and deposition, regionally and globally (Andreae and Rosenfeld, 2008; Li et al., 2013; Zhao et al., 2017). Various anthropogenic aerosol particles from biomass burning, coal combustion, industrial activities, and long-range transport have adverse health effects (Shao et al., 2006; 2016).

Rapid industrialization and urbanization have led to increased air pollution in China, similar to that in developed nations (Huang et al., 2014). Extremely severe and persistent haze is a serious problem and has been a concern for decades. Severe air pollution occurs frequently in Beijing, the capital of China, particularly in winter (Wang et al., 2014; Zhang et al., 2014; Niu et al., 2016). Because of very complex sources and the evolution of aerosol particles, air pollution control remains a great challenge in Beijing (Sun et al., 2013b). The causes of haze episodes and rapid dispersion remain some uncertainties (Wang et al., 2016).

Most researchers used a variety of “bulk” sample methods to study the overall physical and chemical properties of particulate matter and focused on the mass concentrations of different constituents such as nitrate, sulfate, organic matter, black carbon, metals, and dust. For example, Hu et al. (2017) and Wu et al. (2017) used aerodynamic high-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS) to measure the concentration and size distribution of submicron non-refractory species including organic and inorganic aerosols in Beijing. Huang et al. (2016) analyzed the seasonal variations of size-segregated water-soluble inorganic ions during pollution episodes in Beijing. Gao et al. (2014) applied inductively coupled plasma atomic emission spectrometry (ICP-AES) to study seasonal and spatial variations of 19 trace elements in multi-sized airborne particulate matter in Beijing. Wang et al. (2016) reported that the SO$_4^{2-}$ concentration increases noticeably during pollution events and that sulfate formation is greatly facilitated by high RH. Sun et al. (2014) found that submicron secondary...
inorganic aerosols play a vital role in haze formation. These data are important to understand the sources and formation of haze particles and their impact on health and climate. However, they cannot directly provide morphologies, elemental compositions, mixing states, and aging process information of individual particles, although these properties are important for the understanding of the particle formation and for modeling climate effects of atmospheric aerosols (Pösfai and Buseck, 2010; Cappa et al., 2012; Laskin et al., 2016; Li et al., 2016).

Previously, several individual particle analyses were conducted using electron microscopy. For example, Li and Shao (2010) applied transmission electron microscopy (TEM) to study the morphology, elemental composition, and mixing state of individual particles during a brown haze episode in Beijing. Adachi and Buseck (2008) analyzed the mixing state and size distribution of soot particles in Mexico. China et al. (2014) analyzed morphological and mixing properties of soot particles near a freeway. Most of the researchers focused on one or two pollution events. In this work, long-term (1 year) individual particle analysis was conducted. The morphologies and elemental compositions of individual particles from Beijing were obtained on peak pollution days between June 2013 and May 2014. Based on backward trajectory analysis, the potential sources of the individual particles are discussed.

MATERIALS AND METHODS

Aerosol Sampling

Aerosol samples were collected from a northwestern urban Beijing site (116.34°E, 39.99°N) from June 2013 to May 2014. Two types of samplers were placed on the fifth floor of a building on the campus of the China University of Mining & Technology in Beijing. A TSP-PM10-PM2.5 sampler (Kingstar Electronic Technology Inc., China) was used to collect PM2.5 samples on glass fiber filters for mass concentration analysis. The sampling time for each sample was 11 hours; 2 samples were collected every day. A KB-2F single-stage cascade impactor (1 L min \(^{-1}\)) was used to collect individual particle samples on copper TEM grids coated with a carbon film (300-mesh copper, China); the sampling time was 30–120 s depending on the particle loading (visibility). The RH and ambient temperature were automatically measured with a Kestral 4000 Pocket Weather Meter (Nielsen-Kellermann Inc., USA). The collected samples were sealed in a dry plastic tube and stored in an air dryer at a constant humidity of 20% ± 3% to minimize the exposure to ambient air and preserve the sample for analysis (Li et al., 2010).

Mass Concentration Analysis

In total, 86 glass fiber filter samples were collected and weighted with an electronic microbalance (Mettle Inc., Japan). The daily PM\(_{2.5}\) mass concentration was determined using the following formula: \(C = (M_b - M_a)/V\), where \(C\) represents the daily mass concentration of PM\(_{2.5}\) in Beijing (µg m\(^{-3}\)); \(M_a\) and \(M_b\) represent the mass of the glass fiber filers before and after sampling (µg), respectively; and \(V\) is the volume of the sampled air (m\(^3\)), which depends on the sampling hours and flow rate. The hourly PM\(_{2.5}\) mass concentration in Beijing was downloaded from the U.S. Department of State website (http://www.stateair.net/web/post/1/1.html). The U.S. embassy monitoring site is located ~12 km southeast of our sampling site on the campus of the China University of Mining and Technology in Beijing (Fig. S1). The average 24 h mass concentration was used as the daily PM\(_{2.5}\) mass concentration for comparison with our data.

TEM Analysis

The individual particles were analyzed with TEM coupled with energy dispersive X-ray spectrometry (TEM-EDX; Tecnai G\(^2\) F20). The TEM images were used for morphology analysis. The elemental composition was determined with EDX at 200 kV and a spectral acquisition time of ~30 s; Cu was excluded from our analysis because the TEM grids are composed of Cu. The aerosol particle distribution on the TEM grid was inhomogeneous. Coarser and finer particles were concentrated in the center and periphery, respectively. Therefore, five areas, from the center to the periphery of the sample grid, were analyzed to ensure representative data.

Backward Trajectory Analysis

Backward trajectory analysis can be used to identify the transport path of air mass arriving at the sampling site. For the calculation of air mass arriving at the sampling site, the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSLPLIT) model was applied. The endpoints of the sampling site were set at 500 and 1000 m above the ground level. The Global Data Assimilation System (GDAS) output dataset was used; the vertical motion method of the calculations was selected as the default model (Fan et al., 2016).

RESULTS

PM\(_{2.5}\) Mass Concentration

Based on the data from the U.S. Department of State, the annual average PM\(_{2.5}\) mass concentration from June 1, 2013, to May 31, 2014, was 99 µg m\(^{-3}\), twice more than that of the National Ambient Air Quality Standards (GB3095-2012; annual average PM\(_{2.5}\) mass concentration 35 µg m\(^{-3}\)) released in 2012 by the Ministry of Environmental Protection (MEP) of the People’s Republic of China (http://kjs.mep.gov.cn/hbj/hbz/bzwb/dqghj/hbjghzbz/201203/20120302_224165.htm). There were 63 good days (daily PM\(_{2.5}\) mass concentration 0–35 µg m\(^{-3}\)), 42 moderate days (35–75 µg m\(^{-3}\)), 113 lightly polluted days (75–115 µg m\(^{-3}\)), 79 moderately polluted days (115–150 µg m\(^{-3}\)), and 68 heavily (150–250 µg m\(^{-3}\)) or severely polluted days (> 250 µg m\(^{-3}\)), exclusively considering the daily PM\(_{2.5}\) mass concentration based on the Technical Regulation on Ambient Air Quality Index (HJ633-2012) released by the MEP (http://kjs.mep.gov.cn/hbj/hbz/bzwb/dqghj/hbjghzbz/201203/20120302_224166.htm). There were 50 pollution episodes (lasting ≥ 2 d) during which the daily PM\(_{2.5}\) mass concentration was > 75 µg m\(^{-3}\). The air pollution in Beijing was therefore very serious.
In total, 86 PM$_{2.5}$ glass fiber filters were collected during nine monitoring campaigns and the daily PM$_{2.5}$ mass concentration was calculated for comparison with the data from the U.S. embassy monitoring site. Fig. 1 shows that the daily PM$_{2.5}$ mass concentration we monitored and that from the embassy site are consistent; more pollution events occurred from October to April of the next year. We randomly selected ten TEM samples (H1–H10); the sample information is shown in Table 1.

**Nature of Individual Particles**

Based on the elemental compositions and morphologies, six groups of individual particles were classified including mineral particles, sulfate particles, soot aggregates, fly ash, organic particles, and metal particles.

The mineral particles generally show an irregular shape (Fig. 2(a)) and their elemental compositions are complex; they consist of O, Al, Si, Ca Na, Mg, and Fe (Li and Shao, 2010). Mineral particles are mainly suspended in soil, road dust, and construction dust; they are stable under the electron beam (Shao et al., 2007). The mineral particles tend to have a larger equivalent diameter than other particles. Fig. 2(a) shows a quartz mineral, identified based on the elemental composition (Fig. 2(h)).

The sulfate particles are mainly composed of S and O and minor K, Na, and Ca. Most sulfate particles are spherical and bubble-like in shape (Figs. 2(b) and 2(i)). They are sensitive to the electron beam; after several seconds of irradiation, S-rich residues or inclusions of other particles, such as soot, fly ash or metal particles, are left. Several regular rectangular-shaped CaSO$_4$ grains were also observed (Figs. 2(c) and 2(j)), which are relatively less beam-sensitive.

The soot aggregates are chain-like or compact carbon-bearing spheres (Fig. 2(d)). They are mainly composed of C and minor S and Si with hundreds of C-rich spheres. The diameter of each sphere ranges between 10 and 100 nm; it sometimes reaches up to 150 nm (Li and Shao, 2013). Fig. 2(d) shows an aged soot particle with minor S and K (Fig. 2(k)). Based on the scanning electron microscope study on samples of six different freeways in southern Michigan, the morphologies and mixing state of soot particles can be highly variable because of different combustion sources,

![Variation in daily mass concentrations of PM$_{2.5}$ in Beijing.](image)

**Table 1.** Information of the samples for TEM analysis.

<table>
<thead>
<tr>
<th>ID</th>
<th>Collection date</th>
<th>Season</th>
<th>Temperature (°C)</th>
<th>Humidity (%)</th>
<th>PM$_{2.5}$ (µg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>2013/06/08</td>
<td>Summer</td>
<td>22.2</td>
<td>76.3</td>
<td>187.0</td>
</tr>
<tr>
<td>H2</td>
<td>2013/06/11</td>
<td>Summer</td>
<td>24.0</td>
<td>60.9</td>
<td>82.7</td>
</tr>
<tr>
<td>H3</td>
<td>2013/09/21</td>
<td>Autumn</td>
<td>24.9</td>
<td>51.6</td>
<td>110.8</td>
</tr>
<tr>
<td>H4</td>
<td>2013/10/07</td>
<td>Autumn</td>
<td>21.1</td>
<td>63.2</td>
<td>184.0</td>
</tr>
<tr>
<td>H5</td>
<td>2013/10/28</td>
<td>Autumn</td>
<td>17.1</td>
<td>46.2</td>
<td>216.6</td>
</tr>
<tr>
<td>H6</td>
<td>2013/12/07</td>
<td>Winter</td>
<td>11.3</td>
<td>40.0</td>
<td>241.3</td>
</tr>
<tr>
<td>H7</td>
<td>2013/12/08</td>
<td>Winter</td>
<td>6.9</td>
<td>55.6</td>
<td>173.4</td>
</tr>
<tr>
<td>H8</td>
<td>2014/02/23</td>
<td>Winter</td>
<td>3.5</td>
<td>74.3</td>
<td>210.6</td>
</tr>
<tr>
<td>H9</td>
<td>2014/04/15</td>
<td>Spring</td>
<td>23.0</td>
<td>49.9</td>
<td>91.4</td>
</tr>
<tr>
<td>H10</td>
<td>2014/04/21</td>
<td>Spring</td>
<td>24.7</td>
<td>24.0</td>
<td>97.2</td>
</tr>
</tbody>
</table>
Fig. 2. TEM images of individual particles in Beijing in pollution days. (a) SiO$_2$ mineral image and (h) element composition, (b) sulfate particle image and (i) element composition, (c) sulfate particle (CaSO$_4$) image and (j) element composition, (d) an aged soot aggregates and (k) elemental composition, (e) organic particles, (f) fly ash image and (l) element composition, (g) aggregates of many regular metal Fe and (m) elemental composition.

operation conditions, and aging processes and time (China et al., 2014). It is believed that soot particles originate from the incomplete combustion of fuel or biomass (Adachi and Buseck, 2008).

Based on EDX, organic particles exhibit abundant C and minor O; they are stable under strong electron beam exposure. Regular spherical organic particles with smooth surfaces are referred to as tar balls (Fig. 2(e)). Compared with soot particles, they have a larger diameter and lack a graphitic structure. Tivanski et al. (2007) found that the compositions of tar ball particles resemble atmospheric humic-like substances.

Fly ash (Fig. 2(f)) consists of amorphous spherical particles and is mainly composed of Si, Al, and O and minor Fe, Mn, and Ca (Fig. 2(l)). Fly ash is a typical anthropogenic aerosol originating from coal combustion and other industrial combustion activities in northern China (Shi et al., 2003).
We also determined several metal particles including Fe-rich (Figs. 2(g) and 2(m)) and Zn-bearing particles. The Fe-rich particles are mainly composed of Fe and O; they always act as inclusions of secondary particles such as S-rich particles.

A total of 1297 individual particles were analyzed. During pollution in Beijing, sulfate and mineral particles represent the major fraction with 35.1% and 26.0%, respectively, followed by metal particles (13.5%), fly ash (13.2%), organic particles (5.9%), and soot aggregates (5.7%; Fig. 3).

**Elemental Composition of Non-Carbonaceous Particles**

Based on the EDX spectra of individual particles, non-carbonaceous particles mainly contain O, S, Si, Ca, Fe, K, Na, Mg, Al, Cl, and Ti. The criterion, P(Xi), is used to represent the weight ratio of element “Xi” such as Na, Mg, Al, Si, Cl, K, Ca, Ti, and Fe. The P(Xi) criterion is defined as follows (Okada et al., 2005; Li et al., 2010):

\[
P(X_i) = \frac{X_i}{(Na + Mg + Al + Si + S + Cl + K + Ca + Ti + Fe)}
\]

The particle is defined as X_i-rich particle (e.g., Si-rich) if the weight ratio of element X_i is > 65%, the particle is classified as X_i-dominated subtype. If the highest weight ratio of element X_i is < 65%, the element of X_j with the second highest relative weight percentage is used and the particle is classified as X_i + X_j subtype. For the pollution periods in Beijing, 931 individual non-carbonaceous particles with different compositions were determined (Table 2).

The “S-rich” particles are the main particle type, ranging from 37.4% in spring to 56.7% in summer, with an average of 46.3%. It is believed that high RH might cause this phenomenon. Among the S-rich particles, “S-dominated” and “S + Ca” particles are the main subtypes with 19.8% and 10.8%, respectively, followed by “S + Si” particles (8.5%), “S+Na” particles (4.2%), and “S + K” particles (3.0%).

The “Si-rich” particles account for 30.4%; “Si + Al” particles represent the largest fraction, followed by “Si + Ca”, “Si + S”, and “Si-dominated” subtypes, in descending order.

The “Ca-rich” particles account for 8.0% and are dominated by “Ca + S” particles (6.8%) and “Ca + Si” particles (2.0%); “Ca-dominated” particles are absent. Also, “S + Ca” particles (10.8%) and “Ca + S” particles (6.8%) account for 17.6%. It is reasonable to believe that the “Ca-dominated” particles were sulfated through heterogeneous reactions and that high RH is a key factor.

Several “Fe-rich” particles (10%) were determined, which are partly due to crustal mineral sources (e.g., hematite, iron silicate) or anthropogenic emissions from industries or iron welding (Li et al., 2008). The “K-rich” particles are known to be tracers of biomass burning (Adachi and Buseck, 2008) and account for 4.4%.

Based on the elemental composition, 63% of the observed particles contain S as the first or second weighting constituent. The individual particles are highly sulfated.

**Backward Trajectory Analysis**

The 24 h isentropic backward trajectories during the sampling period in Beijing are illustrated in Fig. 4. The trajectories show that most of the air masses originated from adjacent areas south of Beijing.

The H-1 air mass originated from the Bohai Sea, Tianjin...
Table 2. Types of non-carbonaceous individual particles in Beijing in pollution days.

<table>
<thead>
<tr>
<th>Particle types</th>
<th>Winter</th>
<th></th>
<th>Summer</th>
<th></th>
<th>Autumn</th>
<th></th>
<th>Winter</th>
<th></th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>NP</td>
<td>Average P values (1)</td>
<td>N</td>
<td>NP</td>
<td>Average P values</td>
<td>N</td>
<td>NP</td>
<td>Average P values</td>
</tr>
<tr>
<td>S-rich</td>
<td></td>
<td></td>
<td>S(79.1 ± 11.3)</td>
<td>67</td>
<td>37.4</td>
<td>S(83.2 ± 4.5)</td>
<td>119</td>
<td>56.7</td>
<td>S(76.4 ± 8.5)</td>
</tr>
<tr>
<td>S-dominated</td>
<td>33</td>
<td>18.4</td>
<td>S(53.7 ± 4.4)</td>
<td>33</td>
<td>18.4</td>
<td>S(52.7 ± 3.9)</td>
<td>55</td>
<td>27.6</td>
<td>S(57.4 ± 6.5)</td>
</tr>
<tr>
<td>Si-rich</td>
<td>65</td>
<td>36.3</td>
<td>S(86.3 ± 0.8)</td>
<td>65</td>
<td>36.3</td>
<td>S(76.9 ± 9.5)</td>
<td>65</td>
<td>36.3</td>
<td>S(79.6 ± 4.3)</td>
</tr>
<tr>
<td>Si-dominated</td>
<td>4</td>
<td>2.2</td>
<td>Si(86.3 ± 0.8)</td>
<td>4</td>
<td>2.2</td>
<td>Si(76.9 ± 9.5)</td>
<td>4</td>
<td>2.2</td>
<td>Si(79.6 ± 4.3)</td>
</tr>
<tr>
<td>Si + S</td>
<td>33</td>
<td>18.4</td>
<td>S(50.9 ± 1.1)</td>
<td>33</td>
<td>18.4</td>
<td>S(50.8 ± 6.5)</td>
<td>33</td>
<td>18.4</td>
<td>S(52.7 ± 5.8)</td>
</tr>
<tr>
<td>Si + Ca</td>
<td>S(34.3 ± 8.0)</td>
<td>37</td>
<td>Si(49.3 ± 3.6)</td>
<td>37</td>
<td>20.7</td>
<td>Si(47.5 ± 3.3)</td>
<td>37</td>
<td>20.7</td>
<td>Si(47.5 ± 3.3)</td>
</tr>
<tr>
<td>Si + Al</td>
<td>S(47.2 ± 7.4)</td>
<td>18</td>
<td>Si(36.3 ± 5.8)</td>
<td>18</td>
<td>10.1</td>
<td>Si(36.3 ± 5.8)</td>
<td>18</td>
<td>10.1</td>
<td>Si(36.3 ± 5.8)</td>
</tr>
<tr>
<td>Ca-rich</td>
<td>16</td>
<td>8.9</td>
<td>Ca(53.6 ± 9.1)</td>
<td>16</td>
<td>8.9</td>
<td>Ca(53.6 ± 9.1)</td>
<td>16</td>
<td>8.9</td>
<td>Ca(53.6 ± 9.1)</td>
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<tr>
<td>Ca + Si</td>
<td>Ca(53.6 ± 9.1)</td>
<td>5</td>
<td>Ca(57.8 ± 9.2)</td>
<td>5</td>
<td>2.8</td>
<td>Ca(57.8 ± 9.2)</td>
<td>5</td>
<td>2.8</td>
<td>Ca(57.8 ± 9.2)</td>
</tr>
<tr>
<td>Ca + S</td>
<td>Ca(52.4 ± 5.5)</td>
<td>11</td>
<td>Ca(59.3 ± 3.5)</td>
<td>11</td>
<td>6.1</td>
<td>Ca(59.3 ± 3.5)</td>
<td>11</td>
<td>6.1</td>
<td>Ca(59.3 ± 3.5)</td>
</tr>
<tr>
<td>Fe-rich</td>
<td>20</td>
<td>11.2</td>
<td>Fe(78.0 ± 4.4)</td>
<td>20</td>
<td>11.2</td>
<td>Fe(85.9 ± 2.4)</td>
<td>20</td>
<td>11.2</td>
<td>Fe(85.9 ± 2.4)</td>
</tr>
<tr>
<td>Fe-dominated</td>
<td>Fe(78.0 ± 4.4)</td>
<td>7</td>
<td>Fe(85.9 ± 2.4)</td>
<td>7</td>
<td>3.9</td>
<td>Fe(85.9 ± 2.4)</td>
<td>7</td>
<td>3.9</td>
<td>Fe(85.9 ± 2.4)</td>
</tr>
<tr>
<td>Fe + Ca</td>
<td>Fe(50.1 ± 3.4)</td>
<td>13</td>
<td>Fe(51.4 ± 2.2)</td>
<td>13</td>
<td>7.3</td>
<td>Fe(51.4 ± 2.2)</td>
<td>13</td>
<td>7.3</td>
<td>Fe(51.4 ± 2.2)</td>
</tr>
<tr>
<td>K-rich</td>
<td>11</td>
<td>6.1</td>
<td>K(51.4 ± 2.7)</td>
<td>11</td>
<td>6.1</td>
<td>K(53.4 ± 4.8)</td>
<td>11</td>
<td>6.1</td>
<td>K(53.4 ± 4.8)</td>
</tr>
<tr>
<td>K + S</td>
<td>K(51.4 ± 2.7)</td>
<td>11</td>
<td>K(53.4 ± 4.8)</td>
<td>11</td>
<td>6.1</td>
<td>K(53.4 ± 4.8)</td>
<td>11</td>
<td>6.1</td>
<td>K(53.4 ± 4.8)</td>
</tr>
</tbody>
</table>

(1) Average weight percentage and standard deviation (wt. %), (2) Number percentage of analyzed individual particles.
Province, and northern Shandong Province. The air mass from the Bohai Sea leads to high RH; the last 6-hour trajectory is notably shorter than the previous 18-hour trajectory, indicating that the air mass stayed in south Beijing for a long time and accelerated the sulfation, which results in a larger proportion of S-rich particles (52.3%). The H-2 air mass originated in the Hebei, Shandong, Henan provinces and stayed more than 12 hours in the industrial area of the southeastern Hebei Province, causing a large proportion of S-rich particles (60.6%).

The H-3 and H-5 air masses are mainly influenced by local emissions and stayed in Beijing longer than 24 hours and the S-rich particles account for 57.2% and 50.6%, respectively. The H-4 air mass also originated from the Bohai Sea, Tianjin Province, and northern Shandong Province. The RH is lower (51.2%) than that of H-1 (76.3%), the sulfation is lower, and S-rich particles account for 39.6%.

It is common that coals and other materials are served as fuels in northern China in winter. Acid gaseous emissions are released and individual particle sulfation is favored. The H-6 air mass originated in the southwest of Beijing in the Hebei Province and stayed more than 12 hours in Beijing. The H-7 air mass came from Inner Mongolia and the Hebei Province and stayed in Beijing for a long time. These air masses contain 40.9% and 41.8% S-rich particles, respectively. The H-8 air mass originated from high-industry areas of the southern and eastern Hebei Province; it comprises 46.5% S-rich particles.

The H-9 air mass originated in the south of Beijing, including the Hebei, Shandong, Henan, and Anhui provinces, and contains 44.0% S-rich particles. It is known that aerosol dust enters Beijing from the desert area in spring (Hu et al., 2016). The H-10 air mass came from Inner Mongolia; its mineral particles account for 44.7% (more than that of H-7; 26.9%), alleviating the abundance of S-rich particles (33.3%).

**DISCUSSIONS**

**Influences of RH on Sulfate Particle Formation**

The morphologies and elemental compositions of individual particles during pollution days in Beijing were adequately characterized with TEM. Sulfate particles are most abundant during pollution events in Beijing (Fig. 3). Li et al. (2010) found that sulfate particles are the major inorganic aerosol constituents of haze days and are mainly comprised of (NH$_4$)$_2$SO$_4$. Yao et al. (2003) suggested that the sulfate particles form through chemical reactions between NH$_3$ and H$_2$SO$_4$. A small portion of sulfates, such as CaSO$_4$, showed a regular rectangular shape. These regular CaSO$_4$ particles are relatively insensitive to the electron beam. Shao et al. (2008) suggested that these regular rectangular particles form through secondary reactions. Takahashi et al. (2008) believed they might form via the reaction between calcite and SO$_2$. However, Zhang et al. (1999) suggested that they might form from crystallized construction dust. Wu et al. (2012) proposed that not all CaSO$_4$ particles form through secondary reactions but also from re-suspension of surface soil of deserts such as the Taklimakan Desert.

Interestingly, the relative frequency of sulfate particles is positively correlated with the RH (correlation coefficient of 0.84; Fig. 5), suggesting that high RH can accelerate the
formation of secondary sulfate particles. This result is consistent with previous “bulk” sample studies, which reported that high RH promotes sulfate particle formation. For example, Liu et al. (2015) found that sulfates, together with nitrates, significantly contribute to wintertime pollution episodes in Beijing and suggested that sulfate is due to heterogeneous reactions with abundant aerosol water under wet conditions. Sun et al. (2013a) described a strong and positive RH dependency of the sulfur oxidation ratio, indicating that aqueous processing might play a more important role in sulfate formation. All these facts suggest that sulfate formation, which is greatly facilitated by high RH, plays a key role in the formation of persistent and severe haze.

Possible Sources of Aerosol Particles

The backward trajectories illustrate the sources of air mass arriving in Beijing (Fig. 4). The trajectories of the H3 and H5 air masses are very short, indicating that local emissions attributed to the pollution. The H1, H4, and H8 air masses originated from the southeast, H2 and H9 came from the south, and H6 came from the southwest, suggesting that most samples collected on pollution days in Beijing were influenced by air masses from southern areas of Beijing. This result is consistent with that of previous studies. For example, Sun et al. (2013b) reported that high PM pollution episodes in Beijing are generally related to southerly and easterly winds with low wind speeds. Ma et al. (2017) suggested that regional transport from the south is the major reason for the initial PM increase in Beijing and that heterogeneous reactions further enhance the PM. The trajectories near Beijing are very short, indicating that the long stay in Beijing favors heterogeneous reactions. The H7 and H10 air masses came from northwestern Inner Mongolia. Mineral dust particles are lifted into the atmosphere by strong surface winds, are transported over a long distance, and influence the climate. The air mass from Inner Mongolia always includes mineral particles, causing high PM pollution and low RH (Yuan et al., 2008) and alleviating the abundance of S-rich and other particles. The samples were randomly selected; most of the backward trajectories indicate local and southern sources. It is reasonable to believe that high pollution in Beijing is affected by local emissions or air masses originating from adjacent areas south of Beijing.

Heterogeneous Reaction and Sulfation Mechanism

Based on the elemental compositions of individual particles, 63% non-carbonaceous particles were observed with S as the first or second weight constituent, suggesting high sulfation of individual particles. The stability of the atmospheric layer and high RH inhibit the diffusion of emissions, causing a high PM$_{2.5}$ concentration. As a result, anthropogenic emissions (e.g., SO$_2$, NO$_x$) are not transported over a long distance and a series of atmospheric reactions can occur near the emission source. Many studies demonstrated the positive correlation between heterogeneous reactions on mineral particle surfaces and RH of the atmosphere (Li and Shao, 2013; Zhao et al., 2013), indicating that high RH could enhance heterogeneous reactions and increase both the size and hygroscopic properties of mineral particles.

Fig. 6 shows a typical complex heterogeneously reacted particle, which consists of a mineral core with Si, Al, Fe, Mg, and Ca and a mixed hydration layer comprising crystallized particles. Li and Shao (2013) reported that the presence of CaSO$_4$ particles in mineral coatings is likely the result of SO$_2$ absorbed by aqueous nitrate coatings and then converted into CaSO$_4$ crystalline particles through aqueous chemical reactions. Based on the TEM images and elemental compositions, we propose a three-step sulfation mechanism on the individual particle surface explaining the above-mentioned secondary heterogeneous formation (Fig. 7). Firstly, these non-carbonaceous particles (Figs. 7(a) and 7(a)’) absorb water vapor on the surface and form a hydration layer (Figs. 7(b) and 7(b)’). The SO$_2$ and NO$_x$ are
Fig. 6. A complex heterogeneous particle under surface sulfation.

Fig. 7. Diagram showing mechanism of sulfation of individual particles during pollution episodes.

then absorbed, forming a hydration layer containing H₂SO₄ (Figs. 7(c) and 7(c')). This is consistent with the suggestion that sulfate particles mainly form during aqueous processes (Sun et al., 2016). Finally, H₂SO₄ interacts with alkali metals (e.g., Ca, Na, Mg, and K; Fig. 7(d1)) and other mineral elements (e.g., Si, Al; Fig. 7(d2)) and CO₂ is released as shown in Fig. 7(d').

CONCLUSIONS

Based on the morphologies and elemental compositions, six different types of individual particles were classified including mineral particles, sulfate particles, metal particles, soot aggregates, organic particles, and fly ash. Among the 1297 analyzed individual particles, sulfate and mineral particles were predominant with 35.1% and 26.0%, respectively, followed by metal particles (13.5%), fly ash (13.2%), organic particles (5.9%), and soot aggregates (5.7%). The sulfate particles show a positive correlation with RH. Based on the elemental compositions, “S-rich” particles are predominant, ranging from 37.4% in spring to 56.7% in summer, followed by “Si-rich”, “Ca-rich”, “Fe-rich”, and “K-rich” particles.

High RH might accelerate the sulfation of individual particles. The high pollution in Beijing is probably influenced by local emissions and polluted areas south of Beijing. The air mass from Inner Mongolia always carries high concentrations of mineral particles, which might alleviate the abundance of S-rich particles.

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