



## OPEN

## SUBJECT AREAS:

ATMOSPHERIC  
CHEMISTRYENVIRONMENTAL  
MONITORING

# Mineral dust and NO<sub>x</sub> promote the conversion of SO<sub>2</sub> to sulfate in heavy pollution days

Hong He<sup>1</sup>, Yuesi Wang<sup>2</sup>, Qingxin Ma<sup>1</sup>, Jinzhu Ma<sup>1</sup>, Biwu Chu<sup>1,3</sup>, Dongsheng Ji<sup>2</sup>, Guiqian Tang<sup>2</sup>, Chang Liu<sup>4</sup>, Hongxing Zhang<sup>1</sup> & Jiming Hao<sup>3</sup>Received  
13 November 2013Accepted  
5 February 2014Published  
25 February 2014

Correspondence and requests for materials should be addressed to H.H. (honghe@rcees.ac.cn) or Y.S.W. (wys@mail.iap.ac.cn)

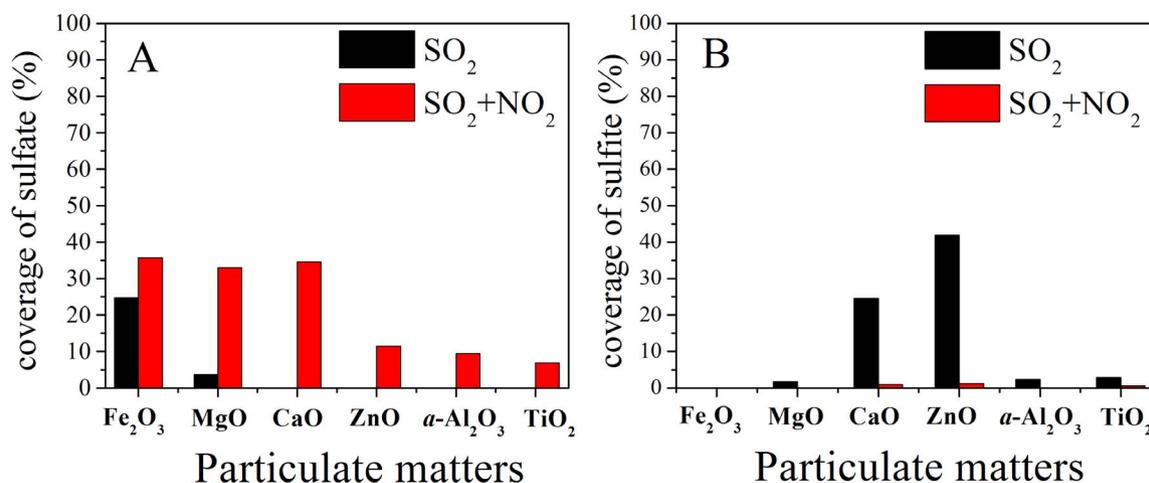
<sup>1</sup>Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China, <sup>2</sup>State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China, <sup>3</sup>State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 10084, China, <sup>4</sup>Chinese Academy of Meteorological Sciences, Beijing 100081, China.

Haze in China has been increasing in frequency of occurrence as well as the area of the affected region. Here, we report on a new mechanism of haze formation, in which coexistence with NO<sub>x</sub> can reduce the environmental capacity for SO<sub>2</sub>, leading to rapid conversion of SO<sub>2</sub> to sulfate because NO<sub>2</sub> and SO<sub>2</sub> have a synergistic effect when they react on the surface of mineral dust. Monitoring data from five severe haze episodes in January of 2013 in the Beijing-Tianjin-Hebei regions agreed very well with the laboratory simulation. The combined air pollution of motor vehicle exhaust and coal-fired flue gases greatly reduced the atmospheric environmental capacity for SO<sub>2</sub>, and the formation of sulfate was found to be a main reason for the growth of fine particles, which led to the occurrence of haze. These results indicate that the impact of motor vehicle exhaust on the atmospheric environment might be underestimated.

China's air pollution has been a global concern for decades. Reviewing the history, the "Photochemical Smog Event in Los Angeles", which took place in the 1940s–1950s, was mainly caused by photochemical reaction of NO<sub>x</sub> (= NO + NO<sub>2</sub>) and volatile organic compounds (VOCs) from motor vehicle exhaust. The "Great Smog of 1952 in London" was mainly caused by SO<sub>2</sub> emitted from coal burning. The primary pollutants in these events were clearly revealed in these incidents. In contrast, up to now, the main cause of heavy haze in China has been widely studied but not yet fully elucidated. The key factors that affect the formation and evolution of haze include emission of primary pollutants, secondary aerosol formation from homogeneous and heterogeneous reactions, and hygroscopic growth of aerosols<sup>1–3</sup>. However, the intrinsic cause for haze formation is still not clear. The Chinese economy is undergoing high-speed development that is heavily dependent on coal consumption as its main energy source. Coal burning, motor vehicles, and industrial emission pollution, which have been seen in developed countries at different times, all contribute to a high burden and heavy composite atmospheric pollution in China nowadays. This has led to complex air pollution and is a new situation that developed countries have not experienced ever before.

Haze is a phenomenon caused by fine particles (PM<sub>1</sub> or PM<sub>2.5</sub>), resulting in the decline of atmospheric visibility. In recent years, haze in China's eastern region has increased in frequency of occurrence as well as the area of the affected region. According to the statistical data from monitoring by the Chinese Academy of Sciences (CAS), the Beijing-Tianjin-Hebei regions experienced five severe haze episodes (peak concentrations of PM<sub>2.5</sub> over 300 µg/m<sup>3</sup>) in January 2013 alone. Therein, downtown Beijing's PM<sub>2.5</sub> level exceeded the Second Grade National Standard of China (75 µg/m<sup>3</sup>, the Ambient Air Quality Standard planned to be implemented in 2016) for 22 days and exceeded the First Grade National Standard (35 µg/m<sup>3</sup>) for 27 days. According to the safety standard of the World Health Organization (WHO) (10 µg/m<sup>3</sup>), downtown Beijing air conditions exceeded the standard for nearly the whole month. The haze-affected area reached 1,300,000 km<sup>2</sup> in January 2013<sup>4</sup>.

The external cause for the large scope and long duration of haze which frequently appeared in China in January 2013 was the stable synoptic conditions; however, the internal cause was related to the PM<sub>2.5</sub> or PM<sub>1</sub> and their precursor pollutants, such as SO<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub>, and VOCs etc., which heavily exceeded the environmental capacity determined by conditions such as local weather and terrain. Once calm weather persists, pollutants do not disperse easily, and secondary particles produced by homogeneous and heterogeneous atmospheric chemical processes of pollutants readily accumulate, resulting in the formation of haze. Field observations of heavy haze in



**Figure 1** | Surface coverage of (A) sulfate and (B) sulfite species on mineral oxides after heterogeneous reaction of SO<sub>2</sub> or SO<sub>2</sub>+NO<sub>2</sub> for 2 h. Reaction conditions: carrier gases: N<sub>2</sub>(80%) + O<sub>2</sub>(20%) with total flow of 100 mL/min; concentrations of SO<sub>2</sub> and NO<sub>2</sub>: both 200 ppm; T = 303 K. A synergistic effect between SO<sub>2</sub> and NO<sub>2</sub> was also observed when reactant concentrations were at ppb level with long reaction time (see Supplementary Information).

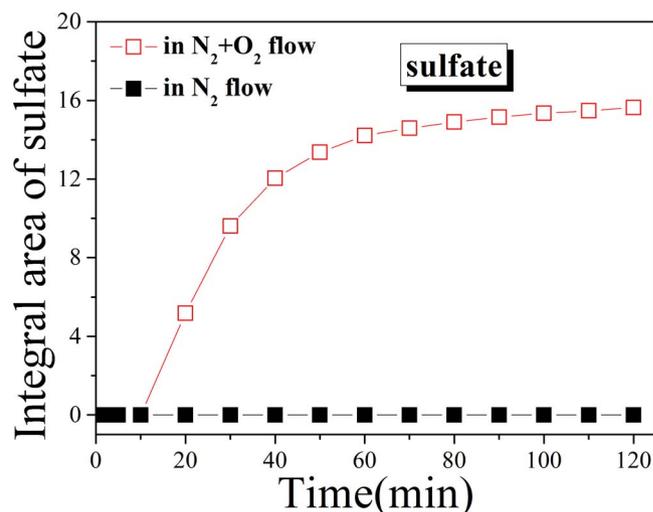
January 2013 also found the occurrence of a dust storm from January 10 to 15 in the Beijing-Tianjin-Hebei regions.

Here, we report on a new mechanism of haze formation, in which the coexistence of NO<sub>x</sub> can reduce the environmental capacity for SO<sub>2</sub>, leading to a gas-particle conversion process and fine particle growth.

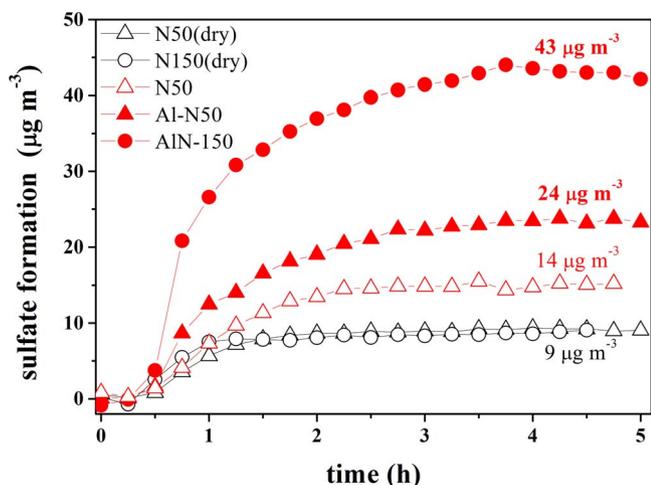
## Results

As one of the most important components of fine particles in the atmosphere, sulfate has been the focus of research studying its formation mechanism. Atmospheric sulfate originates from a variety of sources, including volcanic ash, sea spray, and the oxidation of sulfur dioxide (SO<sub>2</sub>) and other sulfur-containing species<sup>5–8</sup>. A number of models have been applied to predict the formation of sulfate aerosols on a global scale. It has been found that atmospheric SO<sub>2</sub> concentrations are typically overestimated while sulfate tends to be underestimated<sup>9–11</sup>. Sulfur dioxide can be oxidized in the troposphere to form sulfate, which may occur in the gas-phase (principally via reaction with OH to yield H<sub>2</sub>SO<sub>4</sub>), in cloud or fog droplets, or on aerosol particles<sup>12–15</sup>. The oxidation of SO<sub>2</sub> by a stabilized Criegee intermediate (a carbonyl oxide with two free radical sites) or its derivative was recently reported<sup>13,16</sup>. Furthermore, ternary nucleation (H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub>-H<sub>2</sub>O) has been shown to be ubiquitous in the troposphere and a major source of ammonium sulfate in the atmosphere<sup>17,18</sup>. In recent years, field observations and modeling simulation have found large amounts of sulfate in mineral dust aerosol<sup>19–21</sup>, though the formation mechanism remains unclear. Laboratory simulation studies have found that it is difficult for SO<sub>2</sub> to convert to sulfate on the surface of mineral dust other than Fe<sub>2</sub>O<sub>3</sub> and MgO, but the coexistence of O<sub>3</sub> can convert SO<sub>2</sub> to sulfate<sup>22</sup>. As a kind of secondary pollutant, the atmospheric concentration of O<sub>3</sub> is closely related to illumination intensity. Under weak or no UV-light, the concentration of O<sub>3</sub> is low. In addition, both NO<sub>x</sub> and SO<sub>2</sub> are primary pollutants and are emitted from the burning processes of fossil fuels. Our previous research has demonstrated that NO<sub>2</sub> and SO<sub>2</sub> have synergistic effects when they react on the surface of mineral dust, such as Al<sub>2</sub>O<sub>3</sub>, CaO, ZnO, TiO<sub>2</sub>, MgO, and α-Fe<sub>2</sub>O<sub>3</sub>, and thus the formation of sulfate from SO<sub>2</sub> is promoted by the coexistence of NO<sub>x</sub><sup>23,24</sup>. Figure 1 shows the surface coverage of sulfate and sulfite species when NO<sub>2</sub> and SO<sub>2</sub> react on the surface of a mineral oxide. Sulfate cannot be formed on the surface of CaO, Al<sub>2</sub>O<sub>3</sub>, ZnO, and TiO<sub>2</sub> without an oxidant under synthetic air conditions (Fig. 1A). On the surface of Fe<sub>2</sub>O<sub>3</sub> and MgO, although SO<sub>2</sub> alone can produce

sulfate, the coexistence of NO<sub>2</sub> further increased the amount of sulfate. Surface sulfite species were formed on the surface of mineral oxides other than Fe<sub>2</sub>O<sub>3</sub> exposed to SO<sub>2</sub> alone (Fig. 1B). When NO<sub>2</sub> and SO<sub>2</sub> coexisted, the content of sulfite on the surface of all oxides was reduced significantly, or disappeared entirely. This shows that the coexistence of NO<sub>2</sub> significantly promotes the oxidation of surface sulfite to sulfate. Further analysis indicates that, in the process of NO<sub>2</sub> promoting SO<sub>2</sub> oxidation to sulfate, O<sub>2</sub> plays a critical function in the reaction atmosphere. As shown in Fig. 2, sulfate can be formed on the CaO surface only in the presence of O<sub>2</sub>. Similar phenomena were also found on Al<sub>2</sub>O<sub>3</sub>, ZnO, and TiO<sub>2</sub> surfaces (see Supplementary Information). Therefore, O<sub>2</sub> was the key oxidant in the process of SO<sub>2</sub> oxidation, while NO<sub>x</sub> and mineral oxides acted as catalysts to promote the conversion of SO<sub>2</sub> to sulfate on the surface of mineral oxides. The catalytic oxidation mechanism of SO<sub>2</sub> on the surface of mineral oxides by NO<sub>x</sub> is proposed as shown below:



**Figure 2** | Comparison of integral infrared peak area of sulfate when NO<sub>2</sub>+SO<sub>2</sub> was exposed to the surface of CaO with pure N<sub>2</sub> (black solid squares) and synthetic air (80%N<sub>2</sub>+20%O<sub>2</sub>) (red hollow squares) as carrier gas. Reaction conditions: total flow = 100 mL/min; concentrations of SO<sub>2</sub> and NO<sub>2</sub> both 200 ppm; T = 303 K.



**Figure 3** | Sulfate formation in heterogeneous reactions of  $\text{NO}_x$  and  $\text{SO}_2$  in the smog chamber. N50(dry) and N150(dry) represent  $\text{NO}_2$  concentrations of 50 and 150 ppb in the absence of  $\text{Al}_2\text{O}_3$  with a RH of 12%, respectively; N50 represents an  $\text{NO}_2$  concentration of 50 ppb in the absence of  $\text{Al}_2\text{O}_3$  at 50% RH while Al-N50 and Al-N150 represent  $\text{NO}_2$  concentration of 50 and 150 ppb in the presence of  $\text{Al}_2\text{O}_3$  at 50% RH, respectively.

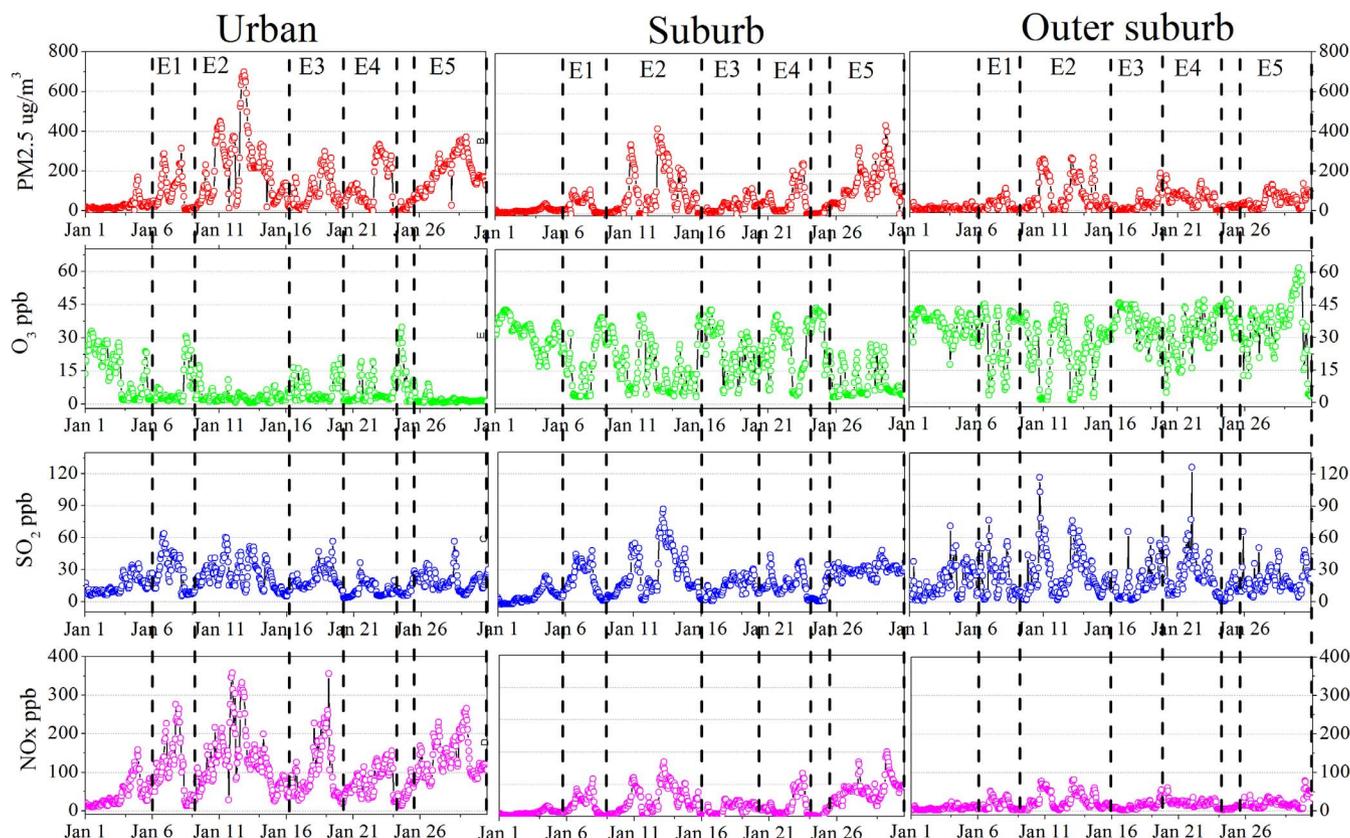


where M represents the surface of mineral oxides. This process is analogous to the lead chamber process for manufacturing sulfuric acid, in which nitrogen oxides serve as a catalyst for conversion of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$ <sup>25</sup>.

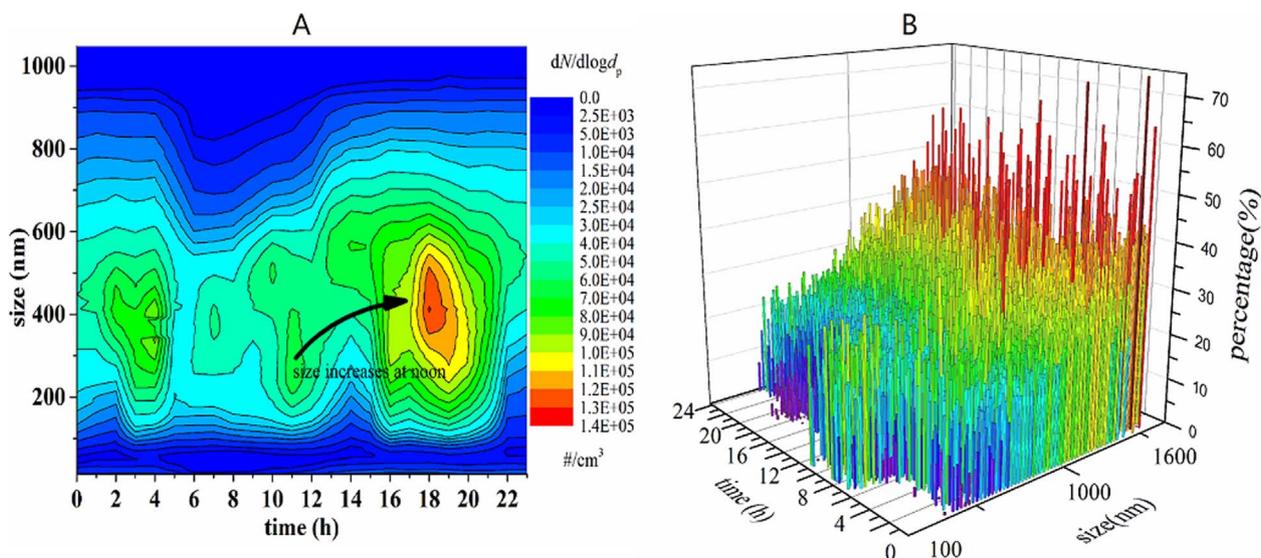
On the other hand, the formed surface nitrate species can promote the hygroscopicity of mineral oxides and content of surface water<sup>26</sup>. This allows the oxidation process of  $\text{SO}_2$  to occur in the liquid phase and improves the efficiency of  $\text{SO}_2$  conversion to sulfate<sup>27</sup>. Under haze weather conditions, the concentration of  $\text{O}_3$  is low while  $\text{NO}_2$  is high, and mineral dust constitutes a high proportion (about 10%) of  $\text{PM}_{2.5}$  in Beijing (see Table S2 in supplementary information). Therefore, the synergistic effect between  $\text{SO}_2$  and  $\text{NO}_2$  on the surface of mineral dust is an important potential source of sulfate aerosol in China. Even in an atmosphere in which the  $\text{O}_3$  concentration is low, the primary pollutant  $\text{NO}_x$  can also promote the oxidation of  $\text{SO}_2$  to sulfate. In addition,  $\text{SO}_2$  oxidized by  $\text{NO}_3$  radicals may also occur under haze conditions<sup>16</sup>.

A 2-m<sup>3</sup> smog chamber, equipped with an aerosol composition speciation monitor (ACSM), was used to investigate sulfate generation in heterogeneous reactions of  $\text{NO}_x$  and  $\text{SO}_2$  on mineral oxides. Detailed conditions of the smog chamber experiments are shown in Table S3 in Supplementary Information. Figure 3 shows the sulfate yields in the smog chamber under different conditions. Without  $\text{Al}_2\text{O}_3$  seed (black empty triangles), the sulfate yields were low ( $\sim 9 \mu\text{g m}^{-3}$ ) and the increase in  $\text{NO}_2$  concentration exhibited no promotion effect on the formation of sulfate (black solid circles). When RH was increased to 50% in the reactor without seed, the formation of sulfate was enhanced slightly ( $\sim 14 \mu\text{g m}^{-3}$ , red empty triangles). In contrast, if  $\text{Al}_2\text{O}_3$  seed aerosols were introduced at 50% RH, sulfate formation increased significantly to  $\sim 24 \mu\text{g m}^{-3}$  (red solid triangles). It is interesting to note that the sulfate yield was further increased ( $\sim 43 \mu\text{g m}^{-3}$ ) by increasing  $\text{NO}_2$  concentration (red solid circles). These results provide distinct evidence that  $\text{Al}_2\text{O}_3$  seed aerosols and  $\text{NO}_2$  greatly promote the formation of sulfate.

Field observations of heavy haze in January 2013 confirmed the above mechanism. Figure 4 shows the variation trend in the



**Figure 4** | Variation trend of  $\text{PM}_{2.5}$ ,  $\text{O}_3$ ,  $\text{SO}_2$ , and  $\text{NO}_x$  concentrations in Beijing (urban site), Mangshan (suburb site) and Xinglong (outer suburb) stations in January 2013.



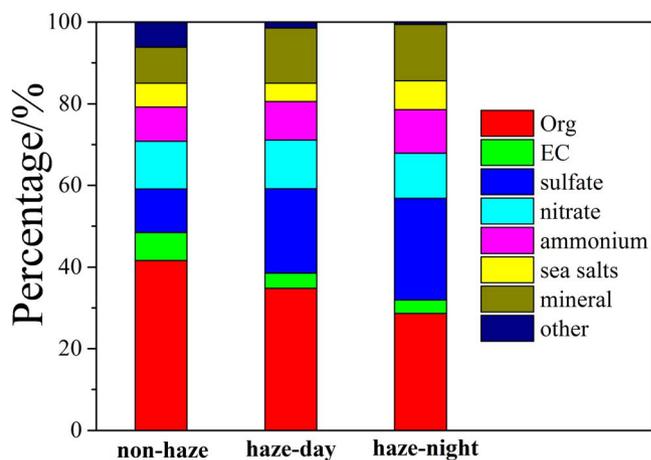
**Figure 5** | Time variations of grain size distribution (A) and size-dependent sulfate mass percentage (B) of fine particles in Beijing station on January 12, 2013. Particle size was measured with a scan mobility particle sizer (SMPS) in the range of 14–1048 nm and sulfate mass fraction was calculated according to the mass concentrations measured by an aerosol mass spectrometer (AMS) with a size range of 90–1758 nm.

concentrations of  $PM_{2.5}$  and gaseous pollutants such as  $O_3$ ,  $SO_2$ , and  $NO_2$  in Beijing (urban), Mangshan (suburban) and Xinglong (outer suburban) monitoring stations in January 2013. Detailed information on the stations is shown in the Supplementary Information. Five episodes of heavy haze (Episode 1–Episode 5) occurred in January 2013 (Fig. 4). In Beijing station, the 1-hour maximum value of  $PM_{2.5}$  reached  $700 \mu g/m^3$ . In Mangshan station, it was  $440 \mu g/m^3$ , while Xinglong station had only  $268 \mu g/m^3$ . However, the concentration of  $O_3$  in Beijing station was lower than the other two stations, especially on the heavy haze days. This illustrates that the photochemical reaction was negligible and  $O_3$  is not the key oxidant causing heavy haze. The concentrations of  $SO_2$  in Beijing, Mangshan, and Xinglong stations were relatively close (monthly mean values were 19 ppb, 20 ppb, and 21 ppb, respectively). But the monthly mean concentrations of  $NO_x$  were 100 ppb (Beijing station) > 42 ppb (Mangshan station) > 18 ppb (Xinglong station). These data strongly corroborate the results of the laboratory simulation study. That is,  $NO_x$  reduced the environmental capacity for  $SO_2$ , so that the oxidation of  $SO_2$  to sulfate was promoted in the presence of high concentrations of  $NO_x$ . Clearly, the high concentration of  $NO_x$  in Beijing station was mainly due to the contribution of vehicle emissions. As seen in Fig. 5A, the fine particle concentration increased rapidly and particle size was enlarged over several hours around noon. Along with the growth in particle size, the relative amount of sulfate increased notably (Fig. 5B). Therefore, the formation of sulfate was a main reason for the growth in size of fine particles (also seen Fig. S4 in SI<sup>28</sup>). Dupart et al.<sup>29</sup> reported that metal oxides present in mineral dust can act as atmospheric photocatalysts promoting the formation of fine  $H_2SO_4$  and sulfate particles, which strongly supports the experimental and observation results from the present study. Moreover, the mass fraction of different components in  $PM_{2.5}$  in Beijing during non-haze and haze episodes also indicated that the formation of sulfate was closely related to mineral content during haze episodes. As seen in Fig. 6, the increase of sulfate fraction on haze days accompanied the increase of mineral fraction, indicating mineral dust may have a promoting effect on the formation of sulfate during haze episodes.

## Discussion

The London smog of 1952 was mainly caused by  $SO_2$  emitted from coal burning. On clear days, the concentration of  $SO_2$  was in the

range of 140–470 ppb while during smog days it reached levels as high as 1.34 ppm<sup>30</sup>. By contrast, cities in northern China had heavy haze pollution even when the concentration of  $SO_2$  was only 60–120 ppb. This indicates that the environmental capacity for air pollutants has declined due to the complex air pollution of coal burning, motor vehicles, and industrial emissions. Therefore haze incidents occur frequently. China's population reached 1.4 billion in 2010, with over half living in cities. Considering its unique megacity scale and high population density, and the fact that the environmental capacity for single pollutants has declined under complex air pollution conditions, eastern China requires a stricter air pollution emission standard than developed countries. In fact, China has implemented an emission standard for coal-fired flue gas emissions that is the most restrictive in the world; however, it is still necessary to strengthen law enforcement. Considering the environmental sensitivity toward  $NO_x$  leading to haze, and the increasing trend of total  $NO_x$  emissions, China should prioritize the reduction of  $NO_x$  emissions. Emission control of vehicles is critical in megacities. Vehicle exhaust emission standards in China should catch up with the current



**Figure 6** | Mass fraction of different chemical compositions in  $PM_{2.5}$  in Beijing station. Non-haze, haze-day, and haze-night represent the sampling times of 12:00 on Jan. 9th, 12:00 on Jan. 12th, and 00:00 on Jan. 13th, 2013, respectively.



standard of the EU, and China must progress to a stricter standard suitable for its severe and complex air pollution.

Solving China's haze pollution problems requires judicious energy structure planning, a reduction in coal and oil usage as well as other traditional energy sources, an increase in the proportion of clean energy, rational industrial distribution planning, the elimination of productive force lags, an upgrade of industries, and the development of environmental protection. With such measures, China will mitigate complex air pollution and achieve sustainable development.

## Methods

Heterogeneous reactions of NO<sub>x</sub> and SO<sub>2</sub> on mineral oxides were investigated by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The experimental methods and integral IR peak area of surface species can be referenced to a previous study<sup>24</sup>.

The smog chamber is a 2-m<sup>3</sup> cuboid reactor, constructed with 50 μm-thick FEP-Teflon film (Toray Industries, Inc.). The reactor was irradiated by 40 black lights (GE F40T12/BLB, peak intensity at 365 nm) and located in a temperature-controlled room (Escpec SEWT-Z-120) at a constant temperature. To generate Al<sub>2</sub>O<sub>3</sub> seed aerosols, liquid alumisol (ALOOH, Kawaken Fine Chemicals Co., Ltd.) was sprayed into droplets by an atomizer and dried by a diffusion dryer. The generated particles were then carried into a corundum tube embedded in a tubular furnace with the temperature maintained at 1373 K. Details on the chamber and experimental methods can be found in previous studies<sup>31,32</sup>. An aerosol composition speciation monitor (ACSM) was used to measure the chemical species in the aerosol phase. The principle and structure of ACSM are similar to aerosol mass spectrometry (AMS). Ng et al.<sup>33</sup> presented a detailed introduction to this instrument and found that measurement results agreed well with AMS.

The urban station is located in downtown Beijing (116°22'21"E, 39°58'28"N), the suburban station is located in Mangshan (116°16'10"E, 40°16'3"N), and the outer suburban station is located in Xinglong (117°34'34"E, 40°23'40"N). All air quality monitoring stations were selected and set up according to US EPA method designations (US EPA, 2007). Concentrations of NO<sub>x</sub>, SO<sub>2</sub>, O<sub>3</sub> and PM<sub>2.5</sub> were measured using a NO-NO<sub>2</sub>-NO<sub>x</sub> chemiluminescence analyzer (Model 42i, Thermo-Fisher Scientific (TE)), a pulsed fluorescence SO<sub>2</sub> analyzer (Model 43i, TE), an ozone analyzer (Model 49 I, TE) and a Tapered Element Oscillating Microbalance (Model 1400A, R&P), respectively. The instruments were operated and maintained properly to ensure data integrity. Scheduled quality control procedures included daily zero and span checks, biweekly precision checks, quarterly multiple-point calibrations, and data validations.

- Ma, J. Z., Xu, X. B., Zhao, C. S. & Yan, P. A review of atmospheric chemistry research in China: Photochemical smog, haze pollution, and gas-aerosol interactions. *Adv. Atmos. Sci.* **29**, 1006–1026 (2012).
- Zhao, X. J. *et al.* Analysis of a winter regional haze event and its formation mechanism in the North China Plain. *Atmos. Chem. Phys.* **13**, 5685–5696 (2013).
- Liu, X. G. *et al.* Formation and evolution mechanism of regional haze: a case study in the megacity Beijing, China. *Atmos. Chem. Phys.* **13**, 4501–4514 (2013).
- Liu, S. *Interpretation from the Ministry of environmental protection experts: how to calculate the area of 1.3 million square kilometers of haze*, <[http://news.xinhuanet.com/tech/2013-01/31/c\\_114561626.htm](http://news.xinhuanet.com/tech/2013-01/31/c_114561626.htm)> (2013-01-31).
- Luria, M. & Sievering, H. Heterogeneous and homogeneous oxidation of SO<sub>2</sub> in the remote marine atmosphere. *Atmos. Environ.* **25**, 1489–1496 (1991).
- Andreae, M. & Crutzen, P. Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry. *Science* **276**, 1052–1058 (1997).
- Laskin, A. *et al.* Reactions at interfaces as a source of sulfate formation in sea-salt particles. *Science* **301**, 340–344 (2003).
- Langner, J., Rodhe, H., Crutzen, P. & Zimmermann, P. Anthropogenic influence on the distribution of tropospheric sulphate aerosol. *Nature* **359**, 712–716 (1992).
- Kasibhatla, P., Chameides, W. & John, J. S. A three-dimensional global model investigation of seasonal variations in the atmospheric burden of anthropogenic sulfate aerosols. *J. Geophys. Res.- Atmos.* **102**, 3737–3759 (1997).
- Barrie, L. A. *et al.* A comparison of large-scale atmospheric sulphate aerosol models (COSAM): Overview and highlights. *Tellus B* **53**, 615–645 (2001).
- Berglen, T. F., Bernsten, T. K., Isaksen, I. S. A. & Sundet, J. K. A global model of the coupled sulphur/oxidant chemistry in the troposphere: The sulfur cycle. *J. Geophys. Res.- Atmos.* **109**, D19310 (2004).
- Seinfeld, J. H. & Pandis, S. N. *Atmospheric chemistry and physics: From air pollution to climate change*. (John Wiley: New York, 1998).
- Sarwar, G. *et al.* Potential impacts of two SO<sub>2</sub> oxidation pathways on regional sulfate concentrations: aqueous-phase oxidation by NO<sub>2</sub> and gas-phase oxidation by Stabilized Criegee Intermediates. *Atmos. Environ.* **68**, 186–197 (2013).
- Zhang, R. *et al.* Nucleation and growth of nanoparticles in the atmosphere. *Chem. Rev.* **112**, 1957–2011 (2012).

- Harris, E. *et al.* Enhanced Role of Transition Metal Ion Catalysis During In-Cloud Oxidation of SO<sub>2</sub>. *Science* **340**, 727–730 (2013).
- Mauldin III, R. L. *et al.* A new atmospherically relevant oxidant of sulphur dioxide. *Nature* **488**, 193–196 (2012).
- Kulmala, M., Pirjola, L. & Mäkelä, J. Stable sulphate clusters as a source of new atmospheric particles. *Nature* **404**, 66–69 (2000).
- Kulmala, M. How particles nucleate and grow. *Science* **302**, 1000 (2003).
- Zhang, X. *et al.* Characterization of soil dust aerosol in China and its transport and distribution during 2001 ACE-Asia I. Network observations. *J. Geophys. Res.* **108**, 8032–8039 (2003).
- Sullivan, R., Guazzotti, S., Sodeman, D. & Prather, K. Direct observations of the atmospheric processing of Asian mineral dust. *Atmos. Chem. Phys.* **7**, 1213–1236 (2007).
- Fairlie, T. D. *et al.* Impact of mineral dust on nitrate, sulfate, and ozone in transpacific Asian pollution plumes. *Atmos. Chem. Phys.* **10**, 3999–4012 (2010).
- Usher, C. R., Michel, A. E. & Grassian, V. H. Reactions on mineral dust. *Chem. Rev.* **103**, 4883–4940 (2003).
- Ma, Q. X., Liu, Y. C. & He, H. Synergistic effect between NO<sub>2</sub> and SO<sub>2</sub> in their adsorption and reaction on gamma-alumina. *J. Phys. Chem. A* **112**, 6630–6635 (2008).
- Liu, C. *et al.* Synergistic reaction between SO<sub>2</sub> and NO<sub>2</sub> on mineral oxides: a potential formation pathway of sulfate aerosol. *Phys. Chem. Chem. Phys.* **14**, 1668–1676 (2012).
- Jones, E. M. Chamber process manufacture of sulfuric acid. *Ind. Eng. Chem.* **42**, 2208–2210 (1950).
- Ma, Q. X., He, H. & Liu, Y. C. In situ DRIFTS study of hygroscopic behavior of mineral aerosol. *J. Environ. Sci.* **22**, 555–560 (2010).
- Sievering, H. *et al.* Removal of sulphur from the marine boundary layer by ozone oxidation in sea-salt aerosols. *Nature* **360**, 571–573 (1992).
- Wang, Y. *et al.* Mechanism for the formation of the January 2013 heavy haze pollution episode over central and eastern China. *Sci. China Earth. Sci.* **57**, 14–25 (2014).
- Dupart, Y. *et al.* Mineral dust photochemistry induces nucleation events in the presence of SO<sub>2</sub>. *Proceed. Natl. Acad. Sci. USA* **109**, 20842–20847 (2012).
- Authority, G. L. *50 Years on: The Struggle for Air Quality in London Since the Great Smog of December 1952*. (Greater London Authority, 2002).
- Chu, B. *et al.* The remarkable effect of FeSO<sub>4</sub> seed aerosols on secondary organic aerosol formation from photooxidation of α-pinene/NO<sub>x</sub> and toluene/NO<sub>x</sub>. *Atmos. Environ.* **55**, 26–34 (2012).
- Liu, C. *et al.* Effect of mineral dust on secondary organic aerosol yield and aerosol size in α-pinene/NO<sub>x</sub> photo-oxidation. *Atmos. Environ.* **77**, 781–789 (2013).
- Ng, N. L. *et al.* An Aerosol Chemical Speciation Monitor (ACSM) for routine monitoring of the composition and mass concentrations of ambient aerosol. *Aerosol Sci. Technol.* **45**, 770–784 (2011).

## Acknowledgments

This work was funded by the “Strategic Priority Research Program” of the Chinese Academy of Sciences (XDB05010300) and National Natural Science Foundation of China (21107129 and 51221892). The authors thank Prof. Zhongli Ding, Jianmin Chen, Xinming Wang, Liangfu Chen, Maofa Ge, and Dr. Shaomeng Li and A. Ravishankara for their instructive discussions, thank Prof. Jianhui Bai for the work at Xinglong Station and thank Prof. Xiaoke Wang for the work at Mangshan Station.

## Author contributions

H.H. initiated the project and designed the experiments, Q.M. and J.M. performed the laboratory experiments, B.C. and C.L. performed the smog chamber experiments, Y.W., D.J., G.T. and H.Z. conducted the field measurements. H.H., Y.W., Q.M., J.M. and B.C. analyzed the data and contributed to the interpretation and to manuscript preparation. J.H. contributed to new tools. Correspondence and requests for materials should be addressed to H. He (honghe@rcees.ac.cn) and Y. Wang (wys@mail.iap.ac.cn).

## Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: He, H. *et al.* Mineral dust and NO<sub>x</sub> promote the conversion of SO<sub>2</sub> to sulfate in heavy pollution days. *Sci. Rep.* **4**, 4172; DOI:10.1038/srep04172 (2014).



This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported license. To view a copy of this license, visit <http://creativecommons.org/licenses/by-nc-nd/3.0>