



A case study of Asian dust storm particles: Chemical composition, reactivity to SO₂ and hygroscopic properties

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Abstract

Mineral dust comprises a great fraction of the global aerosol loading, but remains the largest uncertainty in predictions of the future climate due to its complexity in composition and physico-chemical properties. In this work, a case study characterizing Asian dust storm particles was conducted by multiple analysis methods, including SEM-EDS, XPS, FT-IR, BET, TPD/mass and Knudsen cell/mass. The morphology, elemental fraction, source distribution, true uptake coefficient for SO₂, and hygroscopic behavior were studied. The major components of Asian dust storm particles are aluminosilicate, SiO₂ and CaCO₃, with organic compounds and inorganic nitrate coated on the surface. It has a low reactivity towards SO₂ with a true uptake coefficient, 5.767×10^{-6} , which limits the conversion of SO₂ to sulfate during dust storm periods. The low reactivity also means that the heterogeneous reactions of SO₂ in both dry and humid air conditions have little effect on the hygroscopic behavior of the dust particles.

Key words: DRIFTS; mineral dust; SO₂ reaction; water adsorption

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Introduction

Mineral dust is an important and complex constituent of the atmospheric system. It impacts the Earth's climate and the atmospheric environment in several ways. First, atmospheric mineral dust affects climate directly through scattering and absorption of solar radiation and indirectly by acting as cloud condensation nucleus (CCN) (Ramanathan et al., 2001). The complexity of the aerosol-cloud-climate system makes the negative forcing due to atmospheric aerosols the largest current source of uncertainty in predictions of the future global climate (IPCC, 2007). Second, mineral dust particles can undergo heterogeneous reactions during the transport in the atmosphere, altering the chemical balance of the atmosphere and the physiochemical properties of the mineral dust aerosol itself (Cwiertyny et al., 2008; Usher et al., 2003). Heterogeneous chemical transformations can potentially form dust particles that are more hygroscopic and more efficient CCN (Hanke et al., 2003; Ravishankara, 1997). Finally, cloud processing and heterogeneous chemistry can alter the impact of mineral dust on ocean biogeochemical cycles (Desboeufs et al., 2001; Hand et al., 2004; Meskhidze et al., 2005). For example, Fe-containing mineral dust deposited into the Earth's oceans can modify bio-productivity and biogeochemical cycles (Jickells et al., 2005).

Mineral dust aerosol comprises one of the largest mass fractions of the total global aerosol loading. The annual production of mineral dust is estimated to be 1000–3000

Tg (Bauer et al., 2004; Ginoux et al., 2001). The majority of sources are situated in the arid regions of the Northern Hemisphere, which lie in a broad band that extends from the west coast of North Africa, over the Middle East, Central and South Asia, to China (Prospero et al., 2002). Asian dust storms, which originate from desert areas of Mongolia and China and frequently sweep over northern China, have become increasingly intense since 1999 (Cyranoški, 2003; Gong et al., 2003), which has resulted in the concentration of total suspended particles (TSP) reaching 6000 µg/m³ during storm periods (Zhuang et al., 2001). The occurrence, development processes, transportation mechanisms, and impact on ambient air quality of sand-dust storms have been studied by many researchers (Gao et al., 1992; Jeong, 2008; Ro et al., 2005; Shi et al., 2005; Xie et al., 2005; Sullivan et al., 2007a; Sun et al., 2001, 2004a, 2004b; Zhang and Iwasaka, 1999; Zhang et al., 1996, 2003). The composition, source, and size distribution of spring dust storms in China and their effects on the global environment have also been reported by Zhuang et al. (2001). The physical and chemical characteristics of the aerosols in the air during sand-dust storms have been found to be remarkably different from those on days with normal weather, with the ambient aerosol during sand-dust storms coming primarily from local natural sources (Yang et al., 2002). Since information about the heterogeneous reactivity and hygroscopic properties of mineral dust is crucial in predicting its impacts on climate and the atmospheric environment, many field and laboratory studies have been conducted on mineral dust and its main

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components (Hanisch and Crowley, 2000; Koehler et al., 2009; Laskin et al., 2005b; Maxwell-Meier et al., 2004; Shi et al., 2008; Sullivan et al., 2009; Ullerstam et al., 2003; Zhang et al., 2006).

Sulfur dioxide (SO₂) is the predominant sulfur-containing atmospheric trace gas. It is released to the troposphere by fossil fuel combustion and volcanic emissions as well as through oxidation of dimethyl sulfide (DMS) and other sulfur compounds of biogenic origin. Field, laboratory and modeling studies provide convincing evidence that mineral dust can play an important role in the chemistry of SO₂ (Dentener et al., 1996; Li et al., 2006; Prince et al., 2007; Song and Carmichael, 1999; Ullerstam et al., 2002, 2003; Zhang et al., 2006). Field studies have recorded anti-correlations between the concentration of SO₂ and Saharan (Andreae et al., 2003; Hanke et al., 2003) or Chinese (Tang et al., 2004) desert dust loading. However, several observation-based studies have reported that although East Asian dust particles have long contact times with sulfate and nitrate precursors, they contain only small amounts (typically, less than 10%–50%) of sulfate and nitrate (Maxwell-Meier et al., 2004; Ro et al., 2005; Zhang and Iwasaka, 1999). A recently field study by Xie et al. (2005) also showed that, during dust periods, the conversion rate of SO₂ to sulfate was very low because of the low relative humidity. Song et al. (2007) analyzed the composition of fine dust particles sampled in the ACE-Asian experiment and found that excessively high reaction probability (γ) values were used in previous model simulations. Model studies predict that heterogeneous reactions on dust can have a significant impact on the abundance and distribution of SO₂ and sulfate, but the impact is strongly dependent on the SO₂ uptake coefficient. Therefore, further laboratory study is needed on the reactivity of authentic dust storm particles towards SO₂. In addition, sulfate coated on mineral dust always plays an important role in the hygroscopic behavior of mineral dust, which could determine the CCN activity, precipitation effect, and heterogeneous reactivity of mineral dust towards reactive gaseous pollutants. In this work, we used the Knudsen cell/mass system to investigate the reactivity of dust particles with SO₂, and used *in situ* diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) to investigate the hygroscopic behavior of dust particles. These results will improve our knowledge of the effects of dust storm particles on the atmosphere.

1 Experiment

1.1 Sampling

The dust particles were collected with a clean jar placed on the roof of a building (about 20 m high) of the Research Center of Eco-Environmental Sciences, Chinese Academy of Sciences (116.3°E, 39.9°N, Beijing), on 16–17 April, 2006 during a heavy dust storm period. The dust episode originated from Mongolia and reached Beijing on 16 April. The dust particles were collected for 24 hr during a dust storm period where the ambient conditions were in a

dust storm atmosphere. With a particle collection jar, both coarse particles and fine particles were collected without segregation by size. The collected particles were sealed in a Teflon package before analysis and experiments. The size distribution measured by laser size analysis showed that the $d_{0.5}$ of the particles was 20 μm . The BET area determined from nitrogen adsorption-desorption isotherms at 77 K was 5.43 m²/g.

1.2 FESEM-EDS and XPS analysis

Morphological and elemental analysis was performed with a high-resolution digital field emission scanning electric microscope (FE-SEM, SUPERA 55, ZEISS, Germany). The energy dispersive X-ray (EDX) spectrometer was coupled with a circular high-performance In-lens SE detector. The acceleration voltage was 15.0 KeV in this study. The sample was diluted in super-purity water (18 m Ω) with ultrasonic dispersion, and was then deposited on a 3×3 mm² Cu substrate and dried in a closed box at room temperature. A backscattered electron detector was used to image the samples. Quantification was done using a 200×100 μm area of the same sample. A detection limit of 0.5 atomic% was chosen for quantification purposes.

For X-ray photoelectron spectroscopy analysis, dust samples were pressed into indium foil and mounted onto a copper stub. The copper stubs with the dust samples were introduced into the transfer antechamber under ambient conditions and pumped to about 5×10⁻⁷ Torr. Once this pressure was achieved, samples were introduced into the surface analysis chamber, which was maintained at a pressure in the 10⁻⁹ Torr range during analysis.

1.3 TPD characterization

Desorption of surface species and decomposition of bulk materials were characterized with a Temperature Program Desorption (TPD) experiment which was conducted in a tubular reactor coupled with a mass spectrometer (Hiden, 2000, UK). The carrier gas was Ar with a flow of 50 mL/min and the temperature rise rate was 20 K/min.

1.4 FT-IR/DRIFTS experiments

Infrared spectroscopy (IR) experiments were performed with a Nicolet 6700 (FT-IR spectrometer) (Thermo Nicolet, USA). For the analysis of particle composition, a Deuterated triglycine sulfate (DTGS) detector was used in transmission mode, and the aerosol particles were diluted with KBr with a pure KBr pellet used as reference. All *in situ* DRIFTS experiments were conducted in a flow system with an *in situ* diffuse reflection chamber and a high-sensitivity mercury-cadmium telluride (MCT) detector. Typically, the samples (about 13 mg) were finely ground and placed in a ceramic crucible in the *in situ* chamber. The samples were purged overnight under a flow of dry nitrogen to remove surface water. Mass flow controllers and a sample temperature controller were used to simulate real reaction conditions. The relative humidity (RH) of the stream was controlled by the addition of a flow of humidified nitrogen and the RH was recorded with a hygrometer (CENTER 314, \pm 2% RH). All *in situ* DRIFTS

experiments were conducted at 300 K and in a total flow of 100 mL/min. All DRIFTS spectra reported were recorded at a resolution of 4 cm⁻¹ for 100 scans.

1.5 Knudsen cell/mass experiments

A Knudsen cell was used for the analysis of loss from the gas phase due to surface reactions or adsorption, as described in a previous article (Liu et al., 2008). The Knudsen cell consisted of a Teflon-coated reaction chamber with an inlet valve, a sample holder, and an escape aperture. The reaction chamber was connected to a quadrupole mass spectrometer (HAL 3F PIC, Hiden, UK). The mass spectrometer was differentially pumped using two turbomolecular pumps (Pfeiffer, 60 L and 240 L/sec) to approximately 10⁻⁸ Torr.

The particle samples were dispersed evenly on the sample holder with alcohol and then dried at 393 K for 2 hr. The pretreated samples and reactor chamber were evacuated at 323 K for 6 hr to reach a base pressure of approximately 5.0 × 10⁻⁷ Torr. After the system was cooled to 300 K, the sample cover was closed. The 2.01% SO₂ gas (balance N₂) was introduced into the reactor chamber through a leak valve. The pressure in the reactor was measured using an absolute pressure transducer (BOC Edward). Prior to the experiments, the system was passivated with SO₂ for 150 min to give a steady QMS signal, while the samples were isolated from the gas by the sample cover. Parameters for the Knudsen reaction chamber can be found in Table 1.

2 Results and discussion

2.1 SEM-EDS analysis

Figure 1 illustrates a typical example of the morphology and X-ray spectrum of the particles deposited on the

Table 1 Knudsen reactor parameters

Knudsen reactor parameter	Value
Reactor volume, <i>V</i>	94.0 ± 0.5 mL
Experimental temperature, <i>T</i>	300 ± 0.1 K
Geometric sample area, <i>A_s</i>	5.26 ± 0.05 cm ²
Escape orifice area, <i>A_h</i>	0.40 ± 0.03 mm ²
Escape rate ^a , <i>k_{esc}</i>	1.8 sec

^a Calculated from $\ln(\frac{I_0 - I'}{I_0 - I}) \propto t$, *I*₀, *I'*, and *I* are the QMS signal intensities of N₂ for first steady state, second one and the signal intensities between these two steady state, respectively.

copper substrate. Particles were generally sharp-edged, irregular in shape and contained mostly crustal elements such as Si, Al, Fe and Ca. The amounts of two major crustal elements, Al and Si, were less than those in the Earth's crust, as shown in Table 2. This result suggests that anthropogenic aerosols and aerosols from other sources always mixed with the dust storm particles during transport. Moreover, C and Cl were detected with a larger weight fraction than their crustal abundance. The unexpectedly high fraction of C was possibly due to the mixture of carbonaceous aerosols during the dust event. Carbonaceous aerosol emissions from biomass burning in China, including bio-fuel combustion, field burning of agricultural crop residue, and forest and grassland fires, are the major contributor to organic aerosols in China, as has been summarized by Streets et al. (2003). It is seen that the fine particles coated with carbonaceous species showed a more spherical shape, in agreement with the results of a TEM study (Shi et al., 2005). Another source of C may arise from the uptake of organic vapors by dust particles (Falkovich et al., 2004; Prince et al., 2008; Russell et al., 2002; Sullivan and Prather, 2007). The high concentration of Cl was possibly due to the presence of polyvinylchloride plastic in trash-burning and coal burning (Sun et al., 2004a), or from the chemical process between HCl and dust particles (Sullivan et al., 2007b; Zhang and Iwasaka, 2001). The amount of sulfur was below the detection limit, which indicates little sulfur species were present on the particles' surfaces.

The mineral particles with chemical stability are widely considered to be a good indicator for atmospheric movements (Zhang et al., 1996). There hardly exists a spectral element unique to specific Chinese dust source regions that can be used as a real tracer, but it is reasonable to expect the ratios of some elements to vary with source areas. Several researchers found that Si/Fe, Ca/Fe, Si/Al, Fe/Al, Mg/Al, and Sc/Al could be used to identify the origin of the dust from different areas in China (Sun et al., 2004; Zhang et al., 1996, 2003). Recently, the ratio of Mg/Al have been used as an indicator in determining the contribution of local and non-local sources of airborne particulate pollution at Beijing (Han et al., 2005). The ratio of Mg/Al was about 0.32 in our work. The reference values for the ratio of Mg/Al are 0.45 for Beijing soil, 0.12 for Duolun in Inner Mongolia which was the original area of this dust storm, and 0.15 for Fengning which is located between Beijing

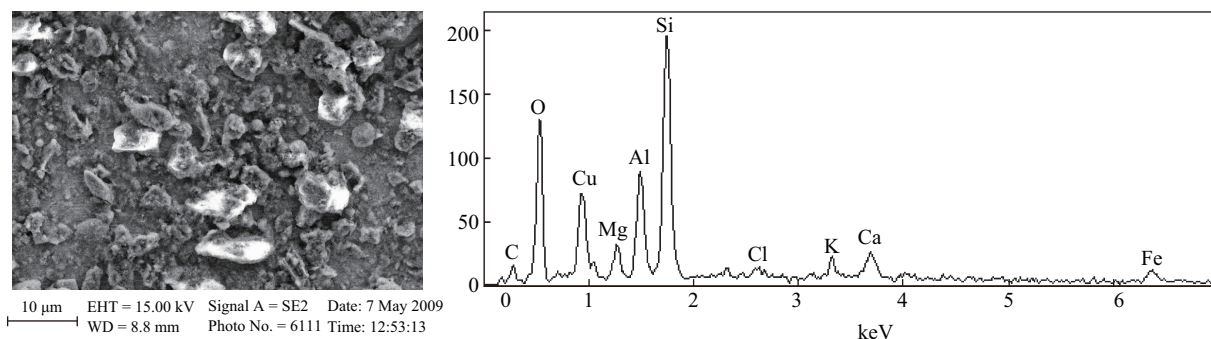


Fig. 1 SEM image of dust particle sample and the EDS spectrum.

Table 2 FESEM-EDS and XPS elements distribution

	C	O	Mg	Al	Si	Cl	K	Ca	Fe	S	N
Crustal abundance (%)	0.003	46.0	1.33	8.04	30.8	1.0×10 ⁻⁴	2.4	3.0	3.5	3.5×10 ⁻⁴	0.5×10 ⁻⁴
Weight% error	22.06 ± 5.09	49.44 ± 1.80	1.80 ± 0.16	5.59 ± 0.23	12.26 ± 0.32	0.78 ± 0.13	1.28 ± 0.15	3.04 ± 0.15	3.75 ± 0.42	n.d.	n.d.
Atom% error	31.44 ± 7.26	52.89 ± 1.93	1.27 ± 0.11	3.54 ± 0.15	7.47 ± 0.20	0.38 ± 0.06	0.56 ± 0.06	1.30 ± 0.10	1.15 ± 0.13	n.d.	n.d.
XPS	14.94 ± 0.72	57.09 ± 0.39	2.62 ± 0.12	6.26 ± 0.62	14.14 ± 0.69	n.d.	n.d.	1.88 ± 0.15	1.59 ± 0.16	n.d.	n.d.

Data are presented as average concentration from 3 measurements, N was not detected due to the spectral overlap.
n.d.: not detected or below detection limit.

and Duolun (Han et al., 2005). Due to the uncertainty of EDS, it is not possible to make accurate evaluations of the contributions of each source. However, the ratio implies that other components were continually deposited on the dust particles during transport, which made the particles a mixture of different species.

2.2 TPD and FT-IR experiments

Temperature programmed desorption, a useful method for analyzing surface species in surface science, was used in this work to gain insight into the major components on dust particle surfaces. The desorbed species CO₂ ($m/e = 44$), H₂O ($m/e = 18$), CO ($m/e = 28$), NO ($m/e = 30$), SO₂ ($m/e = 64$), O₂ ($m/e = 32$) and NO₂ ($m/e = 46$) were monitored by mass spectrometer. As seen from Fig. 2A, four peaks for water ($m/e = 18$) at 362, 423, 643 and 838 K were observed. It is well known that some water is adsorbed on the particles' surface from the ambient atmosphere and that some hydroxyl groups are present on the dust particles' surface. During the desorption program, physically adsorbed water molecules desorbed at low temperature and the water from hydroxyl groups desorbed at high temperature. Another source of water desorbed at high temperature was the oxidation product of organic species adsorbed on the particles, which will be discussed later. The intense desorption peak of CO₂ ($m/e = 44$) with the fractional peak CO ($m/e = 28$) at 976 K was due to the decomposition of calcium carbonate, which has always been reported as a major component of Asian dust particles. In addition, both the mass signal intensities of CO₂ and CO increased gradually when the temperature was above 540 K, which may be due to the burning of organic species. Although the whole program was in an Ar atmosphere, residual O₂ ($m/e = 32$) was present and was

consumed when the temperature was above 540 K (Fig. 2A). Moreover, the sample turned from brown to black after the TPD process due to residual carbon black. These results show that there were many carbonaceous species coated on these particles, which is consistent with the higher C weight percent in the EDS spectrum. Desorption of NO was observed which indicates surface nitrate species were present. It is well known that atmospheric HNO₃ readily adsorbs on mineral dust containing calcite due to its basicity (Usher et al., 2003). The complete conversion of authentic mineral dust samples through heterogeneous reaction between CaCO₃ and HNO₃ in laboratory study and in field measurements was reported (Laskin et al., 2005a, 2005b). No SO₂ desorption indicates there was little sulfur species on the surface of particles, which was in good agreement with the EDS and XPS results. The unexpectedly low amount of sulfur species disagrees with some previous research where sulfur species were always detected in Asian dust storm particles (Ro et al., 2005; Shi et al., 2008; Song and Carmichael, 1999; Sullivan et al., 2007a; Zhang and Iwasaka, 1999). However, EDX analysis of individual dust storm particles also implied that almost no sulfate is formed on the surface of dust storm particles during their transport from source areas to Beijing (Zhang and Iwasaka, 1999). In addition, it was reported that more than 90% of Asian dust particles collected in Qingdao, China during three Asian dust events in the spring of 2001 were not disturbed by sulfate, nitrate, and/or sea-salts (Zhang et al., 2000). It seems the dust storm particles have low reactivity towards SO₂, since SO₂ emissions are high in China.

To further identify the composition of the dust particles, FT-IR was used to characterize the surface species and the structure of the substrate. The sample was heated in air for

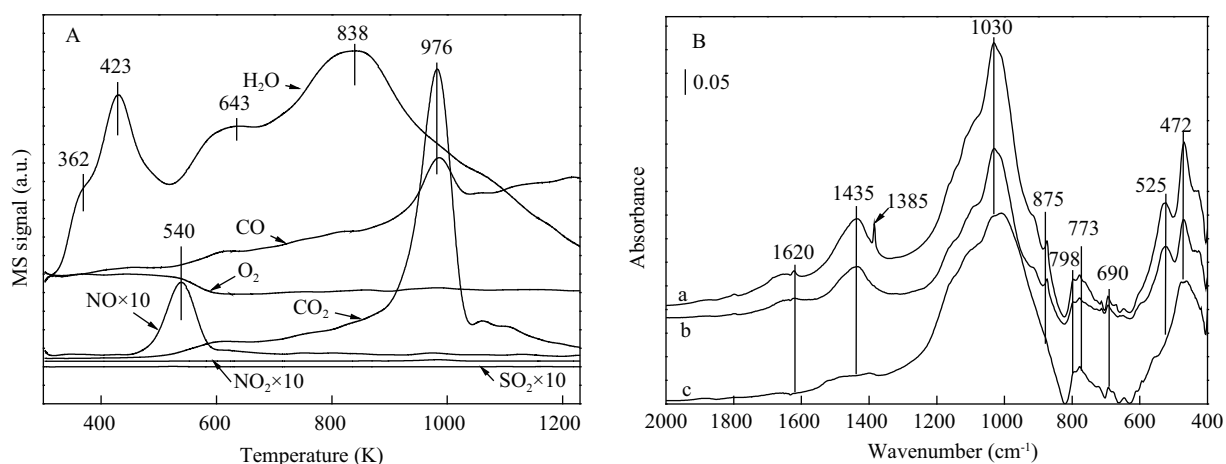


Fig. 2 Characterization of Asian dust storm particles. (A) TPD spectra, conditions: carrier gas Ar = 50 mL/min, $\beta = 20$ K/min, $m_{\text{sample}} = 200$ mg. (B) FT-IR spectra of fresh sample (line a), and samples heated in air for 12 hr at 573 K (line b), and 973 K (line c).

12 hr at 573 and 973 K to remove different surface species to study the structural information of the substrate. The IR spectra of a fresh sample as well as samples heated at different temperatures are shown in Fig. 2B. Several bands at 1030, 798, 773, 690 and 472 cm^{-1} were observed for all three samples, which can be attributed to the stretching of Si–O, Si–O–Al and Al–O (Mashburn et al., 2006). It is suggested that the thermal treatment did not destroy the skeleton structure of the aerosol particle. The bands observed on the fresh sample at 1435, 875, and 525 cm^{-1} , which are also present for the samples heated at 573K, disappeared after heating at 973 K. These bands at 1435 and 875 cm^{-1} are assigned to the asymmetric stretch (ν_3), and in-plane bend (ν_4) of CO_3^{2-} in calcium carbonate, respectively (Al-Hosney and Grassian, 2005). Since the CaCO_3 particles exposed to the ambient atmosphere are terminated by a $\text{Ca(OH)(CO}_3\text{H)}$ surface layer (Al-Hosney and Grassian, 2005), the peak at 525 cm^{-1} can be attributed to ν_7 (OC–OH) (Baltrusaitis et al., 2006). The result is in good agreement with the results of TPD, which showed decomposition of CaCO_3 at 976 K. The band at 1385 cm^{-1} , which was attributed to the H–C bending mode, disappeared after heating at 573 K. This was due to the oxidation of organic species, as shown in the TPD results. The peak at 1620 cm^{-1} may be due to the H–O–H bending mode or the asymmetric stretch (COO) of carboxylic species. The TPD and FT-IR results showed that the major components of the dust particles were aluminosilicate, SiO_2 and CaCO_3 , with mixed organic species, which is in agreement with single-particle characterization results (Ro et al., 2005).

2.3 Knudsen cell experiments

To study the heterogeneous reactivity of mineral dust towards SO_2 , uptake of SO_2 on the dust particles was investigated using a Knudsen cell/mass system. Initially, a steady flow of SO_2 was achieved before the powder was exposed. Upon opening the lid of the sample holder, the SO_2 signal of the parent ion monitored at $m/e = 64$ dropped dramatically. The observed uptake coefficient, γ_{obs} , can be determined from the Knudsen cell equation as follows (Golden et al., 1973):

$$\gamma_{\text{obs}} = \frac{A_h I_0 - I}{A_s I} \quad (1)$$

where, A_h is the effective area of the escape hole, or escape aperture ($A_h = 0.324 \text{ cm}^2$), A_s is the geometric area of the sample holder ($A_s = 5.07 \text{ cm}^2$), and I_0 and I are the QMS intensity measured with sample covered and sample exposed, respectively. The values calculated this way are the initial uptake coefficients, $\gamma_{0,\text{obs}}$, representing the uptake coefficient that is observed at the initial stages of the reaction. As reported by Usher et al. (2002), the uptake coefficient of SO_2 on mineral oxides depends on the sample mass, which has been ascribed to the diffusion of SO_2 into the underlying layers of multilayer powder samples (Underwood et al., 2000). When the uptake coefficient was calculated by Eq. (1), this mass dependence relationship

was not considered. However, this must be accounted for in the determination of a true uptake coefficient.

As seen in Fig. 3a, the QMS intensity decreases when the sample holder lid was open to the dust particle sample. The QMS intensity reverted to its initial level after the closure of the lid. Figure 3b shows the observed uptake coefficient ($\gamma_{0,\text{obs}}$) calculating by Eq. (1). The dependence of the initial uptake coefficient to sample mass is shown in Fig. 4. It is clear that the observed uptake value is dependent on the mass of the sample: as sample mass increases, so does the observed initial uptake coefficient. The plot in Fig. 4 shows only the region where $\gamma_{0,\text{obs}}$ is linearly dependent on the mass.

From the plot in Fig. 4, a mass-independent uptake coefficient (γ_{BET}) can be derived as (Carlos-Cuellar et al., 2003)

$$\gamma_{\text{BET}} = \text{slope} \cdot \frac{A_s}{S_{\text{BET}}} \quad (2)$$

where, slope (mg^{-1}) is the slope of the plot of γ_{obs} versus sample mass in the linear region, and S_{BET} is the specific surface area of the particle sample ($5.43 \text{ cm}^2/\text{mg}$). It can be seen that the BET-surface-area-corrected value of the

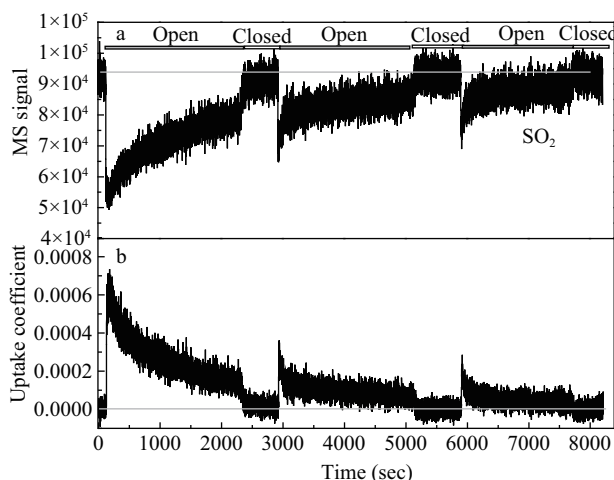


Fig. 3 Uptake of SO_2 on 60 mg dust particles at 300 K. (a) temporal concentration profiles for SO_2 ($m/e = 64$) in the uptake experiment; (b) initial uptake coefficients. SO_2 flow at 2.0% in N_2 balance.

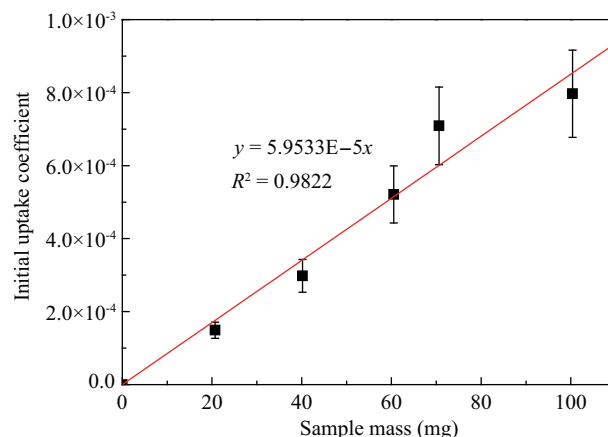


Fig. 4 Linear mass dependence of SO_2 observed uptake coefficients on dust particles at 300 K. SO_2 flow at 2.0% in N_2 balance.

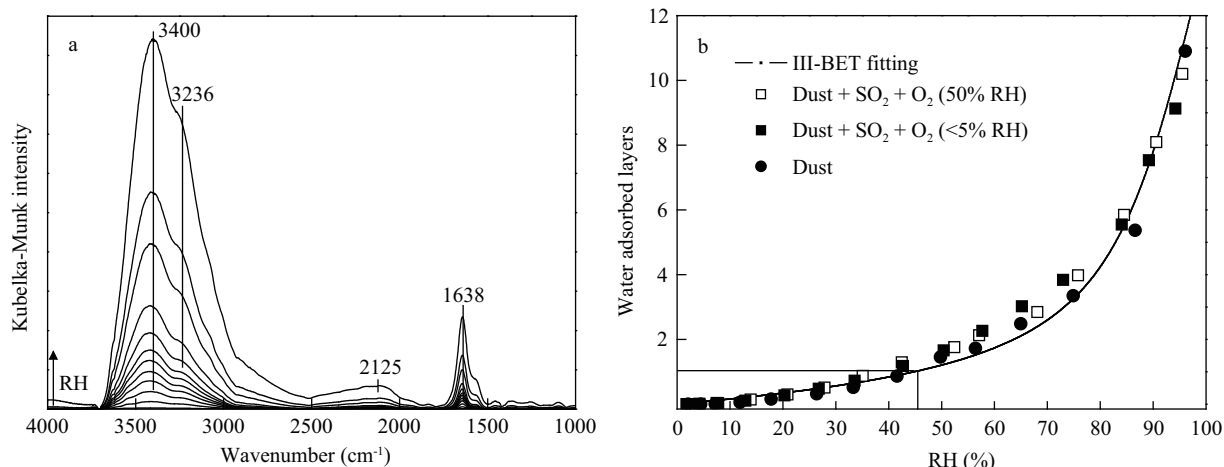


Fig. 5 Water uptake on dust particles obtained at 300 K. (a) DRIFTS spectra as a function of relative humidity (RH) (2.1%, 4.5%, 7.2%, 11.9%, 17.8%, 26.4%, 33.3%, 41.6%, 49.8%, 56.4%, 65.0%, 74.9%, 86.6%, 96.1% RH); (b) isotherms of fresh dust, reacted with SO₂ (200 ppm) + O₂ (20%), and with SO₂ (200 ppm) + O₂ (20%) at RH = 50%. Integrated region was 2700–3700 cm⁻¹.

initial uptake coefficient, $\gamma_{0,BET}$, is 5.767×10^{-6} . The value is lower than that reported in other studies when other authentic mineral dust particles were used. Usher et al. (2002) investigated the uptake of SO₂ on China loess, for which the initial uptake coefficient was determined to be $(3 \pm 1) \times 10^{-5}$. The initial uptake coefficient of SO₂ on Saharan dust was $(6.6 \pm 0.8) \times 10^{-5}$, when a flow tube was used (Adams et al., 2005). The low uptake coefficient value in this study was due to the fact that the major components, aluminosilicate and SiO₂ as shown by EDS, TPD and FT-IR results, have low reactivity towards SO₂. This can also explain the field measurement results, which found that the measured ratio of SO₄²⁻ to (SO₄²⁻ + SO₂) was very low during the dust period (Xie et al., 2005). Xie et al. (2005) explain this phenomenon by reason of the low RH during the dust period. The low uptake coefficient means a low possibility for the first stage of conversion of SO₂ to SO₄²⁻. It should be pointed out that the partial pressure of water in the Knudsen cell was less than 10⁻⁴ Torr, which means the RH was much less than 1% RH. The role of water in the conversion of SO₂ to sulfate could not be accounted for in the Knudsen cell experiments. Therefore, we applied *in situ* DRIFTS to study water uptake on the dust particles as well as the role of water in the heterogeneous reaction of SO₂ with dust particles.

2.4 Hygroscopic measurement

Adsorption of water vapor onto the dust particles was measured at room temperature by means of DRIFTS. The integrated intensity of the O–H stretching region of 2700–3700 cm⁻¹ provides a measure of the amount of water on the surface. The peak in this region is a combination of vibrational modes: symmetric stretch at 3400 cm⁻¹ and asymmetric stretch at 3236 cm⁻¹, which were demonstrated to be sufficiently strong to monitor water adsorption on the surface of the particles (Goodman et al., 2001; Gustafsson et al., 2005). Unlike transmission FT-IR, DRIFTS shows no linear relation between band intensity and concentration of the adsorbate. Gaining quantitative information from the spectra is non-trivial, as the Beer-Lambert law used in transmittance is not applicable.

However, Kubelka-Munk (K-M) theory can be applied to improve the linearity of the dependence of signal intensity upon concentration (Armaroli et al., 2004; Gustafsson et al., 2005). Figure 5a shows the water adsorption DRIFTS spectra. The isotherms of water uptake on fresh dust, and dust reacted with SO₂ in dry and humid air conditions obtained after applying the K-M function are shown in Fig. 5b. The effect of reaction with SO₂ on the hygroscopic behavior of dust samples will be discussed later.

All the isotherms in Fig. 5b exhibit type III characteristics, indicative of a low adsorption enthalpy in the contact layer. In most cases, the two-parameter BET equation with the assumptions of a uniform surface and an infinite number of layers ($n = \infty$) does not fit the experimental data at high relative pressures, when the adsorption isotherm rises indefinitely and an infinite number of layers ($n = \infty$) of adsorbing gas is predicted to build up on the surface. The three-parameter BET equation limits the number of layers of gas adsorbing at high values of P/P_0 , which is as follows:

$$V = \frac{V_m c \frac{P}{P_0}}{1 - \frac{P}{P_0}} \times \frac{1 - (n+1)\left(\frac{P}{P_0}\right)^n + n\left(\frac{P}{P_0}\right)^{n+1}}{1 + (c-1)\left(\frac{P}{P_0}\right) - c\left(\frac{P}{P_0}\right)^{n+1}} \quad (3)$$

where, V is the volume of gas adsorbed at equilibrium pressure P , V_m is the volume of gas necessary to cover the surface of the adsorbent with a complete monolayer, and P_0 is the saturation vapor pressure of the adsorbing gas at the temperature where the adsorption process occurs. n is an adjustable parameter given as the maximum number of layers of the adsorbing gas and is related to the pore size and properties of the adsorbent. As a result, multilayer formation of the adsorbing gas is limited to n layers at large values of P/P_0 . The parameter c is the temperature-dependent constant related to the enthalpies of adsorption of the first and higher layers through Eq. (4):

$$c = \exp\left(-\frac{\Delta H_1^0 - \Delta H_2^0}{RT}\right) \quad (4)$$

where ΔH_1^0 is the standard enthalpy of adsorption of the first layer, ΔH_2^0 is the standard enthalpy of adsorption on

subsequent layers and is taken as the standard enthalpy of condensation, R is the gas constant, and T is the temperature in Kelvin.

A curve-fitting software program was used to fit the 3-parameter BET equation for the water adsorption isotherm of the fresh dust sample (Ma et al., 2010). The result is shown in Fig. 5b with a correlation coefficient $r = 0.99$. The fitting result gave fit values for n (27.6), c (1.52) and V_m . With the V_m , we can convert the integrated K-M area to layers of water adsorption. On this basis, we calculated that one monolayer of water was formed at 46% RH. The ambient RH is about 20%–80%, which means about 1–4 layers of water can be adsorbed on the particle surface.

DRIFTS studies of SO_2 adsorption on dust particles under dry and humid (50% RH) air conditions were also conducted. After the adsorption processes, the samples were purged with dry N_2 for one hour to remove gaseous-phase and physically-adsorbed SO_2 , and then the spectra were collected. As shown in Fig. 6a and b, both spectra under dry and humid air conditions show no absorbance features of sulfate species, which further confirms the low reactivity of dust particles towards SO_2 . Only the peaks due to residual adsorbed water were observed at 1650 and 3600 cm^{-1} . This suggests that the relatively small amount of water adsorbed at ambient RH cannot significantly enhance the conversion of SO_2 to sulfate during the dust storm period. On the other hand, the effect of the reaction with SO_2 on the hygroscopic behavior of dust particles was also studied, which is shown in Fig. 5b. These results show that the heterogeneous reactions of SO_2 only have a slight effect on the hygroscopic properties of these dust particles. There are several reasons to explain this phenomenon. First, SiO_2 and aluminosilicate, as the major components, are inactive towards SO_2 . Second, the mixed organic species and other secondary materials limited the extent of reaction of SO_2 with mineral dust. Third, the sample collected in this study has a large fraction of coarse particles, which often experience relatively less atmospheric processing than fine particles (Ro et al., 2005; Song and Carmichael, 1999; Sullivan et al., 2007a). Finally, for

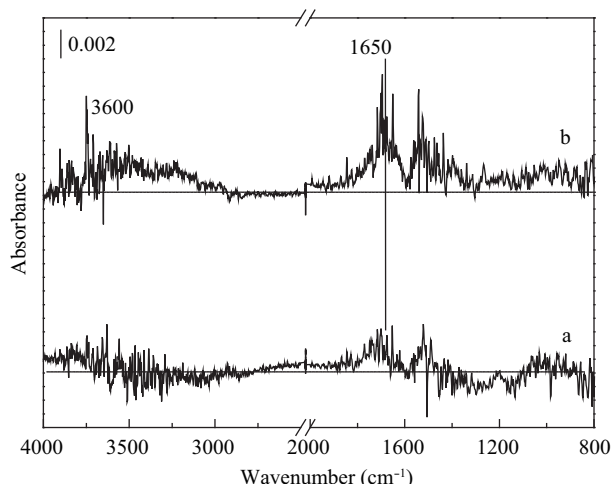


Fig. 6 DRIFTS spectra of SO_2 (200 ppm) adsorption on dust particles in air (20% $\text{O}_2 + \text{N}_2$) at 300 K for 2 hr in dry conditions (a) and humid conditions RH = 50% (b).

conversion of SO_2 to sulfate on mineral dust, an oxidant, such as H_2O_2 , O_3 , HNO_3 or NO_2 , is needed (Li et al., 2006; Ma et al., 2008; Ullerstam et al., 2002, 2003). Therefore, the effect of SO_2 reaction on the hygroscopic changes of dust particles was limited.

SO_2 emissions are high in China, and sulfur compounds have been detected in Asian dust storm particles in previous studies (Ro et al., 2005; Shi et al., 2008; Song and Carmichael, 1999; Sullivan et al., 2007a; Zhang and Iwasaka, 1999). However, a recent model calculation conducted by Manktelow et al. (2010) indicated that the sulfate species on Asian dust particles may mainly derive from the uptake of H_2SO_4 rather than from reaction of SO_2 with the dust surface. The results in this study imply that the heterogeneous reaction of SO_2 with dust particles makes little contribution to the sulfur compounds in the dust.

3 Conclusions

Asian dust storms are one of the largest primary sources of global aerosols. Most of the dust storm particles are deposited during transport, which has a significant effect on the atmospheric environment of the passed cities. In this study, dust storm particles collected in Beijing was analyzed by SEM-EDS, XPS, FT-IR, and TPD experiments. The major components of the dust particles were SiO_2 , aluminosilicate, and CaCO_3 , which were mixed with some organic and nitrate species. These particles contained large fractions from anthropogenic sources and local sources after long transportation. Knudsen cell experiments demonstrated that the observed SO_2 uptake coefficient showed a linear mass dependence relation. The reactivity towards SO_2 was very low, with a true uptake coefficient of 5.767×10^{-6} . The isotherm of water adsorption on dust particles showed a III-type BET curve, with a monolayer formed at 46% RH, and only 1–4 layers of water adsorbed in the ambient RH range (20%–80%). Adsorbed water molecules show no enhancement effect for the conversion of SO_2 to sulfate species on the dust particles. On the other hand, the heterogeneous reaction of SO_2 in both dry and humid air conditions has little influence on the hygroscopic behavior of the dust particles.

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References

- Adams J W, Rodriguez D, Cox R A, 2005. The uptake of SO_2 on Saharan dust: a flow tube study. *Atmospheric Chemistry and Physics*, 5(10): 2679–2689.
- Al-Hosney H A, Grassian V H, 2005. Water, sulfur dioxide and nitric acid adsorption on calcium carbonate: A transmission and ATR-FTIR study. *Physical Chemistry & Chemical Physics*, 7: 1266–1276.
- Andreae M O, Andreae T W, Meyerdierks D, Thiel C, 2003.

- Marine sulfur cycling and the atmospheric aerosol over the springtime North Atlantic. *Chemosphere*, 52(8): 1321–1343.
- Armaroli T, Bécue T, Gautier S, 2004. Diffuse reflection infrared spectroscopy (Drifts): Application to the *in situ* analysis of catalysts. *Oil & Gas Science and Technology*, 59(2): 215–237.
- Baltrusaitis J, Jensen J H, Grassian V H, 2006. FTIR spectroscopy combined with isotope labeling and quantum chemical calculations to investigate adsorbed bicarbonate formation following reaction of carbon dioxide with surface hydroxyl groups on Fe₂O₃ and Al₂O₃. *Journal of Physical Chemistry B*, 110(24): 12005–12016.
- Bauer S E, Balkanski Y, Schulz M, Hauglustaine D A, Dentener F, 2004. Global modeling of heterogeneous chemistry on mineral aerosol surfaces: Influence on tropospheric ozone chemistry and comparison to observations. *Journal of Geophysical Research–Atmosphere*, 109: D02304.
- Carlos-Cuellar S, Li P, Christensen A P, Krueger B J, Burrichter C, Grassian V H, 2003. Heterogeneous uptake kinetics of volatile organic compounds on oxide surfaces using a Knudsen cell reactor: Adsorption of acetic acid, formaldehyde, and methanol on α -Fe₂O₃, α -Al₂O₃, and SiO₂. *Journal of Physical Chemistry A*, 107(21): 4250–4261.
- Cwiertny D M, Young M A, Grassian V H, 2008. Chemistry and photochemistry of mineral dust aerosol. *Annual Review of Physical Chemistry*, 59(1): 27–51.
- Cyranoski D, 2003. China plans clean sweep on dust storms. *Nature*, 421(6919): 101.
- Dentener F J, Carmichael G R, Zhang Y, Lelieveld J, Crutzen P J, 1996. Role of mineral aerosol as a reactive surface in the global troposphere. *Journal of Geophysical Research–Atmosphere*, 101(D17): 22869–22889.
- Desboeufs K V, Losno R, Colin J L, 2001. Factors influencing aerosol solubility during cloud processes. *Atmospheric Environment*, 35(20): 3529–3537.
- Falkovich A H, Schkolnik G, Ganor E, Rudich Y, 2004. Adsorption of organic compounds pertinent to urban environments onto mineral dust particles. *Journal of Geophysical Research–Atmosphere*, 109: D02208.(13)
- Gao Y, Arimoto R, Zhou M Y, Merrill J T, Duce R A, 1992. Relationships between the dust concentrations over eastern Asia and the remote North Pacific. *Journal of Geophysical Research–Atmosphere*, 97(D9): 9867–9872.
- Ginoux P, Chin M, Tegen I, Prospero J M, Holben B, Dubovik O et al., 2001. Sources and distributions of dust aerosols simulated with the GOCART model. *Journal of Geophysical Research–Atmosphere*, 106(D17): 20255–20273.
- Golden D M, Spokes G N, Benson S W, 1973. Very low-pressure pyrolysis (VLPP); A versatile kinetic tool. *Angewandte Chemie International Edition*, 12(7): 534–546.
- Gong S L, Zhang X Y, Zhao T L, McKendry I G, Jaffe D A, Lu N M, 2003. Characterization of soil dust aerosol in China and its transport and distribution during 2001 ACE-Asia: 2. Model simulation and validation. *Journal of Geophysical Research–Atmosphere*, 108: 4262–4284.
- Goodman A L, Bernard E T, Grassian V H, 2001. Spectroscopic study of nitric acid and water adsorption on oxide particles: Enhanced nitric acid uptake kinetics in the presence of adsorbed water. *Journal of Physical Chemistry A*, 105(26): 6443–6457.
- Gustafsson R J, Orlov A, Badger C L, Griffiths P T, Cox R A, Lambert R M, 2005. A comprehensive evaluation of water uptake on atmospherically relevant mineral surfaces: DRIFT spectroscopy, thermogravimetric analysis and aerosol growth measurements. *Atmospheric Chemistry and Physics*, 5(12): 3415–3421.
- Han L H, Zhuang G Z, Sun Y L, Wang Z F, 2005. Local and non-local sources of airborne particulate pollution at Beijing–The ratio of Mg/Al as an element tracer for estimating the contributions of mineral aerosols from outside Beijing. *Science in China Series B: Chemistry*, 48(3): 253–264.
- Hand J L, Mahowald N M, Chen Y, Siefert R L, Luo C, Subramaniam A et al., 2004. Estimates of atmospheric-processed soluble iron from observations and a global mineral aerosol model: Biogeochemical implications. *Journal of Geophysical Research–Atmosphere*, 109: D17205.
- Hanisch F, Crowley J N, 2001. The heterogeneous reactivity of gaseous nitric acid on authentic mineral dust samples, and on individual mineral and clay mineral components. In: International Discussion Meeting of the Deutsche-Bunsen-Gesellschaft-fur-Physikalische-Chemie, Gottingen, Germany, ISI: 000169504900039. 2474–2482.
- Hanke M, Umann B, Uecker J, Arnold F, Bunz H, 2003. Atmospheric measurements of gas-phase HNO₃ and SO₂ using chemical ionization mass spectrometry during the MINATROC field campaign 2000 on Monte Cimone. *Atmospheric Chemistry and Physics*, 3(2): 417–436.
- IPCC (Intergovernmental Panel on Climate Change) 2007. Summary for policymakers. In *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* (Solomon S, Qin D, Manning M et al., eds.). Cambridge University Press, New York. 1–18.
- Jeong G Y, 2008. Bulk and single-particle mineralogy of Asian dust and a comparison with its source soils. *Journal of Geophysical Research–Atmosphere*, 113: D02208.
- Jickells T D, An Z S, Andersen K K, Baker A R, Bergametti G, Brooks N et al., 2005. Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science*, 308(5718): 67–71.
- Koehler K A, Kreidenweis S M, DeMott P J, Petters M D, Prenni A J, Carrico C M, 2009. Hygroscopicity and cloud droplet activation of mineral dust aerosol. *Geophysical Research Letters*, 36: L08805.
- Laskin A, Iedema M J, Ichkovich A, Graber E R, Taraniuk I, Rudich Y, 2005a. Direct observation of completely processed calcium carbonate dust particles. *Faraday Discussion*, 130: 453–468.
- Laskin A, Wietsma T W, Krueger B J, Grassian V H, 2005b. Heterogeneous chemistry of individual mineral dust particles with nitric acid: A combined CCSEM/EDX, ESEM, and ICP-MS study. *Journal of Geophysical Research–Atmosphere*, 110(D10): D10208.
- Li L, Chen Z M, Zhang Y H, Zhu T, Li J L, Ding J, 2006. Kinetics and mechanism of heterogeneous oxidation of sulfur dioxide by ozone on surface of calcium carbonate. *Atmospheric Chemistry and Physics*, 6(9): 2453–2464.
- Liu Y C, He H, Ma Q X, 2008. Temperature dependence of the heterogeneous reaction of carbonyl sulfide on magnesium oxide. *Journal of Physical Chemistry A*, 112(13): 2820–2826.
- Ma Q X, Liu Y C, He H, 2008. Synergistic effect between NO₂ and SO₂ in their adsorption and reaction on γ -alumina. *Journal of Physical Chemistry A*, 112(29): 6630–6635.
- Ma Q X, He H, Liu Y C, 2010. *In situ* DRIFTS study of

- hygroscopic behavior of mineral aerosol. *Journal of Environmental Sciences*, 22(4): 555–560.
- Manktelow P T, Carslaw K S, Mann G W, Spracklen D V, 2010. The impact of dust on sulfate aerosol, CN and CCN during an East Asian dust storm. *Atmospheric Chemistry and Physics*, 10(2): 365–382.
- Mashburn C D, Frinak E K, Tolbert M A, 2006. Heterogeneous uptake of nitric acid on Na-montmorillonite clay as a function of relative humidity. *Journal of Geophysical Research-Atmosphere*, 111: D15213.
- Maxwell-Meier K, Weber R J, Song C H, Orsini D, Ma Y, Carmichael G R et al., 2004. Inorganic composition of fine particles in mixed mineral dust-pollution plumes observed from airborne measurements during ACE-Asia. *Journal of Geophysical Research-Atmosphere*, 109: D19S07.
- Meskhidze N, Chameides W L, Nenes A, 2005. Dust and pollution: A recipe for enhanced ocean fertilization? *Journal of Geophysical Research-Atmosphere*, 110: D03301.
- Prince A P, Kleiber P, Grassian V H, Young M A, 2007. Heterogeneous interactions of calcite aerosol with sulfur dioxide and sulfur dioxide-nitric acid mixtures. *Physical Chemistry & Chemical Physics*, 9(26): 3432–3439.
- Prince A P, Kleiber P D, Grassian V H, Young M A, 2008. Reactive uptake of acetic acid on calcite and nitric acid reacted calcite aerosol in an environmental reaction chamber. *Physical Chemistry & Chemical Physics*, 10(1): 142–152.
- Prospero J M, Ginoux P, Torres O, Nicholson S E, Gill T E, 2002. Environmental characterization of global sources of atmospheric soil dust identified with the Nimbus 7 Total Ozone Mapping Spectrometer (TOMS) absorbing aerosol product. *Review of Geophysics*, 40: 1002.
- Ramanathan V, Crutzen P J, Kiehl J T, Rosenfeld D, 2001. Aerosols, climate, and the hydrological cycle. *Science*, 294(5549): 2119–2124.
- Ravishankara A R, 1997. Heterogeneous and multiphase chemistry in the troposphere. *Science*, 276(5315): 1058–1065.
- Ro C U, Hwang H J, Kim H, Chun Y, Van Grieken R, 2005. Single-particle characterization of four “Asian Dust” samples collected in Korea, using low-Z particle electron probe X-ray microanalysis. *Environmental Science and Technology*, 39(6): 1409–1419.
- Russell L M, Maria S F, Myneni S C B, 2002. Mapping organic coatings on atmospheric particles. *Geophysics Research Letters*, 29: 1779.
- Shi Z B, Shao L Y, Jones T P, Lu S L, 2005. Microscopy and mineralogy of airborne particles collected during severe dust storm episodes in Beijing, China. *Journal of Geophysical Research-Atmosphere*, 110: D01303.
- Shi Z B, Zhang D Z, Hayashi M, Ogata H, Ji H Z, Fujie W, 2008. Influences of sulfate and nitrate on the hygroscopic behaviour of coarse dust particles. *Atmospheric Environment*, 42(4): 822–827.
- Song C H, Carmichael G R, 1999. The aging process of naturally emitted aerosol (sea-salt and mineral aerosol) during long range transport. *Atmospheric Environment*, 33(14): 2203–2218.
- Song C H, Kim C M, Lee Y J, Carmichael G R, Lee B K, Lee D S, 2007. An evaluation of reaction probabilities of sulfate and nitrate precursors onto East Asian dust particles. *Journal of Geophysical Research-Atmosphere*, 112: D18206.
- Streets D G, Bond T C, Carmichael G R, Fernandes S D, Fu Q, He D et al., 2003. An inventory of gaseous and primary aerosol emissions in Asia in the year 2000. *Journal of Geophysical Research-Atmosphere*, 108(D21): 8809.
- Sullivan R C, Guazzotti S A, Sodeman D A, Prather K A, 2007a. Direct observations of the atmospheric processing of Asian mineral dust. *Atmospheric Chemistry and Physics*, 7(5): 1213–1236.
- Sullivan R C, Guazzotti S A, Sodeman D A, Tang Y H, Carmichael G R, Prather K A, 2007b. Mineral dust is a sink for chlorine in the marine boundary layer. *Atmospheric Environment*, 41(34): 7166–7179.
- Sullivan R C, Moore M J K, Petters M D, Kreidenweis S M, Roberts G C, Prather K A, 2009. Effect of chemical mixing state on the hygroscopicity and cloud nucleation properties of calcium mineral dust particles. *Atmospheric Chemistry and Physics*, 9(10): 3303–3316.
- Sullivan R C, Prather K A, 2007. Investigations of the diurnal cycle and mixing state of oxalic acid in individual particles in Asian aerosol outflow. *Environmental Science and Technology*, 41(23): 8062–8069.
- Sun J M, Zhang M Y, Liu T, 2001. Spatial and temporal characteristics of dust storms in China and its surrounding regions, 1960–1999: Relations to source area and climate. *Journal of Geophysical Research-Atmosphere*, 106(D10): 10325–10333.
- Sun Y L, Zhuang G S, Wang Y, Han L H, Guo J H, Dan M et al., 2004a. The air-borne particulate pollution in Beijing—concentration, composition, sdistribution and sources. *Atmospheric Environment*, 38(35): 5991–6004.
- Sun Y L, Zhuang G S, Yuan H, Zhang X Y, Guo J H, 2004b. Characteristics and sources of 2002 super dust storm in Beijing. *Chinese Science Bulletin*, 49(7): 698–705.
- Tang Y H, Carmichael G R, Kurata G, Uno I, Weber R J, Song C H et al., 2004. Impacts of dust on regional tropospheric chemistry during the ACE-Asia experiment: A model study with observations. *Journal of Geophysical Research-Atmosphere*, 109: D19S21.
- Ullerstam M, Johnson M S, Vogt R, Ljungström E, 2003. DRIFTS and Knudsen cell study of the heterogeneous reactivity of SO₂ and NO₂ on mineral dust. *Atmospheric Chemistry and Physics*, 3(6): 2043–2051.
- Ullerstam M, Vogt R, Langer S, Ljungström E, 2002. The kinetics and mechanism of SO₂ oxidation by O₃ on mineral dust. *Physical Chemistry & Chemical Physics*, 4(19): 4694–4699.
- Underwood G M, Li P, Usher C R, Grassian V H, 2000. Determining accurate kinetic parameters of potentially important heterogeneous atmospheric reactions on solid particle surfaces with a Knudsen cell reactor. *Journal of Physical Chemistry A*, 104(4): 819–829.
- Usher C R, Al-Hosney H, Carlos-Cuellar S, Grassian V H, 2002. A laboratory study of the heterogeneous uptake and oxidation of sulfur dioxide on mineral dust particles. *Journal of Geophysical Research-Atmosphere*, 107(D23): 4713.
- Usher C R, Michel A E, Grassian V H, 2003. Reactions on mineral dust. *Chemical Review*, 103(12): 4883–4940.
- Xie S D, Zhang Y H, Li Q, Tang X Y, 2005. Characteristics of air pollution in Beijing during sand-dust storm periods. *Water, Air, & Soil Pollution: Focus*, 5(3–6): 217–229.
- Yang D Z, Yan P, Xu X D, 2002. Characteristics of aerosols under dust and sand weather in Beijing. *Quarterly Journal of Applied Meteorology*, 13(S1): 185–194.
- Zhang D Z, Iwasaka Y, 1999. Nitrate and sulfate in individual Asian dust-storm particles in Beijing, China in spring of 1995 and 1996. *Atmospheric Environment*, 33(19): 3213–3223.

- Zhang D Z, Shi G Y, Iwasaka Y, Hu M, 2000. Mixture of sulfate and nitrate in coastal atmospheric aerosols: individual particle studies in Qingdao (36°04'N, 120°21'E), China. *Atmospheric Environment*, 34(17): 2669–2679.
- Zhang D Z, Iwasaka Y, 2001. Chlorine deposition on dust particles in marine atmosphere. *Geophysics Research Letters*, 28(18): 3613–3616.
- Zhang X Y, Gong S L, Shen Z X, Mei F, Xi X X, Liu L C et al., 2003. Characterization of soil dust aerosol in China and its transport and distribution during 2001 ACE-Asia. 1. Network observations, *Journal of Geophysical Research-Atmosphere*, 108(D9): 8032–8039.
- Zhang X Y, Zhang G Y, Zhu G H, Zhang D E, An Z S, Chen T et al., 1996. Elemental tracers for Chinese source dust. *Science in China (Series D)*, 39(5): 512–521.
- Zhang X Y, Zhuang G S, Chen J M, Wang Y, Wang X, An Z S et al., 2006. Heterogeneous reactions of sulfur dioxide on typical mineral particles. *Journal of Physical Chemistry B*, 110(25): 12588–12596.
- Zhuang G S, Guo J H, Yuan H, Zhao C Y, 2001. The compositions, sources, and size distribution of the dust storm from China in spring of 2000 and its impact on the global environment. *Chinese Science Bulletin*, 46(11): 895–900.