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Sulfur isotopic fractionation and its implication: Sulfate formation in $PM_{2.5}$ and coal combustion under different conditions

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ABSTRACT

In order to exactly explore sulfur source and sulfate formation under highly polluted atmosphere, we determined $\delta^{34}S$ values of sulfate in $PM_{2.5}$ and atmospheric SO_2 in Nanjing region from 1 to 23 Jan. 2014. The secondary sulfate formation mechanism was discussed based on sulfur isotopic fractionation in the process of SO_2 oxidation. Meanwhile, we synchronously studied $\delta^{34}S$ values of raw coals used locally as well as sulfur isotopic fractionation during the combustion under coal burning and smoldering. The results show that $\delta^{34}S$ average values of SO_2 and sulfate in $PM_{2.5}$ were 1.5‰ and 5.1‰, respectively. $\delta^{34}S$ values of sulfate in $PM_{2.5}$ were consistent with those of coals widely used in Nanjing region and Northern China, indicating coal combustion was an important sulfur source for $PM_{2.5}$. Sulfur isotopic fractionation factors ranged from 1.0014 to 1.0075, implying that SO_2 heterogeneous and homogeneous oxidation were coexisting during the formation of the secondary sulfate. The contribution of SO_2 heterogeneous oxidation to sulfate varied from 40.7% to 64.8% during the observation period. $\delta^{34}S$ values of coals presented moderately positive sulfur isotopic signatures due to organic sulfur in low sulfur coals were mainly formed by plant assimilation. Besides, the negative relationship between $\delta^{34}S$ values of coals and total sulfur contents was also found. In addition, there existed a significant sulfur isotopic fractionation effect during coal combustion. Sulfate in $PM_{2.5}$ in flue gas enriched ^{34}S, while SO_2 in flue gas enriched ^{32}S. There was presence of the difference of $\delta^{34}S$ values in $PM_{2.5}$ and SO_2 in flue gas between coal burning and smoldering, which was related to coal property and combustion temperature.

1. Introduction

Haze is a pollution phenomenon caused by fine particles and stable meteorological condition, which results in the decline of atmospheric visibility and the adverse impacts on human and ecosystem health (Peng et al., 2016). In recent years, haze has increased in the frequency of occurrence as well as the area of the affected regions in China (Cong et al., 2015; Wan et al., 2016; Wang et al., 2016; Y.L. Zhang et al., 2016; Y.J. Zhang et al., 2016; Zhang and Cao, 2015; Guo et al., 2016a, 2016b; Wang et al., 2013).

Sulfate is a major component of $PM_{2.5}$ in the atmosphere. Kulmala et al. (2000) revealed stable sulfate clusters was a source of new atmospheric particles. Wang et al. (2016) found that sulfate concentration of $PM_{2.5}$ in Beijing region increased to 40 μg/m^3 in the polluted atmosphere. Besides, sulfate formation was promoted in the presence of NO_2. Cao et al. (2012) determined chemical composition of $PM_{2.5}$ in Xi'an with sulfate concentration at 16.8μg/m^3. Y.L. Zhang et al. (2016) and Y.J. Zhang et al. (2016) found sulfate concentration obviously increased due to enhanced aqueous-phase production during the spring festival holiday. Generally, sulfate aerosol poses a respiratory hazard and affects global climate through direct and indirect radioactive forcing. Besides, Andreae et al. (2005) concluded that strong present-day aerosol cooling would imply a hot future. Therefore, it is admirable to make clear the main sulfur sources in the atmosphere. Atmospheric sulfate usually originates from a variety of sources mainly including fossil fuels combustion, sea spray, biologic sulfur release and human activities (He et al., 2014; Laskin et al., 2003). However, the detailed sulfur sources and sulfate formation mechanism in $PM_{2.5}$ still remains uncertain particularly under highly polluted conditions.

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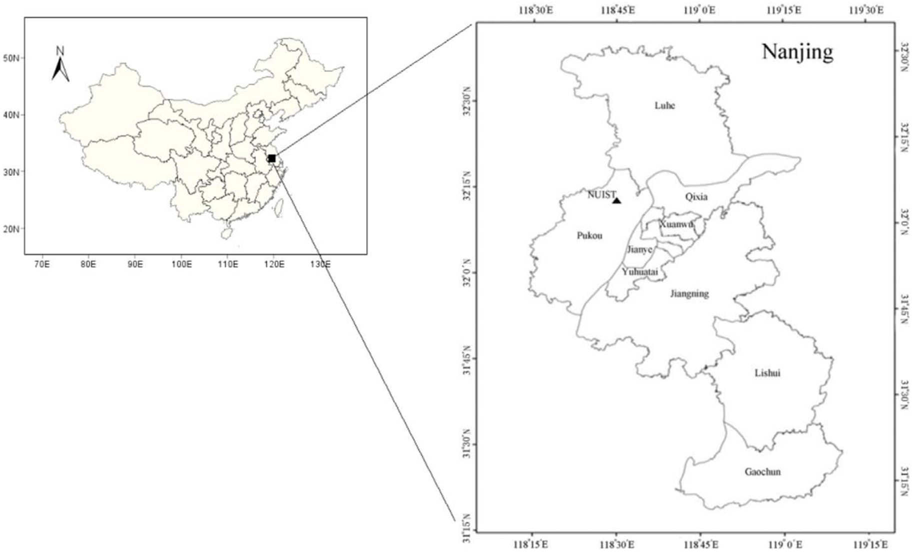

Fig. 1. Sampling site of NUIST in Nanjing, China.

Sulfur isotopic signature is variable in the physical and chemical processes, which depends on the relative difference in the quality of isotopically substituted molecule (Young et al., 2002). This results in the difference of sulfur isotopic compositions from various anthropogenic and natural sources (Guo et al., 2014). Sulfur isotopic composition in sea salt is highly uniform with $\delta^{34}S$ value at 21‰. $\delta^{34}S$ value in DMS from marine biota is at the range from 15 to 20‰ with an average about 18‰ (Calhoun et al., 1991). Bacterial sulfate reduction in anoxic environment produces H_2S, which is isotopically light with $\delta^{34}S$ value near 0‰. Besides, most $\delta^{34}S$ values of anthropogenic sulfate mainly from coal combustion and vehicle exhaust are from 1 to 11‰ (Shaheen et al., 2014). It can be observed that $\delta^{34}S$ values from different sources present a significant discrepancy. Therefore, sulfur isotopic composition ($\delta^{34}S$) of sulfate in $PM_{2.5}$ provides us an insight into seeking for sulfur sources (Wu and Han, 2015; Szynkiewicz et al., 2009).

Nowadays, as an effective indicator, $\delta^{34}S$ has been adopted as a fingerprint to identify sulfur sources of the atmosphere around the world. Han et al. (2016) applied $\delta^{34}S$ value to explore sulfur sources of Beijing aerosol and concluded that biogenic sulfur in summer and the increasing coal combustion in winter were the main contribution. Guo et al. (2016a, 2016b) analyzed $\delta^{34}S$ values of $PM_{2.5}$ in Nanjing region and identified sulfur sources were mainly from coal combustion and vehicle exhaust. Ohizumi et al. (2014) determined sulfur isotopic ratios of sulfate deposition for 28 years and demonstrated that $\delta^{34}S$ value could be used to track the change of emission sources. In addition, Sinha et al. (2008) found that $\delta^{34}S$ value of sulfate aerosol could be used to illuminate mixing process and transport pathway of sulfur-containing pollutants in the atmosphere.

Meanwhile, sulfur isotopic composition is also used to investigate the formation process of the secondary sulfate due to that $\delta^{34}S$ value may be changed when SO_2 is converted into sulfate via homogeneous and heterogeneous oxidation. The measured sulfur isotopic fractionation with respect to SO_2 is about -9‰ for homogeneous oxidation and up to $+16.5$‰ for heterogeneous oxidation (Tanaka et al., 1994). In addition, it is known that homogeneous oxidation of SO_2 is mainly motivated by OH radicals, while heterogeneous oxidation of SO_2 is related to the reactions between SO_2 and H_2O_2, O_2, O_3 and NO_2 in cloud and droplet (Hung and Hung and Hoffmann, 2015; Harris et al., 2013). Guo et al. (2016a, 2016b) determined $\delta^{34}S$ values of SO_2 and sulfate in $PM_{2.5}$ in Nanjing around the Youth Olympic Games (YOG), and concluded that average contribution ratio (48.7%) of SO_2 heterogeneous oxidation was slightly lower than that (51.3%) of SO_2 homogeneous oxidation during sulfate formation processes around the YOG.

It should be pointed out that sulfur isotopic fractionation mechanism is relatively complex, which includes isotopic equilibrium fractionation and kinetic fractionation. Besides, sulfur isotopic fractionation is usually affected by different reaction conditions. For instance, sulfur isotopic fractionation in HSO_3^{-}-SO_2 system may be described by temperature effect. Sulfur isotopic fractionation coefficients in HSO_3^{-}-SO_2 system are 1.0173 and 1.0107 at 25 and 70 °C, respectively (Egiazarov et al., 1971). Therefore, it is significant to study sulfur isotopic fractionation effect between different sulfur-containing substances in the process of sulfur emission such as coal combustion, which is favorable for exploring sulfur sources and transformation processes.

Coal is very abundant in China. Large amount of coals were used as fuel for power generation, central heating and industrial production, which brought about 80% of smoke dust and 90% of SO_2 in the atmosphere. Therefore, it is important to study sulfur emission from coal combustion. In this study, we firstly selected a typical haze case in winter in Nanjing region to study pollution behaviors of $PM_{2.5}$. Meanwhile, we measured $\delta^{34}S$ values of SO_2 and sulfate in $PM_{2.5}$ to trace sulfur sources. Taking into account sulfate formation still remains unclear under heavy polluted condition, we investigated oxidation pathways of SO_2 in the atmosphere based on sulfur isotopic fractionation during SO_2 oxidation to sulfate. Besides, in order to precisely study sulfur sources and the transformation in the atmosphere, it is crucial to clarify sulfur isotopic compositions and fractionation effect during coal combustion due to there usually existed a certain discrepancy in $\delta^{34}S$ value of coals from various regions. So we chose three coals widely used in Nanjing region to measure $\delta^{34}S$ values of raw coal, coal ash as well as SO_2 and $PM_{2.5}$ in flue gas from coal combustion, respectively. Sulfur isotopic fractionation effect was then discussed under coal burning and smoldering.

2. Materials and methods

2.1. Sampling site

$PM_{2.5}$ and SO_2 in the atmosphere were obtained on the roof of library (35 m above the ground) in Nanjing University of Information Science & Technology (NUIST, 32.1° N, 118.5° E). The sampling site of NUIST in Nanjing, China is depicted in Fig.1. It should be pointed out that the sampling site is close to large-scale chemical enterprises such as steel industry, petrochemical companies and thermals power plant, which consume large quantities of coals as the fuel and release lots of flue gas to the atmosphere.

Nanjing is one of the central cities in Yangtze River Delta region in China, which is 6597 km^2 and resident population is > 8 millions. The climate is mainly subtropical monsoon with annual precipitation at 1106 mm and average air temperature at 15.4 °C. Recently, Nanjing has encountered a serious air pollution problem due to rapid development of industrialization process. Lu et al. (2015) found that the concentrations of PM_{10} and gaseous pollutants (SO_2, NO_2) increased in Nanjing region, thereby resulting in a high non-accidental mortality.

2.2. Atmospheric samples and flue gas collection

$PM_{2.5}$ and SO_2 in the atmosphere were collected by the sampler (TH-1000H) with a flow rate of 1.05m^3/min from 1 to 23 Jan. 2015. $PM_{2.5}$ and SO_2 were gathered using quartz filters (203 × 254 mm, Mubktell, Sweden) and glass fiber filters (203 × 254 mm, Tisch Environment INC., USA), respectively. Before sampling, quartz filters were incinerated in a muffle furnace at 450 °C for 4 h, and then placed in the desiccators for 24 h at 20 °C. The sampled filters were reserved in a refrigerator for further chemical analysis.

Three kinds of coals including bitumite and anthracite were obtained from thermal power factory and steel company. Proximate analysis and elemental analysis of different coals were conducted in China University of Mining and Technology (Xuzhou). In addition, coal combustion and flue gas sampling were carried out using self-regulating furnace and sampling system, which is described in Fig.2. Coal samples were placed on self-regulating electric furnace and the transformer was used to adjust input voltage to keep coal combustion at the condition of burning (with continuous open fire) or smoldering (without flame). Flue gas successively entered into the pipe and the sampler by elevating the lifting platform and initiating vacuum pump. Besides, cooling tank was installed in the pipe in order to control the temperature of flue gas to the sampler.

$PM_{2.5}$ and SO_2 in flue gas were simultaneously collected by a modified sampler (TH-1000H, Tianhong Wuhan). As depicted in Fig.2, the double sampling frames were installed in the sampler slot. The upper sampling frame was used to collect $PM_{2.5}PM_{2.5}$, while the lower sampling frame was applied to gather $SO_2PM_{2.5}$. $PM_{2.5}$ and SO_2 in flue gas were sampled with quartz filters and alkaline-soaked glass fiber filters, respectively. Furthermore, coal ash from different combustion conditions was synchronously gathered in foil for sulfur isotopic determination.

2.3. Sulfur extraction and sulfur isotopic analysis

$PM_{2.5}$ samples and coal ash were respectively dissolved by using Milli-Q water. Water soluble sulfate in the solution was precipitated as $BaSO_4$ by adding 1 mol/L $BaCl_2$. After the filtration with 0.22 μm acetate membrane, the precipitate was rinsed with Milli-Q water to remove Cl^-. Finally, $BaSO_4$ powder was calcined at 800°Cfor 2 h to obtain high purity $BaSO_4$. In addition, a small quantity of H_2O_2 was added to oxidize sulfite to sulfate and the extraction of sulfate from the solution referred to that in $PM_{2.5}$.

For sulfur extraction from coal, light magnesium and anhydrous Na_2CO_3 were firstly mixed with mass ratio of 2:1 to prepare aldrin. Then, 2 g aldrin was added to 1 g coal powder to obtain a uniform mixture. The mixture was covered with 1 g aldrin before transferring into 30 mL ceramic crucible. The crucible was introduced into muffle furnace and incinerated at 850 °C for 2 h. The incinerated mixture was then rinsed with 100 mL Milli-Q water. After the filtration, solution pH was adjusted at 1–2 with HCl to remove the influence of CO_3^{2-}. 3 mL 1 mol/L $BaCl_2$ was finally introduced to convert sulfate into $BaSO_4$ powder.

Sulfur isotopic composition was determined in State Key Laboratory of Biogeology and Environmental Geology in China University of Geosciences (Wuhan). Elemental analyzer (EA, Flash 2000, Thermo) and isotopic mass spectrometer (IRMS, Delta V Plus, Finningan) were used to analyze Δ^{34}*s. baso*$_4$ powder was converted into SO_2 in EA in the presence of Cu_2O. SO_2 from EA was ionized and $\delta^{34}S$ value was measured using IRMS. The results are with respect to international standard V-CDT and the precision is within ± 0.2‰.

In our study, coal analysis and the determination of $\delta^{34}S$ value for different samples were carried out in duplicate.

3. Results and discussion

3.1. Sulfur isotopic fractionation during coal combustion

3.1.1. Coal analysis

In order to accurately explore sulfur source and sulfur isotopic fractionation during the conversion of sulfur-containing compounds, we chose three coals used widely in Nanjing region as research objectives. We conducted coal analysis in China University of Mining and Technology (Xuzhou) to study chemical components and the properties of these coals. The corresponding results are shown in Table 1.

As shown in Table 1, the average moisture (M_{ad}) and standard deviation of coals A, B and C were 7.09 ± 0.05%, 1.41 ± 0.03% and 1.98 ± 0.03%, respectively, indicating the moisture of bitumite was much higher compared to those of anthracite. In general, the moisture content of coal decreased with the increasing coalification degree. The ash yield (A_d) of coal was the indicative of mineral substance content. It is observed that ash yield in coal A was lower than those in coals B and C. According to the volatiles (V_{daf}) of the three coals, we inferred that A was high-volatile coal while B and C were low-volatile coals. The fixed

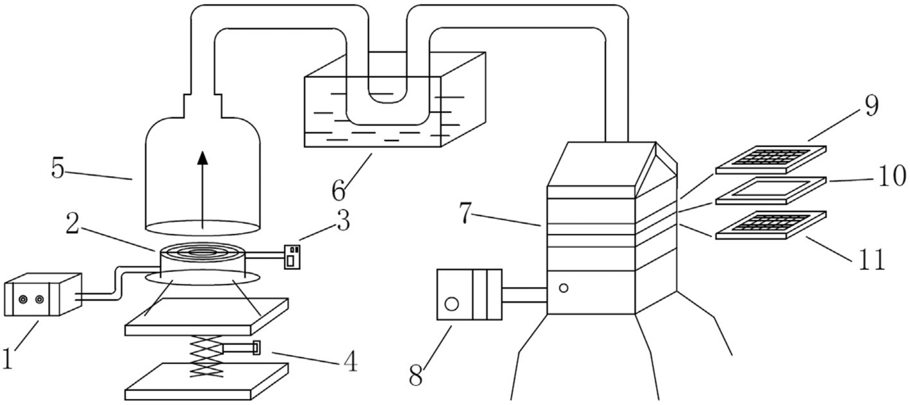

Fig. 2. Schematic diagram of coal combustion and flue gas sampling system. (1. Transformer; 2. Electrothermal furnace; 3. Thermocouple; 4. Lifting platform; 5. Collecting cover; 6. Cooling tank; 7. Large-flow sampler; 8. Vacuum pump; 9. $PM_{2.5}$ sampling plate; 10. Partition; 11. SO_2 sampling plate).

Table 1
Coal analysis of different coal samples.

Coal	Proximate analysis (%)				Elemental analysis (%)					Calorific
	M_{ad}	A_d	V_{daf}	FC_{daf}	C_{daf}	H_{daf}	O_{daf}	N_{daf}	$S_{t,d}$	$Q_{gr,v,ad}$
A	7.09 ± 0.05	3.85 ± 0.05	31.92 ± 0.12	68.08 ± 0.13	81.07 ± 0.07	4.83 ± 0.02	12.23 ± 0.06	1.19 ± 0.02	0.43 ± 0.03	28.71 ± 0.06
B	1.41 ± 0.03	10.76 ± 0.09	9.28 ± 0.03	90.72 ± 0.07	92.04 ± 0.12	3.56 ± 0.04	2.52 ± 0.03	1.43 ± 0.03	0.36 ± 0.02	29.54 ± 0.03
C	1.98 ± 0.03	10.57 ± 0.03	9.72 ± 0.02	90.28 ± 0.05	91.92 ± 0.09	3.47 ± 0.02	2.77 ± 0.04	1.34 ± 0.02	0.51 ± 0.02	30.72 ± 0.05

A belongs to bitumite; B and C belong to anthracite.

carbon (FC_{daf}) was pyrolysis product of coal, which was positive correlation with coalification degree. This can be used to illustrate higher FC_{daf} in B and C than that in A.

According to the results of elemental analysis, we found that the contents of different elements in coals basically followed a decreased order at C, H, O, N and S. Sulfur average content and standard deviation in coals A, B and C were 0.43 ± 0.03%, 0.36 ± 0.02% and 0.0.51 ± 0.02%, respectively. Therefore, these coals were typically low sulfur coals due to sulfur contents were lower than 1.0%. Similar to S, the contents of H and O in coal A were higher than those in coals B and C. On the contrary, the contents of C and N in coal A were lower compared to those in coals B and C.

3.1.2. Sulfur isotopic compositions of coals

For tracing sulfur source in the atmosphere and studying sulfur isotopic fractionation during coal combustion, we measured $\delta^{34}S$ values of raw coal, coal ash as well as $PM_{2.5}$ and SO_2 in flue gas from the combustion under coal burning and smoldering. The results are summarized in Table 2. It is observed from Table 2 that $\delta^{34}S$ average values and standard deviation of raw coals A, B and C were 3.91 ± 0.05‰, 7.51 ± 0.11‰ and 3.65 ± 0.04‰, respectively. The three coals presented moderately positive sulfur isotopic signatures. Generally, pyrite and organic sulfur were the most abundant chemical forms of sulfur in coals. Low sulfur coals used in this study mainly contained non-hydrolysable organic sulfur of original plants and freshwater sulfate (Xiao and Liu, 2011). Due to the assimilation of sulfur by plants only involved a minor change in $\delta^{34}S$ relative to the sulfate in environmental water (Krouse, 1988), sulfur isotopic signature of organic sulfur would be isotopically equivalent to the sulfate. Chou (1997) inferred $\delta^{34}S$ values of the plants would range from 2 to 8‰ if freshwater sulfur available was the principal sulfur source in low sulfur coals. The $\delta^{34}S$ values are in accordance with our results.

In addition, it can be found that there existed a slight discrepancy of $\delta^{34}S$ values in different coals. Compared to bitumite A, 3.60‰ higher $\delta^{34}S$ value of anthracite B and 0.26‰ lower $\delta^{34}S$ value of anthracite C were observed. This was possibly related to coalification degree during coal formation. Coalification processes might result in a sulfur isotopic effect with a positive or negative fractionation factor. Compared to coal B, there were presence of higher coalification degree for coals A and C, which could be described by using the moisture contents of different coals. The relatively lower $\delta^{34}S$ values of coals A and C indicated a certain depletion of $\delta^{34}S$ during coalification process, which might be attributed to bacterial reduction of dissolved sulfate (Dai et al., 2002).

Table 2
$\delta^{34}S$ values of raw coal, coal ash as well as $PM_{2.5}$ and SO_2 in flue gas under burning and smoldering.

	Combustion conditions	A (‰)	B (‰)	C (‰)
Raw coal		3.91 ± 0.05	7.51 ± 0.11	3.65 ± 0.04
Coal ash	burning	3.21 ± 0.04	6.61 ± 0.03	2.89 ± 0.03
	smoldering	3.40 ± 0.08	6.79 ± 0.07	2.95 ± 0.04
Flue gas-$PM_{2.5}$	burning	7.53 ± 0.05	8.74 ± 0.10	6.45 ± 0.07
	smoldering	6.63 ± 0.09	8.29 ± 0.13	6.15 ± 0.05
Flue gas-SO_2	burning	− 2.88 ± 0.03	2.60 ± 0.08	− 2.42 ± 0.04
	smoldering	− 1.21 ± 0.02	3.83 ± 0.09	− 1.08 ± 0.06

The temperature is an important influence factor during the process of coal formation. The products holding typical bitumite and anthracite properties are acquired at 345 °C and 550 °C, respectively. Jugo et al. (2005) found that sulfur isotope might be $\delta^{34}S$ enrichment or depletion at high temperature. Therefore, we inferred that the discrepancy of $\delta^{34}S$ values in different coals was related to the temperature during coal formation. Besides, it is noted from Table 2 that there existed a negative relationship between $\delta^{34}S$ value of coal and total sulfur content. $\delta^{34}S$ value increased with the decreasing total sulfur content in these three coals. Under the condition of low sulfate concentration, organic matter and Fe^{2+} could incorporate H_2S enriched in ^{34}S content, thereby forming organic sulfur and pyrite with high $\delta^{34}S$ values in coals Lei and Ren (1993).

3.1.3. Sulfur isotopic fractionation during coal combustion

It is known that coal combustion can produce a large amount of coal ash and flue gas including particulate matter and SO_2, which may make an important contribution on atmospheric pollution. Therefore, we studied sulfur isotopic composition and the fractionation effect during coal combustion, which are shown in Table 2. Under the condition of coal burning, $\delta^{34}S$ average value and standard deviation of sulfate in coal ash A, B and C were 3.21 ± 0.04‰, 6.61 ± 0.03‰ and 2.89 ± 0.03‰, respectively, which were 0.70‰, 0.90‰ and 0.76‰ lower than those in the corresponding raw coals, indicating there existed a negative deviation of sulfur isotopic composition during coal burning to form coal ash. Sulfur was in present in coal mainly in the forms of pyrite and organic sulfur. $\delta^{34}S$ value of pyrite is much lower than that of organic sulfur in coal due to the earlier formation of pyrite. Consequently, the lighter $\delta^{34}S$ values in coal ash compared to those in raw coals possibly indicated that sulfate in coal ash was mainly from the oxidation of pyrite. In addition, we found that $\delta^{34}S$ average value and standard deviation of sulfate in coal ash A, B and C were 3.40 ± 0.08‰, 6.79 ± 0.07‰ and 2.95 ± 0.04‰ under the condition of coal smoldering, indicating that $\delta^{34}S$ values of sulfate in the ash under coal burning were slightly lower compared to those under coal smoldering. This was chiefly attributed to the influence of the temperature during coal combustion. High temperature was favorable for enriching light sulfur isotope in sulfate of coal ash. Zhang et al. (1995) studied sulfur isotopic compositions in the process of coal combustion and also found there existed a difference of 0.90‰ in $\delta^{34}S$ value between raw coal and coal ash. However, Malgorzata et al. (2007) determined the equivalent $\delta^{34}S$ values of 10.95‰ and 10.92‰ in raw coal and coal ash from Poland Truro power plant. Besides, there was presence of a positive correlation between calorific values of raw coals and the difference of $\delta^{34}S$ values in the ash from coal burning and smoldering, indicating coal property might exert a certain effect on sulfur isotopic fractionation during coal combustion.

Flue gas from coal combustion is usually emitted into the atmosphere, which inevitably facilitates atmospheric pollution. In order to clarify sulfur isotopic fractionation during coal combustion under different conditions, we further measured $\delta^{34}S$ values of $PM_{2.5}$ and SO_2 in flue gas under coal burning and smoldering, and the results are described in Table 2 and Fig. 3. Under the condition of coal burning,

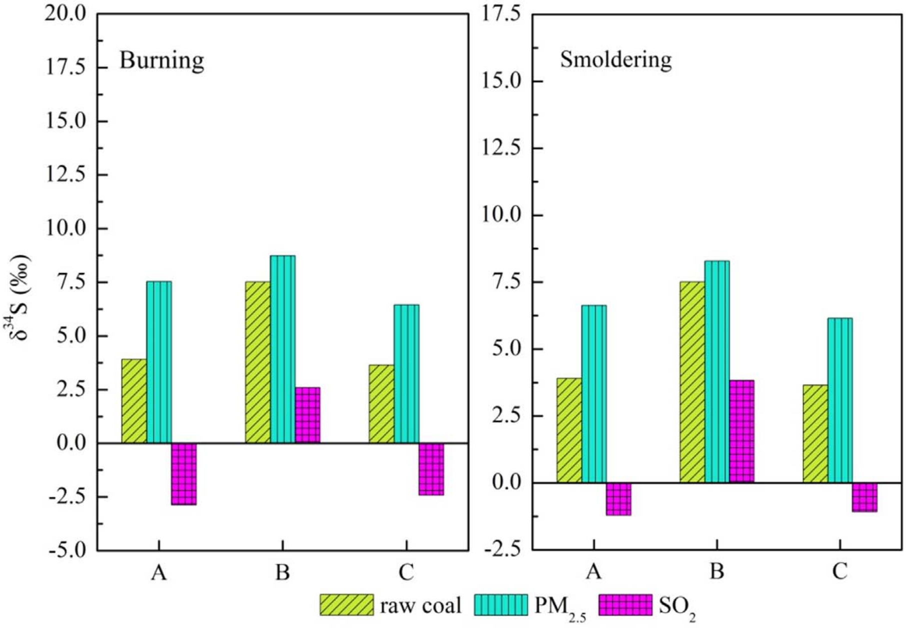

Fig. 3. $\delta^{34}S$ values of $PM_{2.5}$ and SO_2 in flue gas from the combustion under coal burning and smoldering.

$\delta^{34}S$ average value and standard deviation of $PM_{2.5}$ and SO_2 in flue gas were 7.53 ± 0.05‰ and − 2.88 ± 0.03‰ from coal A, 8.74 ± 0.10‰ and 2.60 ± 0.08‰ from coal B as well as 6.45 ± 0.07‰ and − 2.42 ± 0.04‰ from coal C. Compared to those in raw coals, $\delta^{34}S$ values of $PM_{2.5}$ in flue gas increased, while $\delta^{34}S$ values of SO_2 in flue gas decreased (Fig. 3). Specifically, 3.62‰, 1.23‰ and 2.80‰ higher $\delta^{34}S$ values were obtained in $PM_{2.5}$ and 6.79‰, 4.91‰ and 6.07‰ lower $\delta^{34}S$ values were acquired in SO_2 in flue gas from the burning of coals A, B and C, respectively, which suggested that there existed a significant sulfur isotopic fractionation effect during coal burning. Zhang et al. (1995) determined sulfur isotopic composition of $PM_{2.5}$ and SO_2 in flue gas in Guangzhou region with $\delta^{34}S$ values at 11.3‰ and 5.2‰, respectively. The enrichment of ^{34}S in $PM_{2.5}$ and the depletion of ^{34}S in SO_2 were in accordance with our results.

Similarly, under the condition of smoldering, $\delta^{34}S$ average value and standard deviation of $PM_{2.5}$ and SO_2 in flue gas were 6.63 ± 0.09‰ and − 1.21 ± 0.02‰, 8.29 ± 0.13‰ and 3.83 ± 0.09‰, 6.15 ± 0.05‰ and − 1.08 ± 0.06‰ from coals A, B and C, respectively. In comparison to $\delta^{34}S$ values in raw coals, we found 2.72‰, 0.78‰ and 2.50‰ higher $\delta^{34}S$ values in $PM_{2.5}$ and 5.12‰, 3.68‰ and 4.73‰ lower $\delta^{34}S$ values in SO_2 in flue gas from the smoldering of coals A, B and C, respectively. It is noted that the change of sulfur isotopic compositions under coal smoldering was in agreement with that under coal burning. However, the positive deviation of $\delta^{34}S$ values in $PM_{2.5}$ and the negative deviation of $\delta^{34}S$ values in SO_2 under coal smoldering were less than those under coal burning, further illustrating that the temperature had an obvious effect on sulfur isotopic fractionation during coal combustion to produce $PM_{2.5}$ and SO_2 in flue gas. It is known that sulfur atoms with different qualities possessed a different reaction speed. High temperature under coal burning was favorable for sulfur oxidation, thereby facilitating sulfur isotopic fractionation.

In addition, sulfur isotopic fractionation during coal combustion was also affected by $\delta^{34}S$ values of raw coals. As shown in Table 2, the different $\delta^{34}S$ values of three kinds of raw coals were mainly ascribed to coal-forming environment and biochemical processes. Zhang et al. (2002) studied $\delta^{34}S$ values of raw coals and their combustion products in different regions and found there existed a different sulfur isotopic fractionation effect during coal combustion. In summary, coal properties and combustion condition might lead to the difference of sulfur isotopic fractionation. Therefore, it is necessary to synchronously measure $\delta^{34}S$ values of raw coals used locally as well as sulfur isotopic fractionation in the process of releasing particulate matter and SO_2 to the atmosphere in order to accurately explore sulfur source and the transformation pathway using sulfur isotope.

3.2. Pollution characteristics and $\delta^{34}S$ values in the atmosphere

3.2.1. $PM_{2.5}$, SO_4^{2-} and SO_2 concentrations in the atmosphere

As depicted in Fig.4, the concentrations of $PM_{2.5}$, SO_4^{2-} and SO_2 during the period from 1 to 23 Jan. 2014 in Nanjing region changed from 51.1 to 297.2 μg/m³, 22.5 to 92.1 μg/m³ and 42.2 to 78.5 μg/m³ with an average and standard deviation at 144.3 ± 74.2, 48.65 ± 13.2 and 55.5 ± 11.7 μg/m³, respectively. $PM_{2.5}$ concentration was 1.9 times of the Second Grade National Standard of China (75 μg/m³) and 4.1 times of the First Grade National Standard (35 μg/m³). Besides, it can be observed that $PM_{2.5}$ concentration was higher than those in Hong Kong (55.50 μg/m³, Cheng et al., 2015), Guangzhou

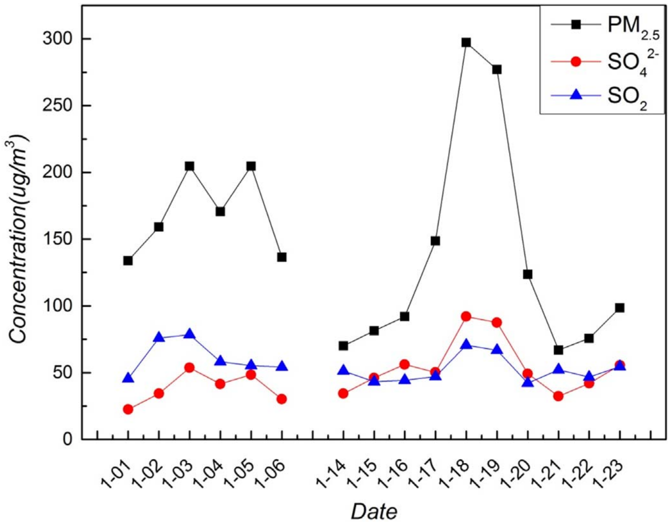

Fig. 4. Temporal variation of $PM_{2.5}$, SO_4^{2-} and SO_2 concentrations during the haze.

(76.80 μg/m^3, Tao et al., 2014), Beijing (115.80 μg/m^3, Hu et al., 2014) and Xi'an (142.60 μg/m^3, Wang et al., 2015), indicating $PM_{2.5}$ pollution was rather serious in Nanjing region during the observation period.

Meanwhile, it is found that the concentrations of $PM_{2.5}$, SO_4^{2-} and SO_2 markedly fluctuated during the whole sampling period. At the early period, $PM_{2.5}$, SO_4^{2-} and SO_2 concentrations remained at the relatively high level. The concentrations of SO_2 were higher compared to those of SO_4^{2-} indicating sulfur source in the atmosphere was mainly from local emission. On 18 Jan., $PM_{2.5}$, SO_4^{2-} and SO_2 concentrations increased to the maximum. Different from the other days, the dominant wind was from north direction on 18 and 19 Jan. The prompt aggravation of $PM_{2.5}$ concentration was mainly due to long-distance transport of air mass from Northern China, where released a great quantity of particulate matter and exhaust gas during coal combustion for central heating. In addition, the concentrations of SO_4^{2-} were found to be much higher than those of SO_2 on 18 and 19 Jan., suggesting that a large portion of SO_4^{2-} in $PM_{2.5}$ was ascribed to the input of the secondary sulfate from Northern China. On 14 and 21 Jan., low $PM_{2.5}$ concentrations were chiefly attributed to the rapid diffusion of the pollutants for the sunny and windy weather during these two days.

3.2.2. $\delta^{34}S$ values of $PM_{2.5}$ and SO_2 in the atmosphere and sulfur source appointment

The regional characteristics of $\delta^{34}S$ value made it meaningful to identify sulfur source in the atmosphere (Han et al., 2016). $\delta^{34}S$ values of $PM_{2.5}$ and SO_2 in the atmosphere during the observation period are shown in Fig.5. It is found that $\delta^{34}S$ values of sulfate in $PM_{2.5}$ ranged from 2.7 to 6.4‰ with an average and standard deviation at 5.1 ± 0.9‰. $\delta^{34}S$ values of SO_2 varied from −1.8 to 4.1‰ with an average and standard deviation at 1.5 ± 1.6‰. It is noteworthy that $\delta^{34}S$ values of sulfate in $PM_{2.5}$ were much higher compared to those of SO_2 during the whole observation period. In the previous study, Guo et al. (2016a, 2016b) found the average $\delta^{34}S$ value of $PM_{2.5}$ in Nanjing around the YOG was 4.15‰. The discrepancy in $\delta^{34}S$ values of $PM_{2.5}$ in winter and summer indicated that there existed different sulfur sources and/or various contribution of sulfur sources to the secondary sulfate. In this study, $\delta^{34}S$ values of sulfate in $PM_{2.5}$ were located at a narrow range, suggesting a relatively stable and simple sulfur source during the sampling period.

It should be pointed out that there was presence of a distinct discrepancy in $\delta^{34}S$ values for the same sulfur source in different regions (Proemse et al., 2012). Especially, there were various types of coals in China. As a result, this inevitably resulted in the uncertainties for source appointment if we did not synchronously determine $\delta^{34}S$ values of locally potential sulfur sources. Therefore, we measured $\delta^{34}S$ values of raw coals widely used in Nanjing region, and the corresponding $\delta^{34}S$ average value and standard deviation were 3.91 ± 0.05‰, 7.51 ± 0.11‰ and 3.65 ± 0.04‰, respectively. It is reported that $\delta^{34}S$ values of coal used in northern China were 4–5‰ (Mukai et al., 2001). $\delta^{34}S$ values of sulfate in $PM_{2.5}$ during the sampling period were basically consistent with those of raw coals. Besides, $\delta^{34}S$ values of SO_2 in the atmosphere (−1.8–4.1‰) were equivalent to those of SO_2 from the combustion of local coals, indicating coal combustion was an important sulfur source for $PM_{2.5}$.

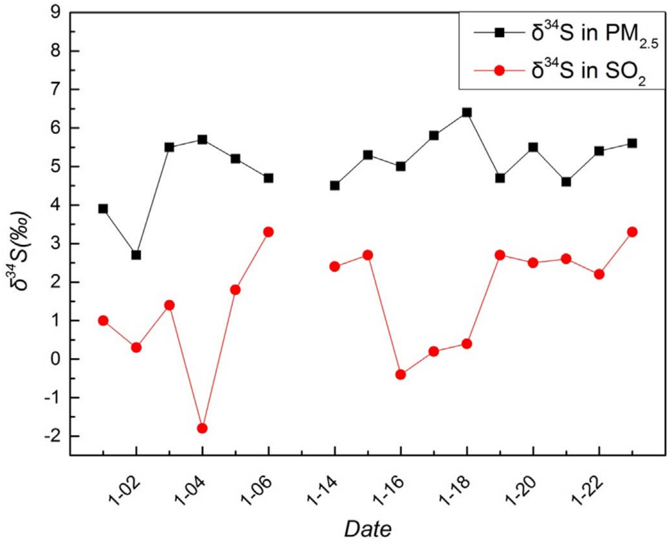

Fig. 5. $\delta^{34}S$ values of $PM_{2.5}$ and SO_2 in the atmosphere during the observation period.

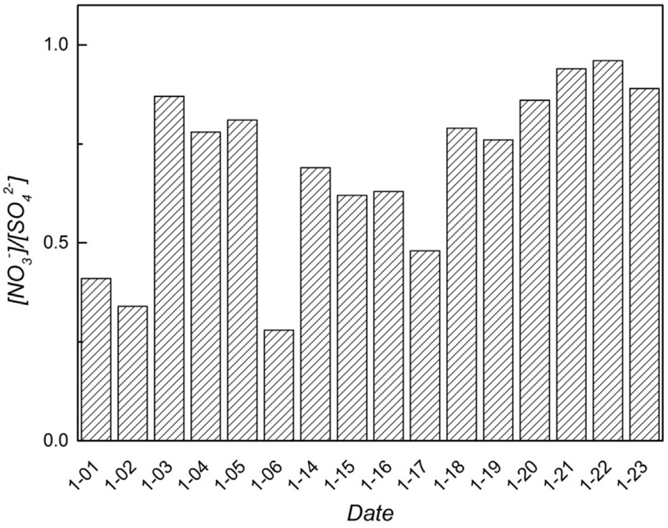

Fig. 6. $[NO_3^-]/[SO_4^{2-}]$ ratios in $PM_{2.5}$ during the observation period.

$[NO_3^-]/[SO_4^{2-}]$ ratio has been used as an indicator to evaluate the importance of stationary sources and mobile sources (Xiao and Liu, 2004). Low $[NO_3^-]/[SO_4^{2-}]$ ratio (< 1) shows the predominance of stationary source over mobile source in participate matter (Arimoto et al., 1996). As described in Fig. 6, $[NO_3^-]/[SO_4^{2-}]$ values of $PM_{2.5}$ during the sampling period ranged from 0.28 to 0.96 with an average and standard deviation at 0.69 ± 0.17. The relatively low $[NO_3^-]/[SO_4^{2-}]$ ratio was mainly ascribed to the consumption of large quantity of coal for central heating and industrial production.

3.2.3. Sulfur isotopic fractionation during SO_2 oxidation

SO_2 can be converted into sulfate by homogeneous and heterogeneous oxidation reactions in the atmosphere. These processes may cause sulfur isotopic fractionation, which is described by fractionation coefficient (α) (Seal, 2006).

$$\alpha = \frac{\frac{\delta^{34}S_{SO_4^{2-}}}{10^3} + 1}{\frac{\delta^{34}S_{SO_2}}{10^3} + 1} \qquad (1)$$

where α is fractionation coefficient, $\delta^{34}S_{SO_4^{2-}}$ and $\delta^{34}S_{SO_2}$ are $\delta^{34}S$ values of sulfate in $PM_{2.5}$ and SO_2, respectively.

Generally, α value is higher than 1 during SO_2 heterogeneous oxidation due to the presence of isotopic equilibrium fractionation and kinetic fractionation. However, α value is lower than 1 during SO_2 homogeneous oxidation for there only exists isotopic kinetic fractionation. At 25 °C, α values of sulfur isotopic equilibrium fractionation and kinetic fractionation were 1.0165 and 0.996, respectively (Eriksen, 1972). As depicted in Fig.7, α values ranged from 1.0014 to 1.0075 with an average and standard deviation at 1.0035 ± 0.0012 in the process of SO_2 oxidation to sulfate during the observation period. It can be observed that α values were absolutely within the scope between

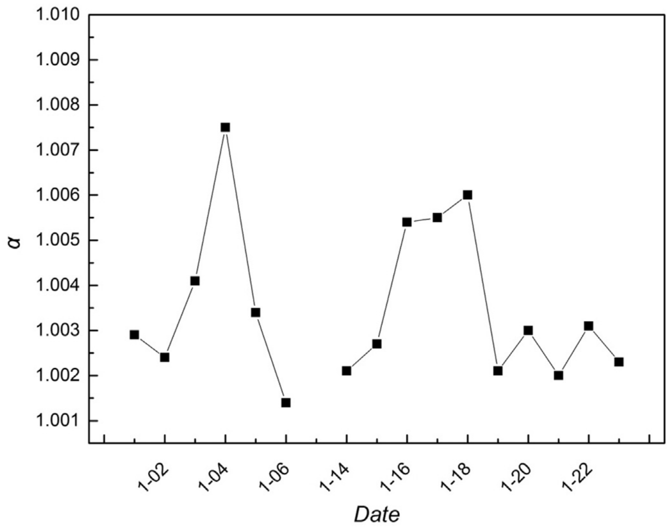

Fig. 7. α values of SO_2 oxidation to sulfate during the observation period.

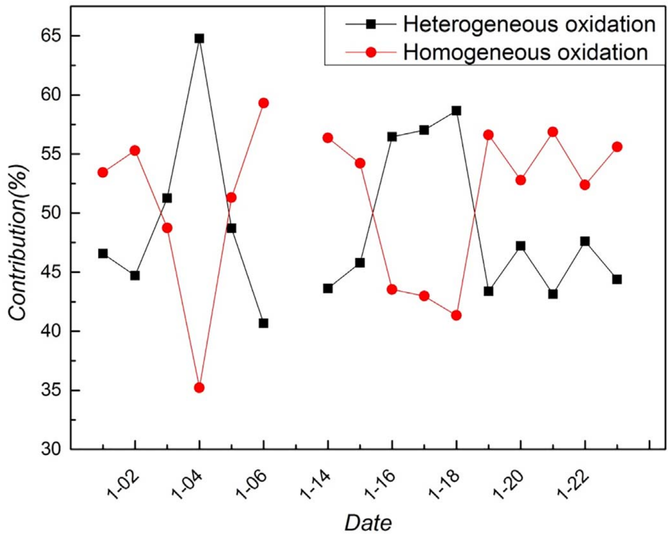

Fig. 8. The contributions of SO_2 heterogeneous and homogeneous oxidation to sulfate.

equilibrium fractionation and kinetic fractionation coefficient, implying that SO_2 heterogeneous and homogeneous oxidation were coexisting during the formation of the secondary sulfate. It is reported that sulfur isotopic fractionation about SO_2 was − 9‰ for homogeneous oxidation (Tanaka et al., 1994) and + 16.5‰ for heterogeneous oxidation (Eriksen, 1972). According to sulfur isotope mass equilibrium during SO_2 oxidation processes (Seal, 2006), we can calculate the contribution of SO_2 heterogeneous and homogeneous oxidation to the secondary sulfate, which is described in Fig.8. It is found that the contribution of SO_2 heterogeneous oxidation ranged from 40.7% to 64.8% with an average and standard deviation at 49.0 ± 6.8%, indicating that average ratio of SO_2 heterogeneous was basically equivalent to that of homogeneous oxidation during the observation period. The high contributions of SO_2 heterogeneous oxidation to the secondary sulfate on 4 Jan. and during 16 to 18 Jan. were chiefly attributed to high relative humidity of the atmosphere, which was favorable for SO_2 dissolution and further oxidized by the oxidants such as H_2O_2, O_3, O_2 and NO_2 in the atmosphere (Hung and Hung and Hoffmann, 2015).

In addition, we noted from Fig.7 that α values scattered in a wide range during the whole observation period, indicating sulfate formation via SO_2 oxidation was relatively complicated. Generally, SO_2 oxidation reactions mainly include OH radical oxidation, aqueous oxidation by H_2O_2 and O_3 and radical chain reactions initiated by transition metal ion. Sulfur isotope fractionation factors are usually different during these SO_2 oxidation processes. For instance, Oxidation by H_2O_2 and O_3 produced sulfate that was enriched in ^{34}S relative to the reactant SO_2, whereas SO_2 oxidation by transition metal ion produced sulfate depleted in ^{34}S (Harris et al., 2013; Harris et al., 2012a). Besides, SO_2 oxidation on clay minerals possessed a distinct fractionation factor of 1.085 ± 0.013 (Harris et al., 2012b). Therefore, α values can be used to evaluate the relative importance of different oxidation pathways. The largest α value of 1.0075 on 4 Jan. was mainly ascribed to SO_2 heterogeneous oxidation by H_2O_2 and O_3 due to high relative humility of 70% in the atmosphere, which was favorable for SO_2 diffusion into water drop. However, we found high $PM_{2.5}$ concentration and low α value on 19 Jan., which indicated that there might be presence of other oxidation pathways such as SO_2 oxidation catalyzed by transition metal ions.

4. Conclusions

Coal combustion was an important sulfur source for $PM_{2.5}$. $\delta^{34}S$ values of SO_2 were much lower compared to those of sulfate in $PM_{2.5}$ during the whole observation period. The average sulfur isotopic fractionation factor of 1.0035 in the process of SO_2 oxidation showed the average contribution of 49.0% for SO_2 heterogeneous oxidation to the secondary sulfate. $\delta^{34}S$ average values of locally used coals were 3.91‰, 7.51‰ and 3.65‰, respectively. The discrepancy of $\delta^{34}S$ values in different coals was related to coalification degree and the temperature during coal formation processes. Compared to those in raw coals, sulfate of $PM_{2.5}$ in flue gas enriched ^{34}S, while SO_2 in flue gas enriched ^{32}S regardless of coal burning or smoldering. Generally, the temperature and coal property could affect sulfur isotopic fractionation during coal combustion.

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