

Sulfur isotopic composition and source identification of atmospheric environment in central Zhejiang, China

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Sulfur dioxide and sulfate aerosols in the atmosphere are significant factors leading to acidification of the atmospheric environment and worsening the pollution of acid deposition. Because of the “fingerprint” characteristics of the stable sulfur isotopic composition, sulfur isotope has been widely adopted in environmental researches concerning sulfur cycle and source identification. In this study, the atmospheric environment of Jinhua City, central Zhejiang Province, was continuously monitored, and the sulfur isotopic composition of SO₂ and sulfate aerosols in the atmosphere was analyzed. The results indicate that the variation of $\delta^{34}\text{S}$ values for SO₂ ranges from 1.0‰ to 7.5‰, and annual average is $4.7\text{‰}\pm 2.3\text{‰}$, whereas that of sulfate aerosols ranges from 6.4‰ to 9.8‰, and annual average is $8.1\text{‰}\pm 1.0\text{‰}$. The $\delta^{34}\text{S}$ values for SO₂ have significant seasonal variations, which are 7.0‰ in winter and 3.3‰ in summer. These variations cannot be attributed to a single factor, and we suggest a temperature-dependent isotope equilibrium fractionation and elevated biogenic sulfur emissions of isotopically light S in summer may be the main controlling mechanisms. Furthermore, we also discuss the $\delta^{34}\text{S}$ model of atmospheric SO₂ oxidation to form sulfate, and suggest that heterogeneous oxidation dominates in the oxidation reactions of atmospheric SO₂ in the central Zhejiang Province. We further suggest that the relative humidity in the atmosphere plays an important role in the oxidation mechanism of atmospheric SO₂.

sulfur isotope, SO₂ aerosol, homogeneous oxidation, heterogeneous oxidation

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Atmospheric sulfur is the main air pollutant that causes acid rain, and originates from the release of natural sources and anthropogenic emissions. SO₂ is the major sulfide in anthropogenic emissions, and also the main precursors of acidification in the atmosphere. Due to their relatively active chemical property, those sulfides at low oxidation state (atmospheric SO₂, etc.) are readily oxidized to form sulfate by either homogeneous oxidation in gas phase or heterogeneous oxidation in liquid phase [1, 2]. Sulfate is one of the main aerosol particles in the atmosphere, a major compo-

nent of cloud condensation nuclei in the atmosphere, and a major contributor to acid rain [3, 4]. Sulfate plays an important role in the chemistry of troposphere and lower stratosphere. It can precipitate onto existing particle surfaces or can become aerosol particles through gas particle conversion in the atmosphere [5, 6]. Sulfate aerosols in troposphere can bring acid rain pollution, then affect global climate by the direct and indirect radiative forcing. In addition, they also harm human health by causing respiratory system disease [7–10]. Therefore, the source identification of atmospheric sulfur and its migration and transformation between source and sink are of great significance both in

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quantitatively evaluating the physical and chemical effects of sulfate aerosols at a regional scale, and further studying how atmospheric SO₂ and sulfate aerosols influence the global environment.

Sampling locations are in Jinhua City, which lies in upstream region of Qiantang River in central Zhejiang Province and at the eastern edge of Jinhua-Quzhou Basin. Geographically, this region is characterized by hilly region and basins, high in the north and south, low in the middle region; the climate is of subtropical monsoon, which has discernible seasonal variations and humid and rainy days. In this paper, we monitored the air pollution status in real-time from year 2004 to 2005 in urban areas of the city, and also determined the sulfur isotope composition of atmospheric SO₂ and sulfate aerosols. The objective of the present study was to understand the sulfur isotope compositions and variations of atmospheric SO₂ and sulfate aerosols, to explore the oxidation pathways of sulfur dioxide to form sulfate in the atmosphere, and to identify ultimately various anthropogenic and natural sources of atmospheric sulfur.

1 Experiments

1.1 Sampling and treatment

Sulfate aerosols and atmospheric SO₂ were collected with a total suspended particles collector on an ultra-fine quartz fiber filter (K-49, 20 cm×25 cm) and an alkali-impregnated filter, respectively. The impregnated filters were prepared with quartz fiber filters dipped in 2% K₂CO₃ and 2% glycerol solution, followed by drying at 50°C. The quartz filters collecting sulfate aerosols were dried at 90°C for 6 hours in the oven, and dipped in re-distilled water, followed by drying at 50°C, then immersed into phosphoric acid solution for 30 minutes. Finally, they were washed repeatedly with deionized water till they were neutral. The filters were installed on a double layer frame when sampling, the upper one to collect aerosols and the lower for atmospheric SO₂. One sample was usually collected for 24 hours with a flow rate of 100 L/min [11].

The aerosols samples collected were treated in following steps to extract sulfate. First, took one fourth of the filter and cutting it into pieces in a 50 mL baker, then added 20 mL deionized water into it and stirred evenly; and then the extracted solution was filtrated through a 0.45 μm organic millipore filter. After that, the sulfate in the sample was precipitated as BaSO₄ by adding 1 mL of 2 mol/L BaCl₂ solution. The precipitation of BaSO₄ was separated in a centrifuge. After rinsing with deionized water several times, we finally got pure BaSO₄, followed by drying at 50°C. Sulfur dioxide trapped in the alkaline filter was extracted in a similar manner except for adding H₂O₂ to oxidize sulfite to sulfate at first. Other steps were nearly the same as in the process extracting sulfate from aerosol samples [12].

1.2 Analysis and test

Sulfur isotope analysis was carried out at State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, using IsoPrime continuous flow mass spectrometer. The standard samples adopted were VCDT of IAEA-S-1 (Ag₂S, -0.30‰), NBS-127 (barite, 20.3‰), and GBW04415 (Ag₂S, 22.15‰). The analytical results are expressed in the usual δ³⁴S notation, in per mil, relative to Canyon Diablo Troilite (CDT) standard. The standard deviation of the isotopic measurements is ±0.2‰ (*n* = 10).

2 Results and discussion

2.1 Concentrations of atmospheric SO₂ and NO₂

The statistical analysis was based on the monitoring data of atmospheric SO₂ and NO₂ obtained by automatic air quality monitoring system in Jinhua City during 2004–2005. The results show that daily average concentration of SO₂ in the atmosphere ranges from 0.004 to 0.204 mg/m³, and annual average values for the two year are 0.044 and 0.048 mg/m³, respectively, whereas daily average concentration of NO₂ ranges from 0.010 to 0.135 mg/m³, and annual average values are 0.057 and 0.053 mg/m³, respectively.

The following data in Figure 1 shows the temporal variations of atmospheric concentration of SO₂ and NO₂ from 2004 to 2005, when both pollutants have obviously seasonal variations. Concentrations of SO₂ are higher in winter and spring, and lower in summer and autumn. The highest concentrations occur in December, whereas the lowest in June and July. By contrast, seasonal variations of NO₂ concentrations are not so significant; the concentration increases step by step beginning in October and maintains at this relatively high level until the end of the following April, and then begins to decrease in May. It reaches its lowest value at the end of June and the beginning of August. The concentrations of atmospheric NO₂ show an obvious temporal variation order.

2.2 Compositions of sulfur isotope for atmospheric SO₂ and aerosols

The measurements of sulfur isotope of atmospheric SO₂ and aerosols were carried out in the study areas during 2005. Atmospheric SO₂ and aerosol samples were collected respectively in the middle of each month. Then the sulfur isotopic compositions were measured after the pretreatment to extract sulfate from samples; those analytical results were listed in Table 1.

Analytical results in Table 1 indicate that the δ³⁴S values of atmospheric SO₂ in central Zhejiang Province range from 1.0‰ to 7.5‰, with annual average at 4.7‰±2.3‰, whereas the δ³⁴S values of aerosols range from 6.4‰ to

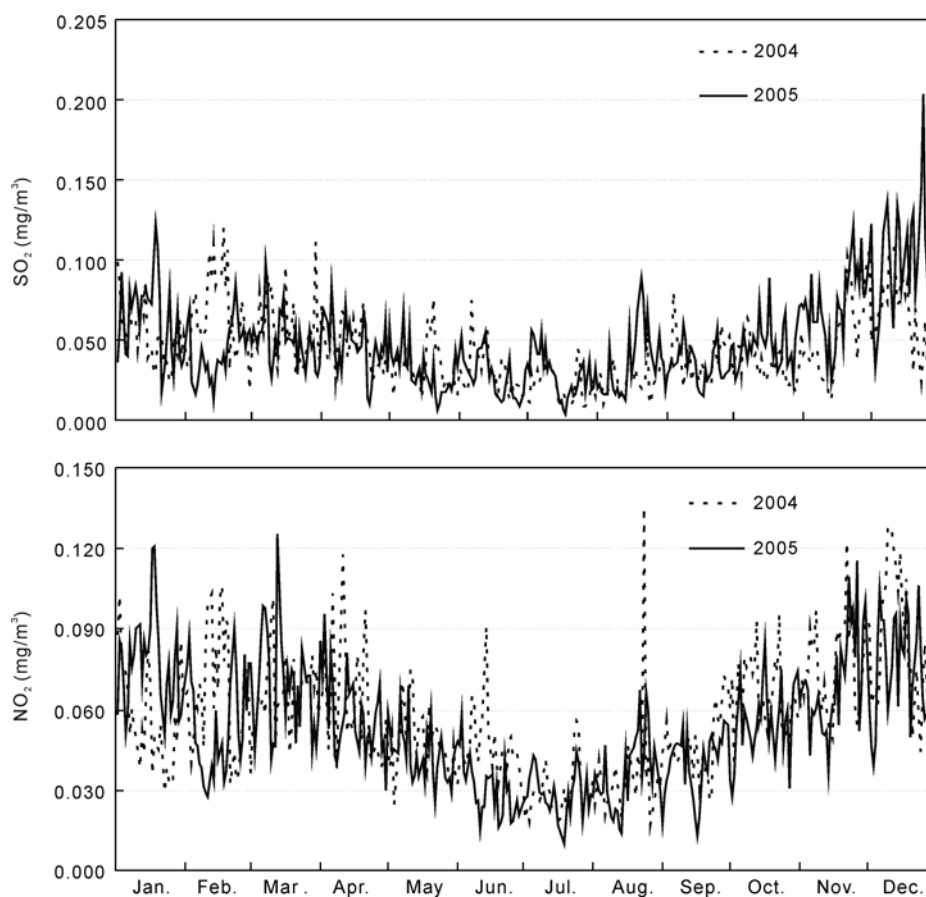


Figure 1 Temporal variation of concentrations of atmospheric SO₂ and NO₂ during 2004–2005.

Table 1 The sulfur isotopic compositions of atmospheric SO₂ and aerosols ($\delta^{34}\text{S}$) in 2005

Month	Atmospheric SO ₂ (‰)	Aerosol (‰)
January	7.5	8.8
February	7.3	7.5
March	6.0	7.5
April	7.5	8.9
May	1.0	9.8
June	3.7	8.3
July	1.5	6.8
August	4.6	8.1
September	2.8	9.0
October	5.1	8.3
November	3.7	6.4
December	6.2	7.6

9.8‰, with annual average at $8.1\text{‰} \pm 1.0\text{‰}$. As a whole, the $\delta^{34}\text{S}$ values of aerosols are higher than those of atmospheric SO₂ without exception; the difference in annual average values between atmospheric SO₂ and aerosols is 3.4‰, consistent with the results observed previously both at home and abroad [12–17]. The results are also in accordance with the regular pattern of fractionation of sulfur isotopes during the coal-burning process, i.e., the released atmospheric SO₂ is always enriched in lighter sulfur isotope relative to the

corresponding coal, whereas those particles are always enriched in heavier sulfur isotope [18, 19]. In terms of the temporal variations, the $\delta^{34}\text{S}$ values of atmospheric SO₂ show an obvious seasonal variation, in which the highest values occur from winter to April in spring, and the lowest values at the end of the spring to summer. The $\delta^{34}\text{S}$ values are slightly higher in autumn than in summer (Figure 2). The $\delta^{34}\text{S}$ values of precipitation in the study area vary from 0.5‰ to 14.2‰, averaging 5.0‰, and exhibit a seasonality, i.e., higher in winter and lower in summer [11]. The seasonal variation characteristics of sulfur isotopic compositions of precipitation are consistent with that of atmospheric SO₂. On the other hand, average annual $\delta^{34}\text{S}$ value of atmospheric SO₂ is closer to that of precipitation than aerosols. These results indicate that the influences of atmospheric SO₂ on the sulfur isotopic compositions are more obvious in precipitation. In other words, atmospheric SO₂ contributes greater than aerosols do in the sulfur isotope compositions of precipitation. The $\delta^{34}\text{S}$ values of aerosols vary slightly throughout the year, nearly fluctuating around the annual average value. They are relatively higher in spring and almost exactly the same in other three seasons (Figure 2).

Some researches on the sulfur isotopic compositions of

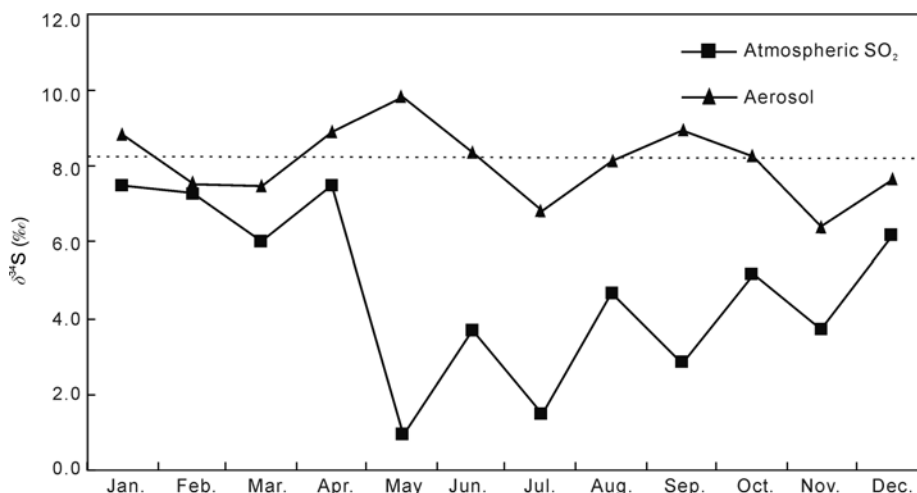


Figure 2 Temporal variations of $\delta^{34}\text{S}$ values of atmospheric SO₂ and aerosols in 2005.

atmospheric SO₂ aerosols have been carried out in China [16, 17, 20, 21]¹⁾. These studies focus on sulfur isotope of atmospheric SO₂ and aerosols in Guiyang and some regions in South China. Figure 3 shows the variation ranges of the isotopic compositions of atmospheric SO₂ and aerosols in different areas. The results in central Zhejiang Province are obviously different from those of Guiyang and the corridor regions between Hunan and Guangxi, and there are still some differences when compared with those of regions of Pearl River Delta and Hengyang in South China. The phenomenon of regional distribution is probably due to the different sources of fossil fuels used in these regions, which may be also the main factors leading to the different distribution of sulfur isotopic compositions of atmospheric SO₂ and aerosols at a regional scale. The sulfur isotopic compositions of fossil fuels from different regions vary significantly because of their different geological backgrounds. Coals consumed in central Zhejiang Province are mainly from North China, which varies greatly in sulfur isotopic compositions when compared with those of Guiyang and the corridor regions between Hunan and Guangxi. The sulfur isotopic compositions of coal in different regions of China are listed in Figure 4. As can be seen from the chart, sulfur isotopic compositions of coal vary greatly due to their different habitats. The regional distribution of sulfur isotope compositions of coal consequently leads to the difference of sulfur isotopic compositions of combustion products such as SO₂ and particles [18]. The similar significant regional distribution of sulfur isotope and lead isotope was also observed in a joint Sino-Japan research carried out in cities including Guiyang, Beijing, Dalian, Changchun, Harbin, Shanghai, Nanjing, and Waliguan in China, and Tsukuba in Japan. The $\delta^{34}\text{S}$ value of atmospheric SO₂ is about 5‰ in northern cities such as Dalian, Changchun, and Harbin, whereas Guiyang, a southwestern city in China, had around

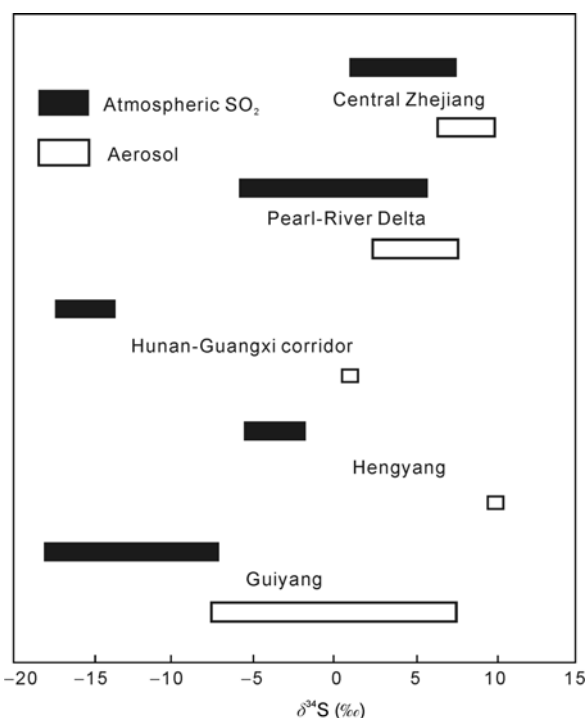


Figure 3 Sulfur isotopic compositions of atmospheric SO₂ and aerosols in different regions of China.

−3‰ sulfur isotope ratio, and the average value of sulfur isotope is about 3‰ in Nanjing and Shanghai. Those scientists suggest that the regional distribution of sulfur isotope of atmospheric SO₂ is consistent with that of coals. They further indicated that the phenomenon of regional distribution resulted from the difference of the sulfur isotopic compositions of fossil fuels [12].

The sulfur isotopic compositions of atmospheric SO₂ and aerosols in the study area are approximately similar to those of Shanghai and Nanjing, and $\delta^{34}\text{S}$ values fall in a range of

1) Hong Y T, Zhang H B, Zhu Y X, et al. Study on sulfur sources of acid rain using sulfur isotopic trace in Southwest China (in Chinese). Guiyang: Institute of Geochemistry, Chinese Academy of Sciences, 1990

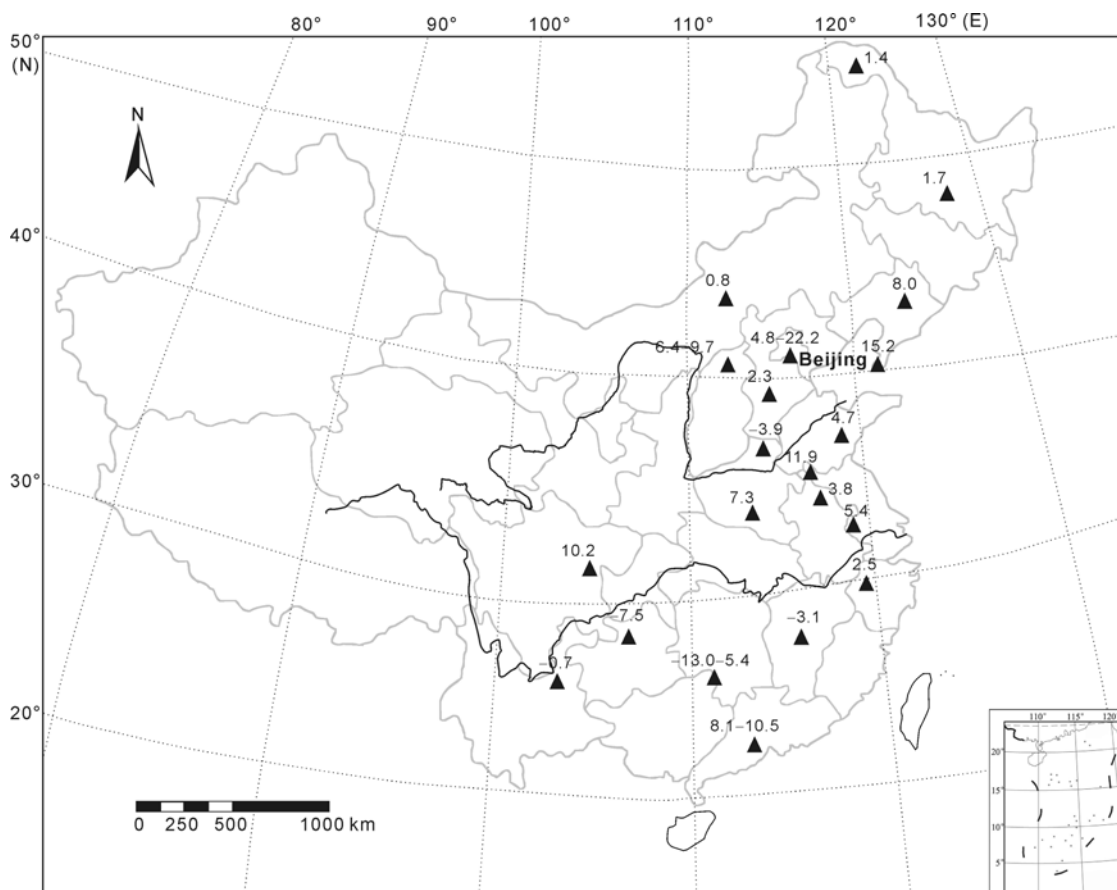


Figure 4 Sulfur isotopic compositions of coals in regions around China ($\delta^{34}\text{S}\text{‰}$).

0–10‰. There are no significant seasonal variations of $\delta^{34}\text{S}$ values of aerosols in the study area and Shanghai. The $\delta^{34}\text{S}$ values of aerosols in Shanghai are 6.3‰ in winter and 5.4‰ in summer, and the difference is very small between winter and summer. However, sulfur isotopic compositions of aerosols in study area are slightly higher than those of Shanghai. The sulfur isotopic compositions of atmospheric SO_2 in regions around China all exhibit seasonal variation at some degree, nearly from 1‰ to 3‰, but variation tendency in Shanghai is in contrast to other regions [12]. Norman et al. [21] and Novak et al. [15] also observed obvious seasonal variation in Canada and Czech in Central Europe, respectively. Norman et al. [21] thought that the seasonal variation at Alert, Canada is due to the different sulfur sources in different seasons, and these sulfur sources have their own particular sulfur isotopic compositions. The variation tendency of sulfur isotopic compositions at Alert is consistent with that of Shanghai, and they are higher in summer and lower in winter. Novak et al. [15] also reported the same seasonality in the sulfur isotope signature of atmospheric SO_2 in the Czech Republic, and suggested that the low $\delta^{34}\text{S}$ values of air-borne SO_2 in winter are influenced by low- $\delta^{34}\text{S}$ emissions from local coal-burning. The coal contains isotopically light sulfur, in which the mean

$\delta^{34}\text{S}$ value is about 1.6‰. In general, there are mainly two explanations for the controlling factors of seasonality in the $\delta^{34}\text{S}$ value of air-borne sulfur species. Some workers stressed the role of isotopically light biogenic sulfur emissions, which lower atmospheric $\delta^{34}\text{S}$ values in the warm summer months [22–25]. As a consequence, the $\delta^{34}\text{S}$ value of atmospheric sulfur in winter becomes heavier than in summer. Other workers suggested that the seasonality of $\delta^{34}\text{S}$ value can be explained by the temperature effects on the equilibrium fractionation associated with the reaction system $\text{HSO}_3^- - \text{SO}_2$ during the formation of sulfate ion rather than a change in the isotopic composition of the sources emitted sulfur [15, 26, 27]. They further point out that the isotopic fractionation factor for sulfur in the reaction system $\text{HSO}_3^- - \text{SO}_2$ decreases from 1.0173 at 25°C to 1.0107 at 70°C, which equals to 0.145‰/°C [28]. In addition, theoretical calculations suggest that sulfur isotope in the reaction system $\text{SO}_3^{2-} - \text{SO}_2$ has a temperature dependence of about 0.08‰/°C [29, 30]. Consequently, the temperature effect of equilibrium fractionation can cause an estimated seasonal variation of 2‰–3‰ according to a temperature gradient coefficient at 0.10‰/°C. In the study area, the $\delta^{34}\text{S}$ values of atmospheric SO_2 are 7.0‰ in winter and 3.3‰ in summer, whereas temperature difference be-

tween winter and summer is 15–20°C. Therefore, it could conclude that single controlling factor cannot fully explain the seasonal variation of sulfur isotope for atmospheric SO₂. The temperature effect of isotope equilibrium fractionation and elevated biogenic sulfur emissions of isotopically light S in summer may be the main controlling mechanisms in the study area.

2.3 The δ³⁴S model of atmospheric oxidation of SO₂ to form sulfate

2.3.1 The oxidation pathways of SO₂ and related reactions

The current concern about acid deposition has focused considerable interest in the conversion mechanism of SO₂ to sulfate aerosol in the atmosphere. Laboratory studies have revealed a multitude of potentially important oxidants and oxidation pathways. However, quantification of the various oxidation mechanisms in atmospheric environment remains elusive. As a result, it is not yet known whether SO₂ oxidation occurs primarily in gas phase, in cloud droplets, or on the wetted surfaces of aerosol particles [13]. During the formation of sulfate, homogeneous and heterogeneous oxidations are two major oxidation pathways (Figure 5). The relative importance of these reaction pathways conditions is controversial. Sulfur isotope ratios can be used to quantify the relative importance of these reaction pathways in the

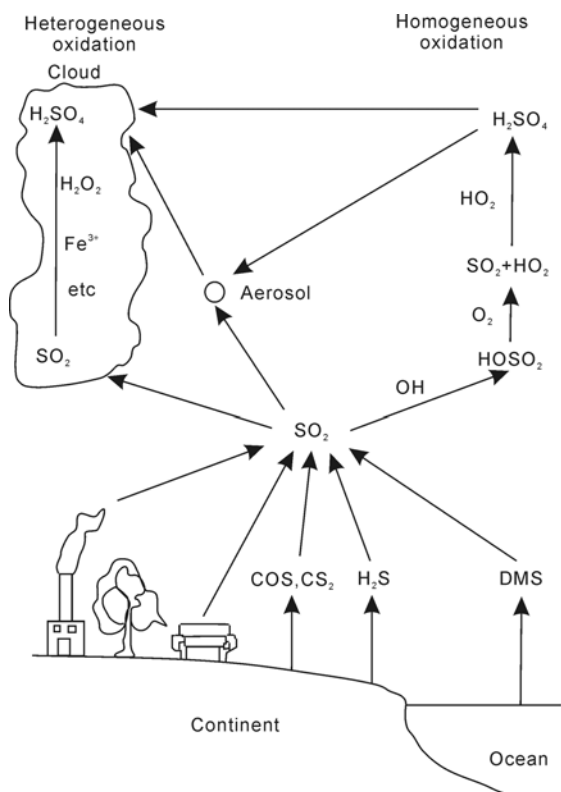
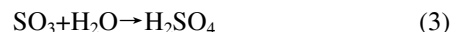
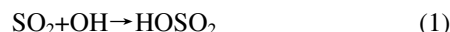


Figure 5 Sources and oxidation pathways of atmospheric SO₂ in the atmosphere.

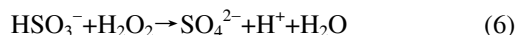
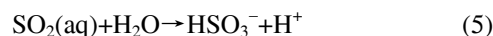
transformation process of atmospheric SO₂ [13, 15, 31].

The homogeneous oxidation reactions of SO₂ are oxidized mainly by free radicals in the atmosphere, such as OH, HO₂ and RO₂. Under normal atmospheric conditions, the ratio of oxidation rate for OH to HO₂ is about 12. In other words, the OH radicals is responsible for the homogeneous oxidation of SO₂ [32]. The homogeneous reaction mechanism has several steps as depicted in the following equations:



Among the above reactions, the formation of the radical HOSO₂ in reaction (1) is the main process dominating the sulfur isotope fractionation. Reactions (2) and (3) have rather small isotopic fractionations because the reaction rates are relatively fast.

The heterogeneous oxidation reactions of SO₂ are dissolved mainly in droplets of cloud and fog, and then being oxidized by H₂O₂, O₂ or O₃ in liquid phase. A major heterogeneous oxidation pathway can be described as follows:



There is also oxidation of SO₂ by Fe(III), Mn(IV), or O₃ in the heterogeneous oxidation reactions. However, according to the study of Martin [33], H₂O₂ dominates the oxidation of SO₂ at pH < 4. The average pH value in precipitation is about 4.5 in central Zhejiang, whereas the acidity of cloud water is usually higher than that of precipitation. Therefore, the following discussion is no longer concerned with the reactions of other oxidants. Moreover, the oxidation rate of S(IV) in clouds is faster than that in the atmosphere at gas phase, and model calculation indicates that the oxidation rate of S(IV) in stratosphere is 2–5 times of that outside the clouds on a global scale [34].

2.3.2 The δ³⁴S pattern in the oxidation process of SO₂

Eriksen [29, 30] and Egiazarov et al. [28] have studied the fractionation factor of sulfur isotope in the system SO₂-HSO₃⁻, and the fractionation factor, α, was experimentally determined to be 1.0165±0.001 at 25°C in reaction (5). They observed simultaneously that heavy sulfur isotope enriched in the reaction products and the fractionation factor increased with the decrease of temperature. The isotopic fractionations associated with reactions (3) and (6) are considerably smaller, with values about 1.001 [30]. Saltzman et al. [13] further established a model to evaluate the relative importance of homogeneous and heterogeneous oxidation, using the isotope fractionation in the oxidation process of SO₂ and sulfur isotopic data of atmospheric SO₂

SO₂ and sulfur isotopic data of atmospheric SO₂ and sulfate aerosols.

Saltzman et al. [13] calculated the fractionation factor between atmospheric SO₂ and sulfate by the formula below:

$$\alpha_m = \frac{\frac{\delta^{34}\text{SO}_4^{2-}}{10^3} + 1}{\frac{\delta^{34}\text{SO}_2}{10^3} + 1}$$

The atmospheric oxidation of SO₂ or HSO₃⁻ is an irreversible process, so isotopic equilibrium of oxidation reaction is generally not attained in the atmosphere. Moreover, reservoir effects may cause the measured isotopic fractionation (α_m) to differ from the true isotopic fractionation, which accompanies sulfate formations [13]. Saltzman et al. [13] suggested that the reservoir effects on α_m can be corrected based on the Rayleigh equation. A new fractionation factor, α_c, corrected for reservoir effects can then be calculated from the formula:

$$\alpha_c = \frac{\ln \frac{\delta^{34}\text{S}_{\text{SO}_2} + 10^3}{\delta^{34}\Sigma\text{S} + 10^3}}{\ln f} + 1,$$

where δ³⁴ΣS is sulfur isotope of total atmospheric sulfur that includes SO₂ and sulfate, and can be described as the following:

$$\delta^{34}\Sigma\text{S} = \frac{[\text{SO}_2] \times \delta^{34}\text{SO}_2 + [\text{SO}_4^{2-}] \times \delta^{34}\text{SO}_4^{2-}}{[\text{SO}_2] + [\text{SO}_4^{2-}]}$$

The oxidation of sulfur dioxide to sulfate in the atmosphere in central Zhejiang Province is associated with an isotope effect. This conclusion could be drawn from a comparison of data on δ³⁴S values in Table 1 and Figure 2, in which the average δ³⁴S value for sulfate aerosols is 3.4‰ higher than that of atmospheric SO₂. Sulfate, the product of atmospheric oxidation of SO₂, contains isotopically heavier sulfur. The overall isotope fractionation consists of two subsequent fractionations: The dissolution of SO₂ (eq. (5), see above) is accompanied by a large equilibrium fractionation. Isotopically heavier sulfur accumulates in the droplets, sulfur of the residual gaseous phase becomes isotopically lighter sulfur. The subsequent sulfur oxidation is accompanied by a kinetic isotope effect, which leads to isotopically lighter accumulation in the resulting sulfate (³²S reacts faster than ³⁴S; α=0.996). Saltzman et al. [13] suggested that the magnitude of kinetic isotope effect varies with different oxidants and reaction mechanisms, and it is probably always considerably smaller than the equilibrium fractionation. Homogeneous oxidation of SO₂ involves only the kinetic fractionation, whereas heterogenous oxidation involves both the kinetic and equilibrium fractionation. It follows that homogeneous oxidation of SO₂ must result in isotopically lighter sulfates, in contrast to heterogenous oxidation which results

in isotopically heavier sulfates (i.e., α>1). Therefore, our analytical data suggest that heterogenous oxidation of SO₂ during the formation of sulfate prevails in the atmosphere of central Zhejiang Province. Those fractionation factors α_m listed in Table 2 are calculated from the measured δ³⁴S values of atmospheric SO₂ and sulfate aerosols, and we cannot directly calculate the corrected fractionation factors α_c because [SO₄²⁻] concentrations in aerosol samples were not measured. The calculation by Saltzman et al. [13] demonstrates that reservoir effects are on the order of 0.001 or less for the Hubbard Brook. Therefore, we can approximately estimate the relative importance of the homogeneous and heterogeneous oxidation with the α_m data. The values of α_m in this study range from 1.000 to 1.009, indicating that heterogeneous oxidation of SO₂ is predominating relative to homogeneous oxidation in the atmosphere. However, the values of α_m are relatively intermediate, also indicating that the role of homogeneous oxidation cannot be underestimated in central Zhejiang Province.

The oxidation mechanism of atmospheric SO₂ in the study area is similar to that of Czech in Central Europe, where heterogeneous oxidation of SO₂ predominates in the atmosphere, but homogeneous oxidation in the study area plays a slightly larger role relative to Czech in Central Europe. Theoretically, SO₂ solubility in water increases with the decrease of temperature, and the photochemical production of gaseous oxidants is probably greatest in summer [13]. Therefore, homogeneous oxidation reactions in the atmosphere play a relatively important role in summer, whereas heterogeneous oxidation reactions are more important in winter. The oxidation of atmospheric SO₂ in the study area does not reflect the above seasonal oxidation mechanism, and Mukai et al. [12] also observed the corresponding characteristics of oxidation reactions in northern China. Only Guiyang in southern China showed a slightly higher fractionation factor even in summer, which is con-

Table 2 The calculated isotope fractionation factors of atmospheric SO₂ in 2005^{a)}

Month	Δδ ³⁴ S	α _m
January	1.3	1.0013
February	0.2	1.0003
March	1.5	1.0015
April	1.4	1.0014
May	8.8	1.0089
June	4.6	1.0047
July	5.3	1.0054
August	3.5	1.0035
September	6.2	1.0061
October	3.2	1.0031
November	2.7	1.0027
December	1.4	1.0014

a) Δδ³⁴S is the difference value of sulfur isotope ratio between aerosols and atmospheric SO₂.

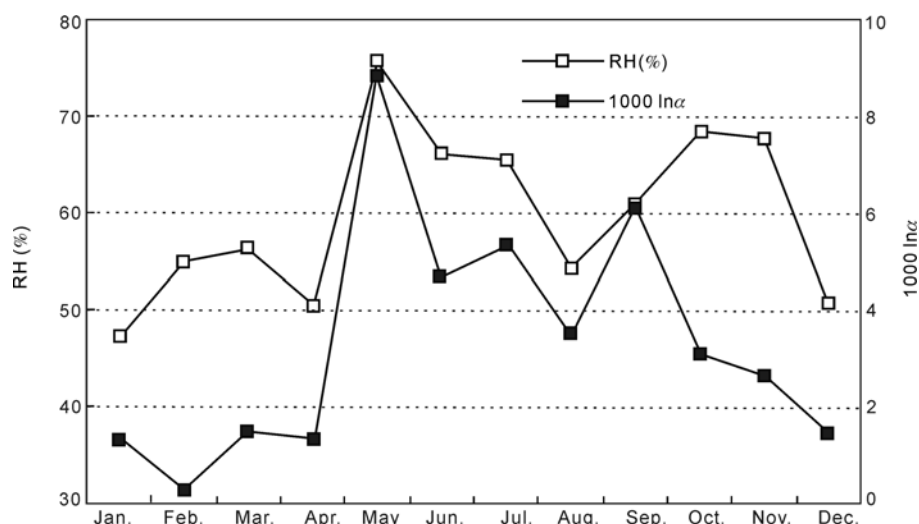


Figure 6 Variations of relative humidity and fractionation factor in the oxidation process of SO_2 .

sistent with that observed in the study area. Two factors may explain this discrepancy. One is the relatively serious air pollution that contains a higher concentration of aerosols in the atmosphere in the Chinese cities. The other reason is that climate in southern China is humid, and relative humidity in spring and summer is extremely high. Consequently, these two factors have enlarged the surfaces of droplets and wet aerosols in the atmosphere, which results in the heterogeneous oxidation reactions of atmospheric SO_2 with oxidants preferentially.

There is an intriguing phenomenon shown in Figure 6 that is surprisingly in accordance with the above analytical conclusion. We can infer that there is a significant dependence between the relative humidity and the fractionation factor α of sulfur isotope in the oxidation process of SO_2 . The highest value of α is observed when the highest relative humidity occurs in May. The result indicates that relative humidity in the atmosphere has a significant influence on the oxidation mechanism of SO_2 .

3 Conclusions

(1) The daily average concentration of SO_2 in the atmosphere ranges from 0.004 to 0.204 mg/m^3 in the study area during 2004–2005, and the annual average values are 0.044 and 0.048 mg/m^3 , respectively, while the daily average concentration of NO_2 ranges from 0.010 to 0.135 mg/m^3 , the annual average values are 0.057 and 0.053 mg/m^3 , respectively. Both pollutants have obviously seasonal variations, with higher concentration of SO_2 in winter and spring than in other two seasons.

(2) The $\delta^{34}\text{S}$ values of atmospheric SO_2 in the study area range from 1.0‰ to 7.5‰, and the annual average value is $4.7\text{‰} \pm 2.3\text{‰}$. The $\delta^{34}\text{S}$ values of aerosols range from 6.4‰ to 9.8‰, and the annual average value is $8.1\text{‰} \pm 1.0\text{‰}$. The

$\delta^{34}\text{S}$ values of aerosols are higher than those of atmospheric SO_2 , and the difference of annual average values between atmospheric SO_2 and aerosols is 3.4‰.

(3) The $\delta^{34}\text{S}$ values of atmospheric SO_2 show an obvious seasonal variation, with the highest values occurring from winter to April in spring and the lowest values at the end of the spring to summer. The $\delta^{34}\text{S}$ values are slightly higher in autumn than in summer. The $\delta^{34}\text{S}$ values of aerosols vary slightly throughout the year, fluctuating around the annual average value; they are relatively high in spring and almost exactly the same in other three seasons.

(4) The $\delta^{34}\text{S}$ values of atmospheric SO_2 are 7.0‰ in winter and 3.3‰ in summer in the study area. A single controlling factor cannot fully explain the seasonal variation of sulfur isotope for atmospheric SO_2 , and instead the temperature effect of isotope equilibrium fractionation and elevated biogenic sulfur emissions of isotopically light S in summer may be the main controlling factors.

(5) Heterogeneous oxidation of SO_2 during the formation of sulfate prevails in the atmosphere, and the role of homogeneous oxidation cannot be underestimated in the oxidation reaction mechanism. In addition, relative humidity in the atmosphere has a significant influence on the oxidation mechanism of SO_2 in the study area.

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