

Sulfur Isotopic Characteristics of Coal in China and Sulfur Isotopic Fractionation during Coal-burning Process

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Abstract

The determined results of the sulfur contents and isotopic composition of coal samples from major coal mines in 15 provinces and regions of China show that the coal mined in the north of China is characterized by higher ^{34}S and lower sulfur content, but that in the south of China has lower ^{34}S and higher sulfur content. During the coal-burning process in both industrial and daily use of coal as fuel the released sulfur dioxide is always enriched in lighter sulfur isotope relative to the corresponding coal; the particles are always enriched in heavier sulfur isotope. The discussion on the environmental geochemical significance of the above-mentioned results also has been made.

Key words: coal; sulfur; isotopic fractionation

Introduction

Coal is a main energy source in China both at present and in the future, and is also one of the important fossil fuel types in the world. The sulfur dioxide and ash particles released from coal-burning process would strongly disturb the geochemical cycle of sulfur in the natural environment and have become a chief factor leading to global atmospheric contamination and acid precipitation. In order to distinguish different sulfur sources, distribution characteristics, flux of emission and long-distance transfer, and to assess quantitatively the relative contribution of anthropogenic and natural emission of sulfur and its effect on environmental air quality, it is considered as a prospective approach to use stable sulfur isotopes as tracers of air pollution (Evanor and Freney, 1983).

First of all, the accumulation of data on sulfur isotopic composition of various kinds of coal is needed for the above purpose. However, systematic analysis of the sulfur isotopic composition of coal from the view point of environmental geochemistry has not yet been initiated in China till now. Possible fractionation of sulfur isotopes during coal-burning process also needs to be studied. In their further investigations of acid rain in Japan, Nakai and Jensen (1967) found it is unsatisfactory to characterize the sulfur isotopic composition of rain water only if the isotopic composition of sulfur in coal and that of biogenic sulfur were involved. Therefore, they assumed there would occur sulfur isotopic fractionation during coal-burning process. In an experiment on coal burning with a set of glass wares in the laboratory, they found, for the first time, that the released gas of sulfur dioxide is rich in ^{32}S relative to the host coal, but it is uncertain what the product of combustion would be, which should be relatively rich in ^{34}S according to the principle of mass balance of isotopes.

Sample and Method

This study will not be conducted from the viewpoints of coal field geology and geochemistry. What we are most concerned with is to gain a full understanding of the sulfur isotopic composition of coal in China, i. e., the sulfur isotopic characteristics and variations of coal in China, as well as regional changes with respect to its distribution, so as to provide the grounds for assessment of the effect of coal-burning on local atmosphere and long-range transport of pollutants. On this account, we collected some typical coal samples from the major coal mines in 15 provinces and regions of China. The samples were quantitatively analyzed for their total sulfur contents and $\delta^{34}\text{S}$ values.

Instead of repeating the experiments by Nakai and Jensen at the laboratory, we made on-the-spot measurements to explore the possible fractionation of sulfur isotopes during the burning process. The No.3 Boiler at the Guiyang Thermal Power Plant was chosen as an example of industrially burning coal. This boiler has a 100-meter-high chimney. Samples were collected in the following procedure.

As a kind of current absorbent in the world, lead dioxide was used in our experiment to absorb the sulfur dioxide released from coal burning. In order to know how the sulfur dioxide in smoke and simultaneously emitted ash particles react upon lead oxide, fibreglass filter film, polyester cloth, common cotton cloth and coarse filter-paper were employed as covering materials respectively, by which the ash particles could be blocked since these materials are different in density. This kind of absorber was put into a bird-cage-like container with a rainproof cover. Taking the advantage of the container which is capable of blocking and precipitating the emitted particles from the chimney, we also collected samples of the particles while lead oxide in the container was absorbing sulfur dioxide gas. Cinder samples were directly taken from boiler's coal cinder. Waste water was also sampled at the drain hole of a water film precipitator of the boiler. After careful investigations of the coal supply sources, 500 g of coal sample was taken from each 5 tons of supply coal, till 5000 g in total, then the 10 small samples were mixed as one sample weighing 5 kg. In this way every coal source under the investigation was sampled so as to guarantee the representativeness of coal samples.

The sampling apparatus mentioned above was put at the top of the 100-meter-high chimney and taken down 7 days later. Through chemical processing, the total sulfur in coal, sulfur dioxide, ash particles and water-soluble sulfide in cinder were determined on a MAT-230 mass spectrometer for their $\delta^{34}\text{S}$ values. In the measurement LTB-2 and LTB-5 (state standard series of China for sulfur isotopes), as well as CSIRD (the standard of Australia) were adopted as the reference for correction. All $\delta^{34}\text{S}$ data in this paper were converted into the international standard values.

Meanwhile, similar experiments and analyses were also carried out of samples from stoves for daily use (made in Beijing).

Results and Discussion

Sulfur isotopic composition and sulfur content of coal in China

1. The results of measurements of coal samples are given in Table 1, which are representative of the coal allocated by the state and of some major coal mines in 15 provinces and regions of China. As shown in Tables 1-2, the sulfur contents of coal samples from some major coal mines of China range from 0.31% to 6.02% with an average value of 1.22%. If the coal with sulfur content > 1% is defined as sulfur-rich (or sulfur-high) coal (Smith and Batts, 1974), generally speaking, the sulfur content of coal in China is slightly higher, but varies greatly from one coalfield to another. The Luzhi Coalfield of Guizhou Province perhaps ranks first with respect to its content of sulfur. However, for most state-owned coal mines or major coal mines, the sulfur contents are lower than 1%, averaging 0.84%.

Table 1. Sulfur isotopic composition and sulfur content of coal samples from 15 provinces and regions of China

Locality	Total sulfur (%)	$\delta^{34}\text{S}_{\text{CDT}}$ (‰)
Heilongjiang :		
Da Hinggan Ling	0.48	+1.40
Dandong	0.56	+11.22
Jilin	0.51	+1.73
Inner Mongolia	1.18	+0.80
Hebei Coalfield :	0.31	+2.30
Handan	0.81	-3.88
West Beijing	0.49	+4.75
Nantong, Sichuan	1.36	+10.19
Datong, Shanxi	0.52	+6.43
Yima, Henan	2.13	+7.33
Fangzi, Shandong	0.73	+4.69
Nanjing, Jiangsu	1.40	+5.36
Zhejiang	1.15	+2.53
Huaibei, Anhui	0.51	+3.79
Lianhua, Jiangxi	0.90	-3.06
Kunming, Yunnan	0.32	-0.65
Guizhou	4.80	-7.52

In China, the major coalfields are located north of the Yangtze River. The sulfur content of coal mined in the north is obviously different from that in the south. The average sulfur content of coal in the north of China is 0.77%, but it is more than double (1.71%) in the south. This difference in sulfur content of coal in China is attributed to its regional distribution, providing an important background for the study of regional air pollution and acid precipitation. As a matter of fact, in China those regions where sulfur-rich coal is mined and those where acid precipitation is serious show a good coincidence.

2. It is well known that the isotopic composition of sulfur in coal varies widely from $\delta^{34}\text{S} = -30$ ‰ to $+30$ ‰ (Long, 1985). However, it does not vary so widely in China (see Table 1 and Fig.1), just within the range of $\delta^{34}\text{S} = -10$ ‰ to about $+10$ ‰. This is an important sulfur isotopic characteristic

feature of coal in China .

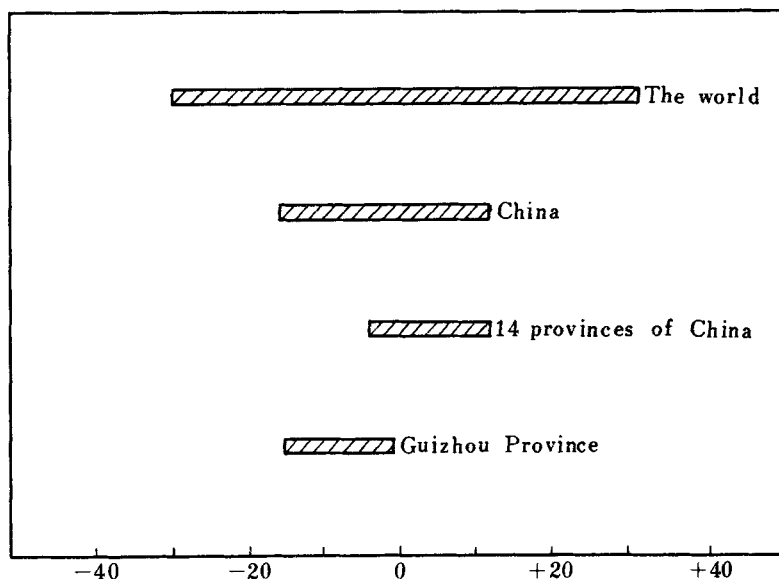


Fig.1. Sulfur isotopic composition of coal in China ($\delta^{34}\text{S}_{\text{CDT}} \text{‰}$).

What should be pointed out is that the coal with lighter sulfur isotope is distributed dominantly in the south of China, especially in the provinces of Guizhou, Yunnan, Jiangxi, etc. The average $\delta^{34}\text{S}$ value of coal from the south is -0.32‰ and that in the north is $+3.68 \text{‰}$, as given in Table 1. This implies that the coal mined in the north of China is characterized by higher $\delta^{34}\text{S}$ and lower sulfur content, but that in the south of China has lower $\delta^{34}\text{S}$ and higher sulfur content.

Nevertheless, the $\delta^{34}\text{S}$ values of coal in China seem not to be correlated with the content of total sulfur. This is just the case as encountered in other parts of the world (Smith and Batts, 1974). As for the existing forms of sulfur in coal and their relations with $\delta^{34}\text{S}$ values, further studies are needed.

3. As mentioned above, among coals mined in all the major coal mines of China, the coal mined in Guizhou is very unique in both isotopic composition and sulfur content. It has been revealed that Guizhou Province is abundant in coal resources, the reserves ranking fourth, only next to Shanxi, Inner Mongolia and Shaanxi, and is the most important coal-producer in the south of China. Coal is widely distributed in Guizhou and coal-series strata occupy an area of 70000 km^2 , accounting for 40% of the whole province. It took a long geological time for coal to be formed in Guizhou. Especially, the Upper Permian coal series is most coal-abundant and most widely distributed. Coal seams occur at shallow depth, thus creating better conditions for exploiting and mining. The proved reserves of coal in Guizhou are distributed mainly in the west, some in the center and a few in the east. Table 2 shows the isotopic composition and content of sulfur in coal samples from the coalfields at Bijie, Northwest Guizhou, Shuicheng and Luzhi, West Guizhou, and in the suburbs of Guiyang, Central Guizhou.

Table 2. Isotopic composition and content of sulfur of coal in Guizhou

Coalfield	Coal	Total sulfur (%)	$\delta^{34}\text{S}_{\text{CDT}} (\text{‰})$
Bijie :	Anthracite		
Dafang		0.62	-4.71
Yaguan		0.99	-9.89
Shuicheng :	Bitumite		
Muchong		2.90	-8.09
Luzhi :	Bitumite		
Dayong		6.02	-5.71
Guiyang suburbs :	Bitumite		
Guojiachong		4.23	-5.22
Shicao		6.23	-8.87
Changpo		8.73	-7.05
Yangjiawan		6.29	-5.51
Onggong		4.08	-10.34
Baiyanping		3.12	-9.61
Guiyang		3.32	-6.49
Mawen		4.89	-9.14
Yanlou		7.01	-12.01
Lanba		5.36	-11.24
Mayuan		4.67	-6.56
Gujiao		9.08	-7.00
Datu		6.92	-2.51
Touqiao		2.80	-5.56

Table 3. Isotopic composition of atmospheric precipitation ($\delta^{34}\text{S}_{\text{CDT}} \text{‰}$).

Location	Sample	Sulfur isotopic composition		Reference
		Range	Average	
China				
Guiyang	Rain	-14.0 - -0.8	-5.4	Hong Y. et al. (1990)
Lasha	Snow		-6.0	Hong Y. et al. (1986)
Beijing	Snow	+6.78 - +8.98		Hong Y. et al. (1990)
Urumuqi	Snow		+7.9	Hong Y. et al. (1990)
Harbin	Snow		+5.3	Hong Y. et al. (1990)
Shenzhen	Rain	-4.9 - +10.8		Hong Y. et al. (1990)
Italy	Rain	-1 - +3	+2.0	Cortecci and Longinelli (1970)
Japan				
Industrial	Rain	+3.2 - +7.3	+6.0	Jensen et al. (1961)
Non-industrial region	Rain	+12.3 - +15.6	+14.0	Jensen et al. (1961)
USSR (former)				
Sakhalin and				
Vladivostok region	Rain	+4.2 - +8.6	+6.9	Chukhrov et al. (1977)
Magodan region	Rain	+3.9 - +7.6	+5.8	Chukhrov et al. (1977)
Siberia	Rain	+3.0 - +21.6	+10.6	Chukhrov et al. (1977)
Kazakhstan				
Steppe region	Rain	+2.1 - +3.7	+3.2	
Mountain region	Rain	+3.6 - +4.6	+4.1	
Kirgizia Mountain	Rain	+5.6 - +8.6	+6.9	Chukhrov et al. (1977)
Tadzikistan				
Mountaineous region	Rain	+3.8 - +12.9	+7.2	Chukhrov et al. (1977)
Kola Peninsula	Rain	+3.8 - +6.2	+4.8	Chukhrov et al. (1977)
Moscow and				
Novgorod region	Rain	+1.6 - +5.9	+4.0	Chukhrov et al. (1977)
Urals	Rain	+5.1 - +5.7	+5.4	Gavrishin et al. (1971)
Rostov region	Rain	+2.8 - +11.3	+7.1	Rabinovich (1971)
Sweden	Rain	+3.2 - +8.2		Jensen et al. (1961)
Canada	Rain	+1.2 - +9.3		Nriagu et al. (1978)
USA				
Pittsfield Mass	Rain		+19.0	Nakai et al. (1967)

From Table 2 it is obvious that the coal in Guizhou is characterized by high sulfur content ranging from 3.12 to 9.08%, averaging 5.5%. The second feature is its low $\delta^{34}\text{S}$ values of total sulfur, mostly negative from -2.51‰ to -12.01‰ with an average value of -7.52‰ . From the first feature it can be seen that the uncontrolled emission of sulfur dioxide from coal burning is an important factor leading to serious environmental contamination, especially in the center of Guizhou where acid-rain pollution is most severe. The low $\delta^{34}\text{S}$ values of coal as the second feature, have stamped the environment in Guizhou with some special isotopic marks. For example, the $\delta^{34}\text{S}$ values of atmospheric precipitants are always negative and distinctly different from those in other areas of the world, as shown in Table 3 (Hong Yetang et al., 1987). The isotopic characteristics and contents of sulfur are of great significance in the study of long-range transport of pollutants from one area to another on the main land of China, and in the investigation of the possible effect of pollutants either from China on adjacent countries or from adjacent countries on China.

It is possible to explain the situation of the atmospheric environment quality on the qualitative basis from the available data on the isotopic composition and sulfur content of coal, but only the isotopic composition data of coal are insufficient to assess quantitatively the sources of sulfur in the atmosphere. Variations in sulfur isotopic composition, i. e., isotopic fractionation, of the released materials also need to be further examined.

Fractionation of sulfur isotopes during the coal-burning process

Table 4 shows the results of the analyses of samples collected from Guiyang Thermal Power Plant is a typical example of industrial use of coal. As can be seen from the table:

1. All of the absorbers, with different lining materials such as can, on which PbO_2 is smeared as absorbent, succeeded in absorbing the sulfur dioxide released from burning coal. Their $\delta^{34}\text{S}$ values are similar to each other, having an average of -15.06‰ . Compared with the $\delta^{34}\text{S}$ value of total sulfur in the corresponding coal (-6.39‰), sulfur dioxide released from burning coal becomes isotopically lighter obviously, with a difference of 8.67‰ . Therefore, Nakai and Jensen's findings that the sulfur isotopic composition of sulfur dioxide in smoke released during the coal-burning process is enriched in the lighter isotope $\delta^{32}\text{S}$ relative to coal itself have been confirmed by the on-the-spot measurements for the first time.

2. Our new findings are: the $\delta^{34}\text{S}$ values of cinder are close to those of coal, with no regular and remarked variations. But the ash particles emitted during the coal-burning process are distinctly enriched in the heavier isotope $\delta^{34}\text{S}$, as compared with coal and sulfur dioxide in smoke. The $\delta^{34}\text{S}$ values of ash particles reach -2.15‰ , 4.24‰ higher than those of coal.

The results of experimental measurements of coal during burning from stoves for daily use provide further support to the fractionation of sulfur isotopes as described above. As shown in Table 5, the sulfur isotopic compositions of sulfur dioxide and particles released from coal stoves for daily use are enriched in lighter and heavier sulfur isotopes relative to coal, respectively. The differences are estimated to be

7.63 ‰ and 5.38 ‰ , respectively .

3. From the above we can , for the first time , put forward a regular pattern of fractionation of sulfur isotopes during the coal-burning process , i . e . , in the industrial and daily use of coal as fuel the released sulfur dioxide is always enriched in lighter sulfur isotope relative to the corresponding coal ; the particles are always enriched in heavier sulfur isotope ; the sulfur isotopic composition of cinder is close to that of coal (Fig.2) .

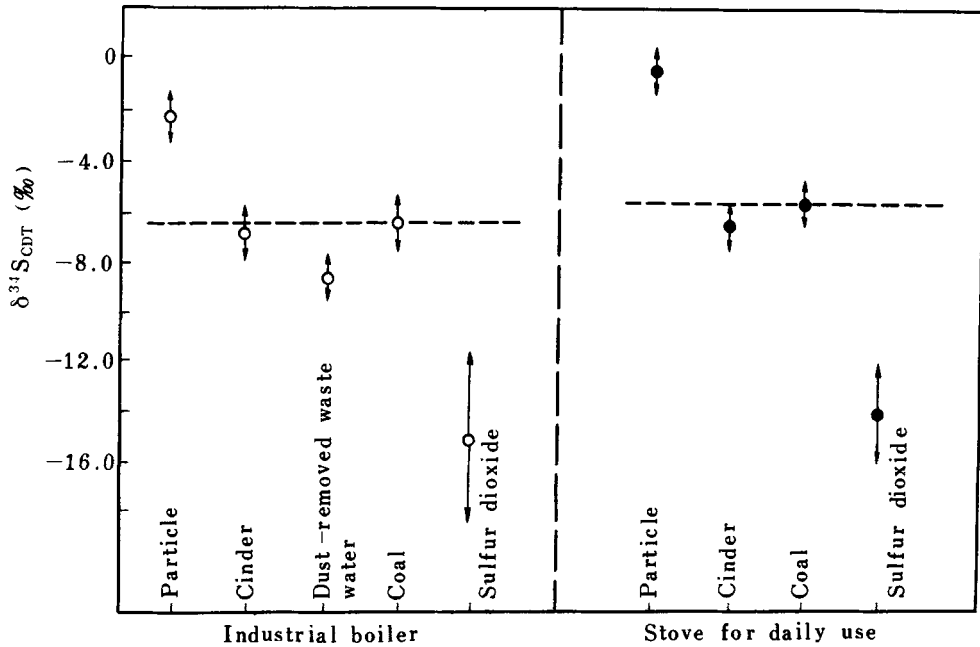


Fig.2 . Fractionation of sulfur isotopes during the coal-burning process .

Table 4 . Actually measured fractionation of sulfur isotopes during industrially coal-burning process

Sample	$\delta^{34}\text{SCDT} (\text{‰})$
Particles collected from the topmost of the chimney	-2.15
SO ₂ in gas (Al can , fibreglass filter film)	-17.06
SO ₂ in gas (filter-paper , outer-wrapped fibreglass filter film)	-17.46
SO ₂ in gas (cotton cloth , outer-wrapped cotton cloth)	-15.75
SO ₂ in gas (polyeaster cloth , outer-wrapped polyeaster)	-14.12
SO ₂ in gas (filter-paper , outer-wrapped filter-paper)	-11.01
Waste water avoid of dust	-8.44
Cinder	-6.88
Coal	-6.39

Table 5 . Actually measured fractionation of sulfur isotopes in stoves for daily use during coal-burning process

Sample	$\delta^{34}\text{SCDT} (\text{‰})$
Ash particle	-0.18
SO ₂ in smoke	-13.97
Cinder	-6.42
Coal	-5.56

The above pattern of fractionation of sulfur isotopes during the coal-burning process is of environmental geochemical significance as described below. On one hand, the evolution trend for the isotopic composition of sulfur in released materials can be predicted with the isotopic composition of sulfur in coal when it burns out; on the other hand, coal-burning results in anthropogenic emission of two kinds of pollutants, sulfur dioxide gas and particles, marked with different isotopic compositions. In the atmospheric environment, owing to differences in their residence time, transport range and physical, chemical and biological reactions involved, they have different ways to affect the environmental quality of the earth. Their sulfur isotopic characteristics provide the basis for tracing and identifying their migration and effects.

4. Table 4 also shows that the particles can interfere the sulfur isotopic composition of sulfur dioxide absorbed by lead dioxide. In case denser fibreglass is used as separating material, the particles containing sulfur have little possibility to get in and react with lead dioxide, and the $\delta^{34}\text{S}$ value of sulfur dioxide absorbed by lead dioxide could truly reflect the sulfur isotopic composition of sulfur dioxide released from coal-burning. In other case that the separating materials are loose cotton cloth, polyester cloth and especially coarse filter-paper respectively, the particles with higher ^{34}S have more chance to pass through the separating materials and react with lead dioxide or adhere to it. In this way the $\delta^{34}\text{S}$ value of the sulfur dioxide absorbed is raised, as shown in Table 4.

It is worth pointing out that the lead dioxide is usually exposed to the air in case a hung flat smeared with lead dioxide is used to absorb sulfur dioxide. If the filter-film is needed as separating material and what kind of filter-film is suitable have not yet been considered carefully, and there is no unified standard up to now, which certainly will affect the accuracy of data and the comparison of data between laboratories. Our experimental results inform us that it is necessary to discuss this problem further.

5. Fractionation of sulfur isotopes during the coal-burning process is a complex process, maybe a sort of dynamic fractionation taking place in oxidizing and burning processes and in the smoke flue. But the exact fractionation mechanism, including the relations of the fractionation extent with the coal type, combustion temperature, and flue condition, still needs to be studied further.

In addition in industrially coal-burning process the smoke and ash particles should be sometimes handled before emitted into the atmosphere. The plant under investigation uses the water-film technique to get rid of the smoke and ash. It is pointed out that there would be no remarkable fractionation sulfur isotopes when the gaseous sulfur dioxide is washed with water (Nriagu and Coker, 1978). Perhaps water-film precipitation could change the size composition of emitted particles, and thus change their $\delta^{34}\text{S}$ values. Even if it is true, it is certain that the particles eliminated by the water-film technique are still relatively heavier in sulfur isotopic composition. As can be seen from Table 4, after removing dust, the pH value of the waste water becomes so low as to be pH=3.16 due to the absorption of a great deal of gaseous sulfur dioxide. The $\delta^{34}\text{S}$ values of the waste water should become so low as to be the same as those of gaseous sulfur dioxide, but still higher than those of gaseous sulfur dioxide, which is reasonably

attributed to the incorporation of ash particles into water by washing. Therefore, the basic pattern of fractionation in the industrial process in the case of dust removing is the same as in the coal-burning process in stoves for daily use without precipitation.

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References

- Hong Yetang et al., 1987, Primary results of measurements of sulfur isotopic compositions of some environmental samples from China, *Environmental Geochemistry and Health*; v. 3, p. 161–164.
- Ivanov, M. V. and J. R. Freney, 1983, *The Global Biogeochemical Sulfur (scope 19)*: Chichester, John Wiley and Sons LTD., 278p.
- Lu Huanzhang and Xu Zhonglun et al. transl. 1985, *Long geochemical tables*: Beijing, Science Press, 283p. (Chinese version).
- Nakai, N. and M. L. Jensen, 1967, Sources of atmospheric sulfur compounds: *Geochemical Journal*, v.1, p. 199–209.
- Nriagu, J. O. and R. D. Coker, 1978, Isotopic composition of sulfur in precipitation within the Great Lakes Basin: *Tellus*, v. 30, p. 365–375.
- Smith, J. W. and B. D. Batts, 1974, The distribution and isotopic composition of sulfur in coal: *Geochimica et Cosmochimica*, v. 38, p. 121–133.