The elemental and isotopic composition of sulfur and nitrogen in Chinese coals

Hua-Yun Xiao *, Cong-Qiang Liu

State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

ABSTRACT

Coal combustion is an important atmospheric pollution source in most Chinese cities, so systematic studies on sulfur and nitrogen in Chinese coals are needed. The sulfur contents in Chinese coals average $0.9 \pm 1.0\%$, indicating that most Chinese coals are low in sulfur. A nearly constant mean $\delta^{34}S$ value is observed in low sulfur (TS < 1) Chinese coals of different ages (D, P_1, T_3 and J_3). High sulfur Chinese coals (OS > 0.8%), often found at late Carboniferous (C_3) and late Permian (P_2) in southern China, had two main sulfur sources (original plant sulfur and secondary sulfur). The wide variety of $\delta^{34}S$ values of Chinese coals ($-15‰$ to $+50‰$) is a result of a complex sulfur origin. The $\delta^{15}N$ values of Chinese coals ranged from $-6‰$ to $+4‰$, showing a lack of correlation with coal ages, whereas nitrogen contents are higher in Paleozoic coals than in Mesozoic coals. This may be related to their original precursor plant species: high nitrogen pteridophytes for the Paleozoic coals and low nitrogen gymnosperms for the Mesozoic coals. Different to $\delta^{34}S$ values, Chinese coals showed higher $\delta^{15}N$ values in marine environments than in freshwater environments.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

China is rich in coal resources. Most coals in China are mined to be used in power plants and in the cement industry. Combustion of coals usually produces large quantities of polluting gases and waste, inducing environmental problems that often lead to health hazards. Both SO_2 and NO_x play important roles in development of acid rain. Deposition of acid compounds from the atmosphere has increased in some Chinese areas during recent decades (e.g. Lü and Tian, 2007) and there is increasing concern that deposition of these compounds is damaging the forest ecosystem. The environmental problems come mainly from the quality of coal used, especially from high sulfur coals. Combustion of sulfur containing fossil fuels and certain industrial processes involving sulfur compounds represent the main anthropogenic sources of primary SO_2 present in the atmosphere (Galloway et al., 1987). Coal combustion is also an important anthropogenic source of NO_x in some cities (e.g. Xu et al., 2000).

Sulfur isotope ratios ($\delta^{34}S$) of atmospheric sulfur has been determined at many sites all over the world because they may hold source specific information that can serve as a fingerprint to identify sulfur sources and, consequently, to assess the relative contribution and impacts of the different sources (Ohizumi et al., 1997; Novák et al., 2001; Xiao and Liu, 2002; Pruett et al., 2004). Atmospheric sulfur with low $\delta^{34}S$ value in most southern Chinese cities

was believed mainly emitted from local coal burning power stations (Mukai et al., 2001; Xiao and Liu, 2002; Xiao et al., 2008, 2009). The $\delta^{34}S$ values of anthropogenic emissions in industrial and consumer processes generally show a wide range depending on the nature of the source (mainly coals in China). Hong and Zhang (1992) found that northern Chinese coals usually have higher sulfur isotopic ratios than southern Chinese coals, but the number of samples they used for statistical analysis is very limited. Although previous studies have been conducted on some coalfields (e.g. Zhou et al., 2000), systematic research on sulfur isotope of coals has not been carried out still for the whole of China. In the literature, some conclusions related to coal sulfur isotope are reached as follows.

Pyrite and organic sulfur are the most abundant chemical forms of sulfur in coals. Previous isotopic studies have suggested that the $\delta^{34}S$ value of organic sulfur in low sulfur coals is representative of isotopically homogeneous, primary plant sulfur, reflecting not influenced by seawater sulfate (Price and Sheih, 1979; Casagrande and Price, 1981; Haciuey and Anderson, 1986). In contrast, the $\delta^{34}S$ values of organic sulfur in high sulfur coals were more variable and typically more negative as a result of bacterial influence (Chambers and Trudinger, 1979; Haciuey and Anderson, 1986; Dellwig et al., 2000; Zhou et al., 2000). Additionally, the $\delta^{34}S$ values of organic sulfur and pyrite exhibited a linear relationship for high sulfur coals (Price and Sheih, 1979, 1986), suggesting a common mechanism of the sulfur incorporation.

Although coal combustion is still believed an important atmospheric pollution source in most of the Chinese cities, new

* Corresponding author. Fax: +86 851 5891609.
  E-mail address: xiaohuayun@vip.skleg.cn (H.-Y. Xiao).

stress from oil combustion was raised due to the increasing quantities of vehicles. Since nitrogen isotope (δ^{15}N) is known to be an effective tool to discriminate nitrogen sources (Freyer, 1978; Heaton, 1987, 1990), contribution of coal combustion can be estimated if their nitrogen isotopic composition is known. The nitrogen isotopic composition in Chinese oils was determined (Chen et al., 2004), but up to now there are no reports on nitrogen isotope data of Chinese coals. Therefore, this study was designed to systematically collect Chinese coals in four main coal producing regions and to analyse their sulfur and nitrogen isotopic composition.

2. Main coal producing regions in China

Five main coal producing regions can be identified in mainland China based on coal forming periods, sedimentary facies, distribution of coal seams, geological structures and geographical factors (Fig. 1). These are the Late Jurassic (J_3) coal producing region in northeastern China (I), the Early-Middle Jurassic (J_{1-2}) coal producing region in northwestern China (II), the Permocarboniferous (C–P) coal producing region in northern China (III), the Late Permian (P_2) coal producing region in southern China (IV), the Mesozoic–Cenozoic (M–C) coal producing region in Yunnan Province and Tibet (V) and the Triassic (T) coal producing region in Taiwan Province (VI) (Wang et al., 1992). The production from 2 of these coal producing regions, C–P and J_{1-2}, comprises about 40% and 33.3%, respectively, of the entire national coal resources. Since the M–C coal producing region (V) and the Triassic (T) coal producing region (VI) have not been extensively exploited and account for less than 1% of the total coal resources (Wang et al., 1992), we did not collect coal samples from these regions for this study.

3. Materials and methods

3.1. Sampling and sample preparation

A sampling plan was designed based on the distribution of coal resources, coal yields, coal ranks and ages. Samples were collected by a channel sampling method as described in the Chinese national standard GB481-93 (State Bureau of Technical Supervision, 1993). First, the weathered surface of a coal exposure was removed and the face of the coal bed was evened. Then, a channel sample (approximately 15 cm wide and 5 cm deep) was taken from the top to the bottom of the coal bed excluding dirt partings thicker than 3 cm. Each collected sample was then further divided and a 5 kg sample was selected for analysis. A total of 179 coal samples were collected in this way from the main coal mines of 26 provinces, autonomous regions and central administrative municipalities of China. Fig. 1 shows the sampling locations.

To prevent contamination and weathering, all samples were stored in plastic bags. Sample preparations were conducted according to the Chinese national standard GB 474-1996 (State Bureau of Technical Supervision, 1996). The samples were prepared by air drying, grinding and sorting through a 200 mesh nylon sieve.

3.2. Determination of sulfur, nitrogen and boron in coals and the classification of coal rank

The determination of elemental contents in coals as well as classifying coal ranks of the samples was carried out in USGS using the methods as follows.
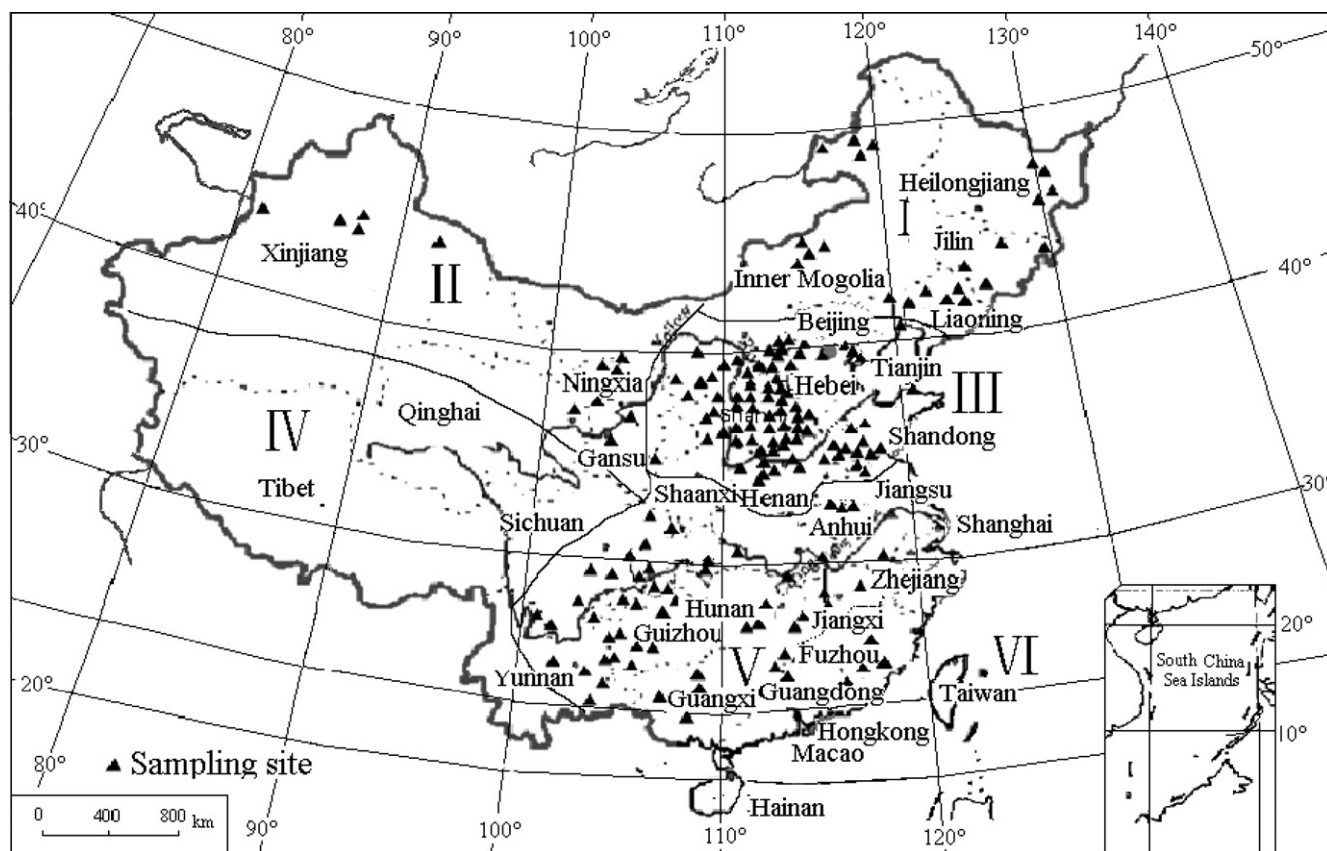

Fig. 1. The map of China showing main coal producing regions and coal sampling sites. (I) Late Jurassic coal producing region in northeastern China; (II) Early-Middle Jurassic coal producing region in northwestern China; (III) Permocarboniferous coal producing region in northern China; (IV) Mesozoic–Cenozoic coal producing region in Yunnan Province and Tibet; (V) Late Permian coal producing region in southern China; (VI) Triassic in Taiwan Province.

The S and N contents of the samples were determined according to the American Society of Testing Materials (ASTM) methods D3177-89 (ASTM, 1989) and D5373 (ASTM, 2002), respectively. Approximately 0.25 g of coal from each sample was weighed in a ceramic combustion boat and burned in a tube furnace at a temperature of 1350 °C in a stream of high purity O_2 to oxidize the S. The released SO_2 was passed through the infrared absorption detector of a sulfur analyzer (LECOR SC132). After conversion in an oxygen stream in their entirety to nitrogen oxides, N is determined by thermal conductivity on a second aliquot additionally treated to reduce all nitrogen oxides to nitrogen and to remove residual oxygen, carbon dioxide and water vapor.

The determination of forms of sulfur in coal was according to the methods by ASTM (1984). Sulfate sulfur is determined by infrared absorption of the SO_2 produced by combustion of whole coal or of the separated forms of sulfur in an oxygen atmosphere. The pyritic sulfur content is measured indirectly by determining the iron concentrations in a separated fraction by flame atomic absorption spectrometry. The organically bound sulfur content is calculated by subtracting the sum of the concentrations of monosulfide, sulfate sulfur and pyritic sulfur from the total sulfur content.

To indicate corresponding paleo-environments, the B contents of the samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP–AES) following the Australian standard AS 1038.10.3-1998 (Standards Australia, 1998). A 0.5 g aliquot of each sample was ignited in contact with Eschka mixture (two parts MgO and one part anhydrous Na_2CO_3) in an oxidizing atmosphere at 800 °C to decompose the organic matter. The residue was then extracted with HCl (density at 20 °C from 1.16 g/ml to 1.19 g/ml), and the B was then determined by ICP–AES. The intensity of the emitted radiation of B at 249.678 nm was used for determining the B contents.

The coal ranks of the samples were classified by ASTM D388-99e1 (ASTM, 1999). Classification of the higher rank coals was based on the amount of fixed C, while the lower rank coals were classified by gross calorific value. A combination of these characteristics was used for differentiating between certain adjacent groups.

3.3. Stable isotopic analyses

Coal samples were oxidized in a Parr bomb to convert all forms of sulfur present to sulfate. To assure complete conversion, hydrogen peroxide was added to all washings. Sulfate was recovered from coal washings by precipitating as $BaSO_4$ with enough 2 mol/l $BaCl_2$ solution. After precipitation for 24 h, the mixture was filtered through a 0.22 μm acetate membrane filter. The precipitates ($BaSO_4$) on the filters were carefully rinsed with enough Milli-Q water to remove Cl^- and then transferred into crucibles with the filters and combusted at 800 °C for 40 min in air. In order to determine the composition of white power in the crucible, it was analyzed with X-ray diffractometry. The results showed >99% $BaSO_4$ in the power. Thermal decomposition of $BaSO_4$ (Yanagisawa and Sakai, 1983) was conducted to prepare SO_2 for sulfur isotopic analysis in a Finnigan MAT-252 mass spectrometer. The standard deviation for the $\delta^{34}S$ analysis of NBS127 (barium sulfate) was better than ±0.2‰ ($n = 5$).

After combustion at 850 °C in am evacuated quartz tube and purification with liquid N, nitrogen isotope ratios of coals were determined on a Finnigan MAT-252 mass spectrometer. Analysis of potassium nitrate standard (MOR2386-01) provided by Shoko Co., Ltd., Tokyo, Japan (+1.9‰) gave a mean (±SD) $\delta^{15}N_{air}$ value of 1.9 ± 0.2‰ ($n = 10$). High purity N_2 reference gas was run with each analysis. Three to five replicate measurements per sample were carried out and values were presented as the average of these measurements. The analytical precision (±SD, $n = 10$) for $\delta^{15}N$ was ±0.2‰.

3.4. Statistical analysis

Statistical analysis was conducted with SPSS 11.5 and graphs were mainly created with SigmaPlot 2000 software (both SPSS Science, Chicago, USA). A multiple comparison test (Tukey HSD, LSD) was used to determine significant differences between mean values and correlations were analyzed by one-way analysis of variance (ANOVA).
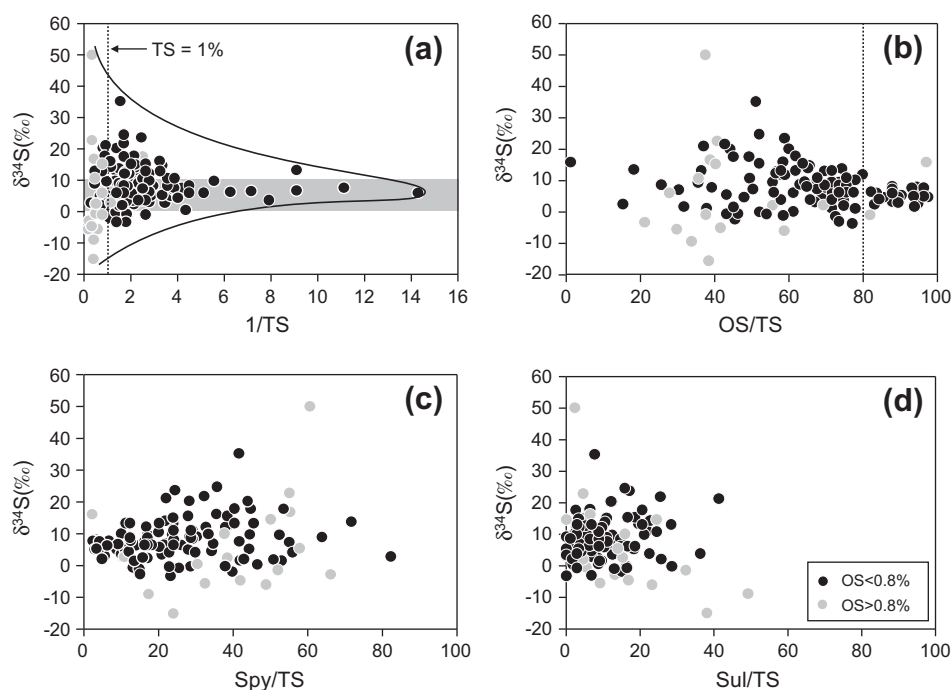

Fig. 2. Variations of the $\delta^{34}S$ values with 1/TS (a), OS/TS (b), Spy/TS (c) and Sul/TS (d).

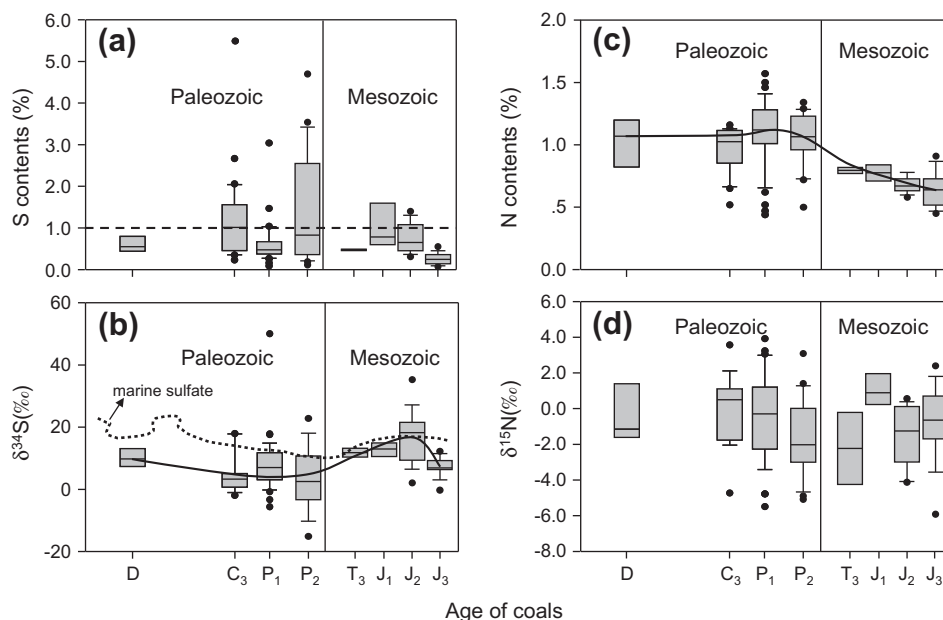**Fig. 3.** Temporal variations of sulfur contents (a), the $\delta^{34}S$ values (b), nitrogen contents (c) and the $\delta^{15}N$ values (d) in Chinese coals. Box plots display the 10th, 25th, 50th, 75th, and 90th percentiles as solid lines. Symbols indicate 5th and 95th percentiles. Different letters above the bars indicate a significant statistical difference between means at the level of $p < 0.05$. The global age curve of the sulfur isotopic composition of marine sulfate was also shown in the figure (Claypool et al., 1980).

4. Results

4.1. Elemental contents and isotopic signatures of sulfur and nitrogen in Chinese coals

The contents of total sulfur (TS) and total nitrogen (TN) in Chinese coals ranged from 0.1% to 5.6% (averaging 0.9 ± 1.0%; Fig. 2a) and from 0.4% to 1.6% (averaging 1.0 ± 0.3%), respectively. Among these samples, only about 11% have an organic sulfur (OS) content of >0.8%. Organic sulfur is the dominant sulfur form in most Chinese coals, with a mean of OS/TS ratios at 0.6 (Fig. 2b).

The $\delta^{34}S$ values of Chinese coals exhibit a very wide range (−15‰ to +50‰), but approximately 70% of the $\delta^{34}S$ values were from 0‰ to +15‰. Although the $\delta^{34}S$ values of organic sulfur and pyrite can provide useful information on coal forming environments (e.g. Casagrande et al., 1977), we did not analyze the $\delta^{34}S$ values of organic sulfur and pyrite (Spy) because it is clear that organic sulfur dominates in low sulfur Chinese coals and pyrite is usually enriched in high sulfur Chinese coals (Ni, 1997). Chinese coals defined as high sulfur based on their organic sulfur contents (OS > 0.8%) show a wide range (−15‰ to +50‰) of sulfur isotope ratios and low sulfur coals (1/TS > 4) exhibit a narrow range (0‰ to +10‰) (Fig. 2a). For samples with OS < 0.8% and OS/TS > 80%, the $\delta^{34}S$ values also showed a similar narrow range (+0‰ to +10‰) (Fig. 2b). As shown in Fig. 2c, the range of the $\delta^{34}S$ values is large when Spy/TS > 40%, indicating that pyrite was formed in different stages. Sulfate contents in most of the Chinese coals are relatively low (Fig. 2d).

Relative to the wide range of $\delta^{34}S$ values (−15‰ to +50‰), the range of the nitrogen isotopic ratios of Chinese coals is narrow (−6‰ to +4‰), similar to those (−2.5‰ to +3.5‰) reported previously for North American and European coals (Hoering, 1955; Bokhoven and Theuwen, 1966) and slightly less negative than those (+3.5‰ to +6.3‰) for a suite of European coals (Stiehl and Lehmann, 1980). Approximately 73% of the $\delta^{15}N$ values ranged from −3‰ to +2‰. These are similar to the range of values found in humic acids from modern lacustrine and swamp environments (0‰ to +3‰; Sweeney et al., 1978).

4.2. Isotopic signatures in Chinese coals of different ages

The total sulfur contents of Chinese coals showed large fluctuation with ages (Fig. 3a). The total sulfur contents of Devonian (D), early Permian (P_1), late Triassic (T_3) and late Jurassic (J_3) coals are <1%, while some coals of late Carboniferous (C_3) and late Permian (P_2) ages contained high sulfur. The $\delta^{34}S$ values of Chinese coals varied with ages as shown in Fig. 3b. The mean $\delta^{34}S$ values in Paleozoic coals ranged from +3.4‰ to +10.2‰ (averaging +6.6‰), roughly parallel the global age curve of the sulfur isotopic composition of marine sulfate (Claypool et al., 1980) and then they increased significantly to be about +12.3‰ in Mesozoic Chinese coals ($p < 0.01$). The mean $\delta^{34}S$ values in Chinese coals of late Triassic (T_3) to middle Jurassic (J_2) are very close to the global age curve of marine sulfate, then decreased to +7.2‰ at late Jurassic (J_3). For those low sulfur Chinese coals of D, P_1, T_3 and J_3 ages, the mean $\delta^{34}S$ values of +7.2‰ to +10.2‰ were determined, consistent with the range for low sulfur coals reported previously (Smith and Batts, 1974; Price and Sheih, 1979; Smith et al., 1982; Westgate and Anderson, 1984; Haciuey and Anderson, 1986).

Both nitrogen contents and $\delta^{15}N$ values of the Chinese coals exhibit different temporal patterns to those for sulfur. Nitrogen contents in Chinese coals of Paleozoic era are significantly higher than those of Mesozoic era ($p < 0.01$) (Fig. 3c), whereas no systematic variation of the $\delta^{15}N$ values was observed with the age of the coals (Fig. 3d). Smith and Hudson (1951) did not observe an age effect of coal nitrogen either. Likewise, the lack of correlation of $\delta^{15}N$ values with ages was observed for Australian coals (Rigby and Batts, 1986). Although natural processes such as nitrification, denitrification and biodegradation result in a wide variation of nitrogen isotope distribution in soils (e.g. Cheng et al., 1964), the $\delta^{15}N$ values in Chinese coals are surprisingly constant (−6‰ to +4‰), possibly reflecting the invariant ^{15}N contents of the precursor organic matter with time.

4.3. Isotopic signatures in Chinese coals of different ranks

Both sulfur contents and $\delta^{34}S$ values of the Chinese coals did not vary continuously with ranks of the coals, but a higher sulfur

content and a less positive $\delta^{34}S$ value are observed for anthracite coals (Fig. 4a and b). In China, the Jurassic coals usually belong to the coals of low rank, while the coals of high ranks are Carboniferous and Permian (Guo, 1992). So the cause for the less positive $\delta^{34}S$ values in anthracite coals may be the same as that for the low $\delta^{34}S$ values in Paleozoic coals.

In Chinese coals, nitrogen contents varied from 0.7 ± 0.3% to 1.0 ± 0.3%, increasing from lignite to anthracite, while the $\delta^{15}N$ values decreased with ranks from +0.9 ± 1.7‰ to −1.7 ± 2.1‰ (Fig. 4c and d). Stiehl and Lehmann (1980) also observed a correlation between the $\delta^{15}N$ values and coal ranks in a suite of European coals. But Rigby and Batts (1986) found no correlation in Australian coals. Since coalification is believed to have little effect on the $\delta^{15}N$ values of coals (Rigby and Batts, 1986), the decreasing $\delta^{15}N$ values of Chinese coals with high ranks in this study may not be due to the isotope effects.

4.4. Isotopic signatures in Chinese coals of different boron contents

Because there is an evident correlation between boron contents of coals and their sedimentary paleo-environments, Goodarzi and Swaine (1994) proposed the following ranges of boron contents to indicate corresponding paleo-environments: (1) up to 50 mg/kg boron: freshwater influenced coals; (2) 50–110 mg/kg boron: mildly brackish influenced coals; (3) >110 mg/kg boron: brackish influenced coals. The boron contents of Chinese coals were determined in this study and the sedimentary paleo-environments in which the coals formed were classified accordingly.

No significant differences of either sulfur contents or $\delta^{34}S$ values in the Chinese coals are found among the three ranges of boron contents (Fig. 5a and b). These are different to the results reported by Price and Casagrande (1991) and Tang and Ren (1996). They all observed a decrease in the $\delta^{34}S$ values when sedimentary paleo-environments turned from freshwater to seawater. In this study, sulfur contents are high in coals when boron contents are within 50–110 mg/kg and low sulfur content occurs at both <50 mg/kg and >110 mg/kg boron contents (Fig. 5a). This suggested that the environment indicated by sulfur contents is different from that by boron contents. High sulfur content indicates marine influenced post-depositional environments (providing marine sulfate

whereas >110 mg/kg boron suggests brackish influenced depositional environments (for plant growth). Additionally, although high sulfur contents are found at 50–110 mg/kg boron content, most of the $\delta^{34}S$ values are within the range of 0‰ to +10‰.

Both nitrogen contents and the $\delta^{15}N$ values in Chinese coals increased slightly with boron contents (Fig. 5c and d). The mean nitrogen content and mean $\delta^{15}N$ value are 0.9 ± 0.3% and −0.9 ± 2.2‰, respectively, in freshwater influenced coals (B < 50 mg/kg), 1.0 ± 0.2% and −0.2 ± 2.2‰ in mildly brackish influenced coals (B = 50–110 mg/kg), and 1.1 ± 0.2% and 1.1 ± 2.8‰ in brackish influenced coals (B > 110 mg/kg).

4.5. Isotopic signatures in Chinese coals of main coal producing regions

The sulfur contents in most coals of southern China (V) are relatively higher and their $\delta^{34}S$ values are less positive (+5‰ ±8.4‰) as compared with those in northern coal producing regions (I–III) (Fig. 6a and b). These are consistent with the results reported by Hong and Zhang (1992). In Chinese coals, the most negative $\delta^{34}S$ values (averaging −7.5‰) are found in Guizhou Province, where high sulfur contents are also observed.

The nitrogen contents in coals of northern China (III) and southern China (V) are relatively higher than those in the other two coal producing regions (I and II), whereas the differences between the $\delta^{15}N$ values in the four coal producing regions are not significant (p > 0.05) (Fig. 6c and d).

5. Discussion

5.1. Isotopic composition of original plant sulfur in coals

Coal that has a total sulfur content of <1% usually shows a moderately positive sulfur isotopic signature (0‰ to +10‰). For example, Smith and Batts (1974) reported that organic sulfur in some low sulfur coals of Australia had $\delta^{34}S$ values between +4.6‰ and +7.3‰. A similar range from +2‰ to +8‰ for organic sulfur was also observed in low sulfur coals from Australia and Gondwanaland by Smith et al. (1982). Measurements by Price and Sheih (1979) and Westgate and Anderson (1984) on low sulfur Pennsylvanian
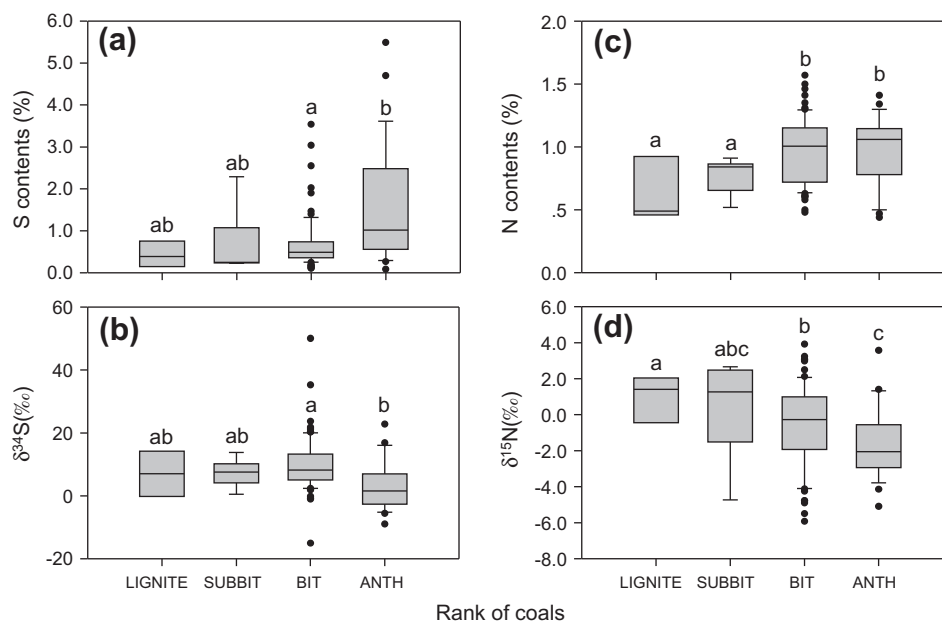

Fig. 4. Relationship of sulfur contents (a), the $\delta^{34}S$ values (b), nitrogen contents (c) and the $\delta^{15}N$ values (d) in Chinese coals with the rank of coals. Different letters above the bars indicate a significant statistical difference between means at the level of p < 0.05.
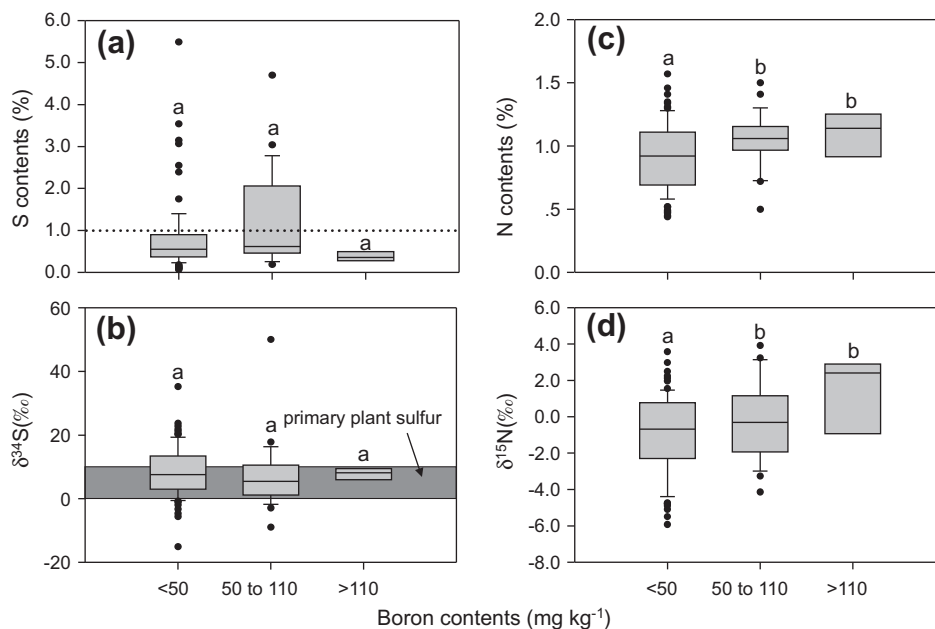
Fig. 5. Relationship of sulfur contents (a), the $\delta^{34}S$ values (b), nitrogen contents (c) and the $\delta^{15}N$ values (d) with the boron contents in Chinese coals. The classification of boron contents is based on the method proposed by Goodarzi and Swaine (1994). Different letters above the bars indicate a significant statistical difference between means at the level of $p < 0.05$.
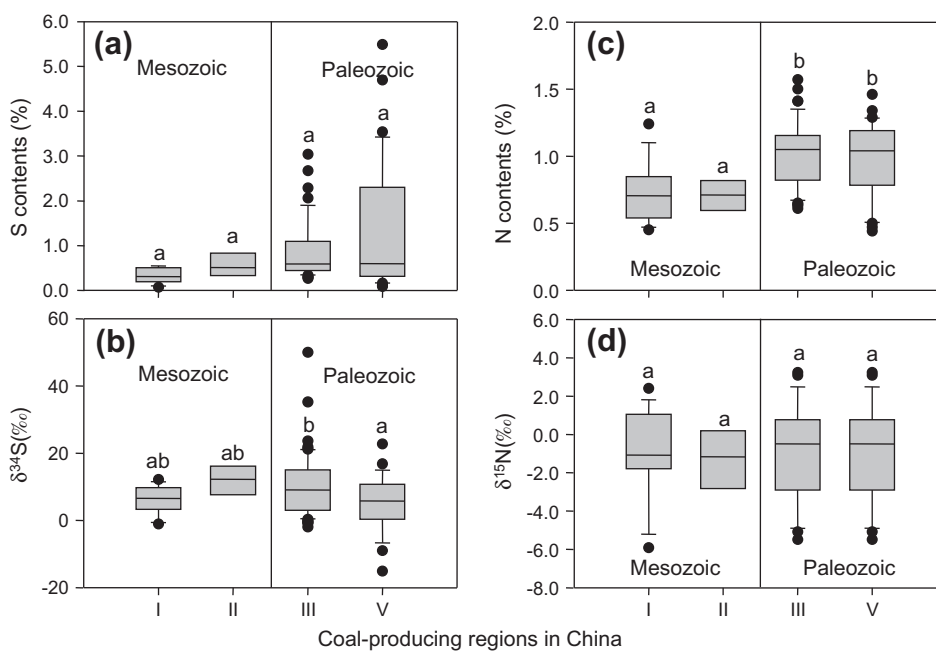

Fig. 6. Regional variations of sulfur contents (a), the $\delta^{34}S$ values (b), nitrogen contents (c) and the $\delta^{15}N$ values (d) in Chinese coals. The number of the main coal producing regions is the same as shown in Fig. 1. Different letters above the bars indicate a significant statistical difference between means at the level of $p < 0.05$.

coals (<0.8% organic S) from the Illinois Basin yielded organic sulfur $\delta^{34}S$ values in the range of +5‰ to +13‰ and of +3.4‰ to +7.3‰, respectively. Coals sampled from the Green River coal region in Wyoming and Colorado also yield $\delta^{34}S$ values of organic sulfur ranging from +2.4‰ to +8.1‰ (Haciuey and Anderson, 1986). Although we did not determine the $\delta^{34}S$ values of organic sulfur, the isotopic data on OS dominated low sulfur Chinese coals (OS/TS > 80%) agree well with those reported previously (Fig. 2b). As shown in Fig. 2a, however, if OS/TS ratios were not taken into consideration, Chinese coals that contained <1% TS presented a wide range of $\delta^{34}S$ values of −2.9‰ to +35.3‰, only those having

<0.25% TS just showed a narrow range isotopically similar to low sulfur coals (<1% TS) previously reported. Nevertheless, a narrow range of mean $\delta^{34}S$ values was also observed for coals having <1% TS formed in D, P_1, T_3 and J_3 (Fig. 3b). These low sulfur coals, most of which have OS/TS > 70%, presented a mean $\delta^{34}S$ value of +10.2‰, +8.2‰, +11.8‰ and +7.2‰, respectively, within the apparently narrow range of values worldwide (Smith and Batts, 1974; Price and Sheih, 1979; Smith et al., 1982; Westgate and Anderson, 1984; Haciuey and Anderson, 1986). This further suggested that sulfur in low sulfur (<1% TS) Chinese coals is mainly in the form of organic sulfur.

The low sulfur coals are reported previously to have similar $\delta^{34}S$ values to that of plant sulfur from freshwater environments and modern freshwater peats. Freshwater peats from the Okefenokee Swamp, Georgia were found to range from +7‰ to +11‰ (Smith and Batts, 1974; Price and Sheih, 1979). The $\delta^{34}S$ values of dissolved sulfate of +4‰ (Mektiyeva et al., 1976), +3.6‰ (Mektiyeva and Pankina, 1968) and +3.5‰ to +8.1‰ (Rabinovich and Grinenko, 1979) are reported in modern freshwater environments whereas they are ~+20‰ in seawater. Because assimilation of sulfur by plants involves only a minor depletion in ^{34}S relative to dissolved sulfate in environmental waters (Mektiyeva et al., 1976; Krouse, 1988), the portion of the organic sulfur produced by plant assimilation will be isotopically equivalent to the sulfate. And thereby, Chukhrov et al. (1980) observed only a difference of <2‰ between the plants of central Yakutia in Russia and the sulfate source. Chou (1997) reported if freshwater sulfur available during plant growth is the principal source of sulfur in low sulfur (<1% total sulfur) coals, the $\delta^{34}S$ values of plants would range between +2‰ and +8‰. Likewise, if sulfur assimilated by plants came from seawater, the $\delta^{34}S$ values of plants would be also close to those of marine sulfate (~+20‰). This reflected coals derived from these two plants would be isotopically different if no isotope effects during post-depositional processes occurred as discussed below. Obviously, this is not the case for Chinese coals as shown in Fig. 5b. Based on the corresponding paleo-environments indicated by the B contents of coals, the $\delta^{34}S$ values of the low sulfur Chinese coals formed in marine environments are also observed within the range similar to those formed in freshwater environments. Accordingly, sulfur in low sulfur coals is considered to have been derived from the swamp vegetation which incorporated sulfur from either the surrounding freshwater or seawater with little isotopic fractionation. Similarly, Kalkreuth and Leckie (1989) reported that sulfur contents are generally very low although there is an important marine influence in Cretaceous coals of North America. This was also demonstrated by Rippon (1984) in a detailed study of the Clowne seam (Duckman-tian, English Midlands).

The post-depositional processes such as sulfur reduction-oxidation and sulfur immobilization-mineralization processes may play an eminent role in the sulfur contents and, to a certain extent, in their sulfur isotopic distribution. Although little work has addressed changes in $\delta^{34}S$ ratios of decomposing plant materials, Schoenau and Bettany (1989) suggested that labile organic sulfur fractions tended to have more positive $\delta^{34}S$ ratios than relatively recalcitrant organic sulfur fractions. So they believed that during the early stages of decomposition and sulfur mineralization, $\delta^{34}S$ values of the residual plant materials should decrease, reflecting the preferential loss of the isotopically heavier fractions. A contrary view was held by Novák et al. (1994), who believed that isotopically light sulfur may be continually released from deep peats over long term diagenesis. If a sulfur isotope effect during coalification did occur in Chinese coals, whether with a positive or negative fractionation factor (ε), the $\delta^{34}S$ values would not be homogeneous in low sulfur Chinese coals formed at D, P_1, T_3 and J_3 unless they underwent coalification of similar degree or the hydrolysable organic matter of original plants had been completely degraded (no isotopic effects). The latter may be right because the ranks of these Chinese coals are different. This suggests that the relatively isotopically homogeneous low sulfur coals in this study and in those previously studies could also possibly reflect constant $\delta^{34}S$ values of non-hydrolysable fraction rather than of the whole original precursor plants.

5.2. Isotopic composition of secondary sulfur epigenetically introduced

Coals attributed to non-marine settings in the world commonly show sulfur contents of <1% (e.g. Ayers and Kaiser, 1984), whereas high sulfur contents in coals are usually explained by the proximity of the original peat to marine waters during deposition. It has been suggested by previous investigators that sulfur was introduced into the coal forming environment primarily as sulfate (Casagrande et al., 1977). Since sulfate concentrations are typically a hundred times higher in seawater than in freshwater, the sulfate ions in seawater provide an abundant source of sulfur for coals (Gibling et al., 1989).

Kaplan (1983) suggested two potential main sources of sulfur in high sulfur coals. These are original plant sulfur assimilated during the growth of plants and secondary sulfur added from post-depositional environments during coalification. It is proposed by Holmes and Brownfield (1992) that secondary sulfur in high sulfur coals can be formed by either biogenic or non-biogenic reactions as follows:

(1) Biogenic secondary sulfur, produced by sulfate reducing bacteria, usually results in coal with a negative $\delta^{34}S$ value. In high sulfur coals, bacterial reduction of seawater sulfate from overlying beds may have produced the largest and most diverse isotopic effect in the sulfur cycle (Chambers and Trudinger, 1979; Dellwig et al., 2000). Sulfate reducing bacteria discriminate against the heavy ^{34}S isotopes and previous culture studies elucidated that the product is depleted in ^{34}S by 5–46‰ relative to the original sulfate source (Kemp and Thode, 1968; Chambers et al., 1975). During these processes, isotopically light sulfur was introduced into coals. Accordingly, the most probable source of ^{34}S depleted sulfur in Chinese coals came from the bacterial reduction of dissolved sulfate during the post-depositional coalification. Similar mechanisms are also found in other studies. For example, due to the addition of ^{34}S depleted secondary sulfur, the low $\delta^{34}S$ values in the Anderson-Wyodak seam have been observed (Haciuey and Anderson, 1986). Alternately, Goldhaber and Kaplan (1974) have suggested that although high sulfate concentrations resulted in significant fractionation during bacterial sulfate reduction (up to 50‰), low sulfate concentrations produce little fractionation under similar conditions. Thereby, possibly varying extents of microbial sulfur production during bacterial reduction of seawater sulfate resulted in the wide variability of the $\delta^{34}S$ values in Chinese coals.

(2) Non-biogenic secondary sulfur in (a) a partially closed system, in which secondary sulfur is derived from the incomplete reduction of epigenetically introduced sulfate, results in coal whose sulfur content is moderately high and whose isotopic signature ranges from +2‰ to −10‰; and (b) a closed system, in which secondary sulfur is derived from the total reduction of all epigenetically introduced sulfate sulfur, results in secondary sulfur having the same isotopic signature as the original sulfate. These have been demonstrated in a previous study on the northern Chinese coals which suggested that pyrite in coals turned isotopically heavier when the positional system turned from open to be closed (Zhou et al., 2000).

Coal influenced by marine incursion is usually believed to be high sulfur coal with a trend toward lighter isotopic sulfur (Westgate and Anderson, 1984). The high sulfur contents (>1% TS) and less positive $\delta^{34}S$ values in Chinese coals of Paleozoic age (Fig. 3a and b) may be associated with the repeated transgression occurring in southern China (IV), while the more positive $\delta^{34}S$ values of Mesozoic coals in northeastern China (I) and northwestern China (II) may be indicative of non-biogenic secondary sulfur. The much heavier sulfur in Chinese coals in this study may be also related to evaporites because evaporites usually have a highly

positive $\delta^{34}S$ values. For example, the $\delta^{34}S$ values of gypsum have a range from +10‰ to +35‰ (Clark and Fritz, 1997). So, the wide range of the $\delta^{34}S$ values in the Chinese coals suggests a complex origin, including biogenic and non-biogenic sulfur and even evaporates.

5.3. Sources of nitrogen in Chinese coals

As shown in Fig. 3c, Chinese coals of Devonian through Paleocene age contain relatively higher nitrogen than Mesozoic Chinese coals. This may be related to their original precursor plant species: The older Chinese coals (Paleozoic) mainly came from pteridophytes, while the important coal forming plants of the younger coals were gymnosperms and to some extent pteridosperms. Usually the former plants have more nitrogen content than the latter. According to Guo (1992), pteridophytes have protein contents of 10–15%, while there is <7% in gymnosperms.

It has been believed that the boron contents in marine and non-marine sediments are significantly different and have been found to be consistently sensitive to varying degrees of salinity (Landergreen and Manheim, 1963). The depositional environments in which the coals formed were classified accordingly (Goodarzi and Swaine, 1994). It is accepted that marine plants have higher $^{15}N/^{14}N$ ratios than terrigenous plants (Wada et al., 1975; Sweeney et al., 1978). Nissenbaum and Kaplan (1972) reported that marine humic acid generally contains more nitrogen than terrigenous humic acid. So it is possible that the nitrogen contents and $\delta^{15}N$ values of Chinese coals formed in marine depositional environments are higher than those in non-marine depositional environments (Fig. 5d). Similar results were found by Rigby and Batts (1986). They reported that tasmanite in marine depositional environment contained more ^{15}N than torbanites in a freshwater environment because the higher $^{15}N/^{14}N$ ratios found in tasmanite (+12.7‰) are in accord with the range reported for modern marine plankton of +3‰ to +13‰ (Miyake and Wada, 1967).

5.4. Nitrogen isotopic alteration during coalification

In this study, no systematic variation of the $\delta^{15}N$ values of the Chinese coals was observed with age (Fig. 3d), but a slight increase of the nitrogen contents and a slight decrease of the $\delta^{15}N$ values with the rank were found (Fig. 4d). Although Stiehl and Lehmann (1980) also found a positive correlation between the nitrogen contents and the rank and an increase in $\delta^{15}N$ values from the lignite to anthracite for a suite of European coals, they did not find a continuous variation of the $\delta^{15}N$ values and the relative nitrogen contents the rank during the coalification process. Rigby and Batts (1986) observed no correlation of $\delta^{15}N$ values with the rank for Australian coals. The decrease in $\delta^{15}N$ values of the Chinese coals with the rank, isotopic fractionation during organic degradation (coalification) and original precursor plant species are discussed below.

Generally, breakdown of pure organic matter preferentially mineralizes ^{14}N, potentially causing an enrichment in ^{15}N in the residue (e.g. Thornton and McManus, 1994). Recent studies by Yano et al. (in press) showed that non-labile N pool accounted for >75% of total N and was only slightly ^{15}N enriched relative to bulk N (by +1.3‰, on average). Nonetheless, it is impossible for the isotope effects to lead to the decrease of the $\delta^{15}N$ values of the Chinese coals with the rank. But some researchers hold a different issue that isotopic fractionation during release of amino compounds or ammonia as a consequence of bacterial degradation of organic matter can be negligible (e.g. Sweeney et al., 1980). So if nitrogen isotope ratios of organic matter do not appear to change by partial degradation during coalification, it might be expected that the $\delta^{15}N$ values of the Chinese coals would reflect primarily

the nitrogen isotope ratio in the non-hydrolysable organic matter of their primary plants. Therefore, the conclusion is reached that enrichment in ^{15}N in the residue after decomposition or that no isotopic fractionation would not result in the slightly decrease of the $\delta^{15}N$ values with the rank for the Chinese coals.

The correlation of both the nitrogen contents and the $\delta^{15}N$ values in Chinese coals with the rank may be associated with original precursor plant species. The bituminous and anthracite coals (high rank) in China occurred mainly at D to P_3, in which original precursor plants were high protein pteridophytes (Guo, 1992). Although we did not know the $\delta^{15}N$ values of their original precursor plants, nitrogen isotopic composition of protein may provide some information. Because the total protein within a cell has been found to be enriched in ^{15}N (~3‰) relative to bulk nitrogen (Macko et al., 1987), it might be expected that the higher protein pteridophytes would show heavier $\delta^{15}N$ values.

6. Summary and conclusions

This study has determined sulfur and nitrogen contents and their isotopic composition of Chinese coals. Some principal conclusions that can be drawn from the study are presented as follows:

(1) A narrow range of $\delta^{34}S$ values (0‰ to +10‰) was observed in low sulfur Chinese coals, which formed in either freshwater or marine environments although the whole original plant sulfur may be within a wide range. Low sulfur coals mainly contain non-hydrolysable organic sulfur of the original plants and are nearly isotopically constant in different ages. High sulfur Chinese coals (OS > 0.8%), often found in late Carboniferous (C_3) and late Permian (P_2) in southern China, contained two main sulfur sources (original plant sulfur and secondary sulfur). If post-depositional environments were influenced by seawater sulfate, secondary sulfur introduced and thus sulfur contents in Chinese coals are high and the $\delta^{34}S$ values ranged widely from −15‰ to +50‰ due to large isotopic effect produced by on-going biogenic or non-biogenic reactions. Repeated transgression occurred at Paleozoic era in southern China resulting in less positive $\delta^{34}S$ values in coals.

(2) The nitrogen contents in Chinese coals are mainly controlled by original precursor plant species. High nitrogen coals were formed in the pteridophytes dominated Paleozoic era and low nitrogen coals in gymnosperm dominated Mesozoic era. These also resulted in variations of nitrogen contents with the rank and different distribution pattern in the four main coal producing regions. As a whole, no systematic variation of the $\delta^{15}N$ values of the Chinese coals was observed with age or coal forming region. However, depositional environments of the original precursor plant influenced the $\delta^{15}N$ values of coals to some extent, with higher $\delta^{15}N$ values in marine environments than in freshwater environments.

References

ASTM, 1984. ASTM D2492: Standard Test Method for Forms of Sulfur in Coal, ASTM International, West Conshohocken, PA. <http://www.astm.org>.

ASTM, 1989. ASTM D3177: Standard Test Methods for total Sulfur in the Analysis Sample of Coal and Coke, ASTM International, West Conshohocken, PA. <http://www.astm.org>.

ASTM, 1999. ASTM D388-99e1: Standard Classification of Coals by Rank, ASTM International, West Conshohocken, PA. <http://www.astm.org>.

ASTM, 2002. ASTM D3179: Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke, ASTM International, West Conshohocken, PA. <http://www.astm.org>.

Ayers, W.B., Kaiser, W.R., 1984. Lacustrine-interdeltaic coal in the Fort Union Formation, Palaeocene, Powder River Basin, Wyoming and Montana, USA. In: Rahmani, R.A., Flores, R.M. (Eds.), Sedimentology of Coal and Coal-bearing Sequences. International Association of Sedimentologists, Special Publication 7, pp. 61–84.

Bokhoven, C., Theuwen, H.J., 1966. Determination of the abundance of carbon and nitrogen isotopes in Dutch coals and natural gas. Nature 211, 927–929.

Casagrande, D.J., Price, F.T., 1981. Sulfur isotope distribution in coal precursors. Geological Society of America Abstracts with Programs 13, 423–424.

Casagrande, D.J., Siefert, K., Breschinski, C., Sutton, N., 1977. Sulfur in peat-forming systems of the Okefenokee Swamp and Florida Everglades: origins of sulfur in coal. Geochimica et Cosmochimica 41, 161–167.

Chambers, L.A., Trudinger, P.A., 1979. Microbiological fractionation of stable sulfur isotopes: a review and critique. Geomicrobiology Journal 1, 249–293.

Chambers, L.A., Trudinger, P.A., Smith, J.W., Burns, M.S., 1975. Fractionation of sulfur isotopes by continuous cultures of *Desulfivibrio desulfuricans*. Canadian Journal of Microbiology 21, 1602–1607.

Chen, C.P., Mei, B.W., Cao, Y.C., 2004. Characteristics of nitrogen isotopic composition of oils in some Chinese basin. Science in China Ser. D 34, 721–727.

Cheng, H.H., Bremner, J.M., Edwards, A.P., 1964. Variations of nitrogen-15 abundance in soils. Science 146, 1574–1575.

Chou, L., 1997. Geological factors affecting the abundance, distribution, and speciation of sulfur in coals. In: Yang, Q. (Ed.), Geology of Fossil Fuels—Coal Proceedings of The 30th International Geological Congress, Part B, vol. 18. VSP, Utrecht, The Netherlands, pp. 47–57.

Chukhrov, F.S., Ermilova, L.P., Churikov, V.S., Nosik, L.P., 1980. The isotopic composition of plant sulfur. Organic Geochemistry 2, 69–75.

Clark, I.D., Fritz, P., 1997. Environmental Isotopes in Hydrology. CRC Press, New York. pp. 1–352.

Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., Zak, I., 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. Chemical Geology 28, 199–260.

Dellwig, O., Watermann, F., Brumsack, H.J., Gerdes, G., Krumbein, W.E., 2000. Sulfur and iron geochemistry of Holocene coastal peats, NW Germany: a tool for palaeo-environmental reconstruction. Paleontology 167, 359–379.

Freyer, H.D., 1978. Seasonal trends of NH_4^+ and NO_3^- nitrogen isotope composition in rain collected at Jülich, Germany. Tellus 30, 83–92.

Galloway, J.N., Zhao, D.-W., Xiong, J.-L., Likens, G.E., 1987. Acid rain: China, United States, and a remote area. Science 236, 1559–1562.

Gibling, M.R., Zentilli, M., McCready, R.G.L., 1989. Sulfur in Pennsylvania coals of Atlantic Canada: geologic and isotopic evidence for a bedrock evaporite source. International Journal of Coal Geology 11, 81–104.

Goldhaber, M.B., Kaplan, I.R., 1974. The sedimentary sulfur cycle. In: Goldberg, E.D. (Ed.), Marine Chemistry. The Sea, vol. 5. Wiley Interscience, New York, pp. 569–655.

Goodarzi, F., Swaine, D.J., 1994. The influence of geological factors on the concentration of boron in Australian and Canadian coals. Chemical Geology 118, 301–318.

Guo, C.T., 1992. Coal Chemistry. Chemical Industrial Press of China, Beijing (in Chinese).

Haciuey, K.C., Anderson, T.F., 1986. Sulfur isotopic variations in low-sulfur coals from the Rocky Mountain region. Geochimica et Cosmochimica Acta 50, 1703–1713.

Heaton, T.H.E., 1987. $^{15}N/^{14}N$ ratios of nitrate and ammonium in rain at Pretoria, South Africa. Atmospheric Environment 21, 843–852.

Heaton, T.H.E., 1990. $^{15}N/^{14}N$ ratios of NO_x from vehicle engines and coal-fired power stations. Tellus 42B, 305–307.

Hoering, T.C., 1955. Variations in nitrogen-15 abundance in naturally occurring substances. Science 122, 1233–1234.

Holmes, C.W., Brownfield, M.E., 1992. Distribution of carbon and sulfur isotopes in Upper Cretaceous coal of northwestern Colorado. In: McCabe, P.J., Parrish, J.T. (Eds.), Controls on the Distribution and Quality of Cretaceous Coals. Geological Society of America, Special Paper, pp. 57–68.

Hong, Y.T., Zhang, H.B., 1992. Sulfur isotope characteristic of coal in China and isotopic fractionation during coal burning. Science in China Ser. B 00B (8), 868–873 (in Chinese).

Kalkreuth, W., Leckie, D.A., 1989. Sedimentological and petrological characteristics of Cretaceous strandplain coals: a model for coal accumulation from the North

American Western Interior Seaway. International Journal of Coal Geology 12, 381–424.

Kaplan, I.R., 1983. Stable isotopes of sulfur, nitrogen and deuterium in recent marine environments. In: Arthur, M.A. (organizer), Stable Isotopes in Sedimentary Geology, SEPM Short Course No. 10. pp. 2/1–2/108.

Kemp, A.L.W., Thode, H.G., 1968. The mechanism of the bacterial reduction of sulphate and of sulphite from isotope fractionation. Geochimica et Cosmochimica Acta 32, 71–91.

Krouse, H.R., 1988. Sulfur isotope studies of the pedosphere and biosphere. In: Rundel, P.W., Ehleringer, J.R., Nagy, K.A. (Eds.), Stable Isotopes in Ecological Research. Springer-Verlag, New York, pp. 424–444.

Landergreen, S., Manheim, F.T., 1963. On the dependence of the distribution of heavy metals on facies. Fortschritte in der Geologe von Rheinland und Westfalen 10, 173–192.

Lü, C., Tian, H., 2007. Spatial and temporal patterns of nitrogen deposition in China: synthesis of observational data. Journal of Geophysical Research 112, D22S05. doi:10.1029/2006JD007990.

Macko, S.A., Fogel, M.L., Hare, P.E., Hoering, T.C., 1987. Isotopic fractionation of nitrogen and carbon in the synthesis of amino acids by microorganisms. Chemical Geology 65, 79–92.

Mektiyeva, V.L., Pankina, R.G., 1968. Isotopic composition of sulfur in aquatic plants and dissolved sulfate. Geochemistry International 5, 624–625.

Mektiyeva, V.L., Gavrilov, E.Y., Pankina, R.G., 1976. Sulfur isotopic composition in land plants. Geochemistry International 13, 85–88.

Miyake, Y., Wada, E., 1967. The abundance of $^{15}N/^{14}N$ in marine environments. Records of oceanographic works in Japan 9, 37–53.

Mukai, H., Tanaka, A., Fujii, T., Zeng, Y., Hong, Y., Tang, J., Guo, S., Xue, H., Sun, Z., Zhou, J., Xue, D., Zhao, J., Zhai, G., Gu, J., Zhai, P., 2001. Regional characteristics of sulfur and lead isotope ratios in the atmosphere at several Chinese urban sites. Environmental Science and Technology 35, 1064–1071.

Ni, J.Y., 1997. Composition Character of Sulfur and Trace Elements in Late Permian Coal of Guizhou Province, China. Ph.D. Dissertation. Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China.

Nissenbaum, A., Kaplan, I.R., 1972. Chemical and isotopic evidence for the in situ origin of marine humic substances. Limnology and Oceanography 17, 570–582.

Novák, M., Wieder, R.K., Schell, W.R., 1994. Sulfur during early diagenesis in Sphagnum peat: insights from $\delta^{34}S$ ratio profiles in ^{210}Pb-dated peat cores. Limnology and Oceanography 39, 1172–1185.

Novák, M., Jačková, I., Přechová, E., 2001. Temporal trends in the isotope signature of air-borne sulfur in central Europe. Environmental Science and Technology 35, 255–260.

Ohizumi, T., Fukuzaki, N., Kusakabh, M., 1997. Sulfur isotopic view on the sources of sulfur in atmospheric fallout along the coast of the sea of Japan. Atmospheric Environment 31, 1339–1348.

Price, F.T., Casagrande, D.J., 1991. Sulfur distribution and isotopic conditions in peats from the Okefenokee Swamp, Georgia and the Everglades, Florida. International Journal of Coal Geology 17, 1–20.

Price, F.T., Sheih, Y.N., 1979. The distribution and isotopic composition of sulfur in coal from the Illinois Basin. Economic Geology 74, 1445–1461.

Price, F.T., Sheih, Y.N., 1986. Correlation between the $\delta^{34}S$ of pyritic and organic sulfur in coal and oil shale. Chemical Geology 58, 333–337.

Pruett, L.E., Kreutz, K.J., Wadleigh, M., Aizen, V., 2004. Assessment of sulfate sources in high-elevation Asian precipitation using stable sulfur isotopes. Environmental Science and Technology 38, 4728–4733.

Rabinovich, A.L., Grinenko, V.A., 1979. Sulfate sulfur isotope ratios for USSR river water. Geochemistry International 16, 68–79.

Rigby, D., Batts, B.D., 1986. The isotopic composition of nitrogen in Australian coals and oil shales. Chemical Geology 58, 273–282.

Rippon, J.H., 1984. The Clowne seam, Marine Band, and overlying sediments in the Westphalian B of north Derbyshire. Proceedings of the Yorkshire Geological Society 45, 27–43.

Schoenau, J.J., Bettany, J.R., 1989. ^{34}S natural abundance variations in prairie and boreal forest soils. Journal of Soil Science 40, 397–413.

Smith, J.W., Batts, B.D., 1974. The distribution and isotopic composition of sulfur in coal. Geochimica et Cosmochimica Acta 38, 121–133.

Smith, P.H., Hudson, B.E., 1951. Abundance of ^{15}N in the nitrogen present in crude oil and coal. Science 113, 577.

Smith, J.W., Gould, K.W., Rigby, D., 1982. The stable isotope geochemistry of Australian coals. Organic Geochemistry 3, 111–131.

Standards Australia, 1998. AS1038.10.3-1998: Coal and Coke – Analysis and Testing: Determination of Boron Content – ICP–AES Method, Standards Australia, Sydney. <http://www.standards.com.au>.

State Bureau of Technical Supervision, 1993. GB 481-93, Sampling Method of Coal Sample for Production. Standardization Administration of the People's Republic of China, Beijing. <http://www.sac.gov.cn> (in Chinese).

State Bureau of Technical Supervision, 1996. GB 474-1996, Preparation of Coal Sample. Standardization Administration of the People's Republic of China, Beijing. <http://www.sac.gov.cn> (in Chinese).

Stiehl, G., Lehmann, M., 1980. Isotopenvariationen des Stickstoffs humöser und bituminijser natürlicher organischer Substanzen. Geochimica et Cosmochimica Acta 4, 1737–1746.

Sweeney, R.E., Liu, K.K., Kaplan, I.R., 1978. Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen. In: Robinson, B.W. (Ed.), Stable Isotopes in Earth Sciences. N.Z. D.S.I.R. Bulletin No. 220, pp. 9–26.

Sweeney, R.E., Kalil, E.K., Kaplan, I.R., 1980. Characterisation of domestic and industrial sewage in Southern California coastal sediments using nitrogen, carbon, sulphur and uranium tracers. Marine Environmental Research 3, 225–243.

Tang, Y.G., Ren, D.Y., 1996. The genesis of pyrites in coal. Geology Review 42, 64–70 (in Chinese).

Thornton, S.F., McManus, J., 1994. Application of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter provenance in estuarine systems: evidence from the Tay estuary, Scotland. Estuarine, Coastal and Shelf Science 38, 219–233.

Wada, E., Kadonaga, T., Matsuo, S., 1975. [15]N abundance in nitrogen of naturally occurring substances and global assessment of denitrification from isotopic viewpoint. Geochemistry Journal 9, 139–148.

Wang, X., Zhu, L., Wang, J., 1992. The Forming and Distribution of Coalfields in China. Science Publishing House, Beijing (in Chinese).

Westgate, L.M., Anderson, T.F., 1984. Isotopic evidence for the origin of sulfur in the Herrin #6 coal member of Illinois. International Journal of Coal Geology 4, 1–20.

Xiao, H.Y., Liu, L.Q., 2002. Sources of nitrogen and sulfur in wet deposition at Guiyang, Southwest China. Atmospheric Environment 36, 5121–5130.

Xiao, H.Y., Tang, C.G., Liu, X.Y., Xiao, H.W., Liu, C.Q., 2008. Sulphur isotopic ratios in mosses indicating atmospheric sulphur sources in southern Chinese mountainous areas. Geophysical Research Letters 35, L19807. doi:10.1029/2008GL034255.

Xiao, H.Y., Tang, C.G., Xiao, H.W., Liu, X.Y., Liu, C.Q., 2009. Identifying the change of atmospheric sulphur sources in China using isotopic ratios in mosses. Journal of Geophysical Research 114, D16304. doi:10.1029/2009JD012034.

Xu, X., Chen, C., Qi, H., He, R., You, C., Xiang, G., 2000. Development of coal combustion pollution control for SO_2 and NO_x in China. Fuel Processing Technology 62, 153–160.

Yanagisawa, F., Sakai, H., 1983. Thermal decomposition of barium sulfate–vanadium pentaoxide–silica glass mixtures for preparation of sulfur dioxide in sulfur isotope ratio measurements. Analytical Chemistry 55, 985–987.

Yano, Y., Shaver, G.R., Giblin, A.E., Rastetter, E.B., 2010. Depleted ^{15}N in hydrolysable-N of arctic soils and its implication for mycorrhizal fungi–plant interaction. Biogeochemistry doi:10.1007/s10533-009-9365-1.

Zhou, C.G., Yang, Q., Kang, X.D., Tang, D.Z., Liu, D.M., 2000. Sulfur isotope evidence of pyrite generation in coal of late Palaeozoic in Northern China. Coal Geology of China 12 (1), 19–22 (in Chinese).