



# Article Distribution of Se in Floating Coals with Densimetric Fractions in China

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Abstract: Scholars at home and abroad have studied the concentrations of Se in coal and the relationship between Se and sulfur assignment. However, little attention has been paid to the study of Se in floating coal, especially the distribution pattern of Se in floating coal of densimetric fractions and the influencing factors. A total of 138 coal samples were collected from 14 provinces and cities in China to test the Se and sulfur concentrations in coal, and we carried out the comparison of Se with forms of sulfur with 81 of them. A total of 10 coal samples were selected for float-and-sink analyses to investigate the distribution pattern of Se in floating coal. The results showed that the average Se concentration of Chinese coal was 2.26 µg/g, which is identical with the results of previous research studies, which found an average Se concentration of 2~3 µg/g. Selenium was not uniformly distributed in floating coals of densimetric fractions but it had some regularity. The main controlling factor was the sulfur content in the coal. The Se concentrations of the high-sulfur coal showed a "linear growth" distribution with an increasing density, the Se concentrations of the floating coal in each densimetric fraction increased slowly and the Se concentrations of the floating coal of a densimetric fraction > 2.00 g/cm<sup>3</sup> increased sharply. The other controlling factor was the ash yield of the coal. The Se concentrations of the low-medium-sulfur floating coal showed a "parabolic-like" distribution, i.e., low Se concentrations at both ends and high Se concentrations at the middle densimetric fraction. With the increase in the ash content of the coal from 18.23% to 51.92%, the densimetric fraction with the highest Se concentration gradually progressed from 1.40 g/cm<sup>3</sup> to 1.50 g/cm<sup>3</sup>, 1.60 g/cm<sup>3</sup> and 1.80 g/cm<sup>3</sup> in order. The correlation between the selenium of the raw coal from different regions and the total sulfur, pyrite sulfur and organic sulfur was not significant. However, there existed a significant correlation between Se, total sulfur, pyrite sulfur and organic sulfur in floating coals from the same mining area and depositional environment, among which pyrite sulfur was the most correlated with Se, followed by total sulfur and organic sulfur.

Keywords: coal; selenium; sulfur; pyrite sulfur; ash content; floating coal

# 1. Introduction

Coal is an important fossil energy source and can be widely used in thermal power generation, the chemical industry, steel, construction, the environment and people's livelihood; among these areas, power generation is the area that uses the most coal, whereby coal is used as a fossil energy source. China is one of the world's richest countries in terms of coal resource reserves and is also the world's largest consumer of coal. In 2021, the production of raw coal was 4.13 billion tons, and coal consumption accounted for 56.0% of China's total energy consumption [1,2]. Coal contains carbon, oxygen, sulfur, hydrogen, nitrogen, silicon, aluminum, iron, titanium, calcium, magnesium, potassium, sodium and other major elements. In addition, coal also contains trace elements such as germanium,



Citation: Zhang, G.; Feng, Q.; Zhao, H.; Zhang, N.; Wu, M.; Wang, X.; Wen, M.; Deng, Y.; Yang, Z. Distribution of Se in Floating Coals with Densimetric Fractions in China. *Minerals* **2023**, *13*, 396. https:// doi.org/10.3390/min13030396

Academic Editors: Jinhe Pan, Wencai Zhang, Wei Cheng and Saeed Chehreh Chelgani

Received: 12 January 2023 Revised: 3 March 2023 Accepted: 7 March 2023 Published: 13 March 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). gallium, uranium, thorium, vanadium, mercury, arsenic, selenium and rare earth due to the coal-forming environment, geological structure and degree of coal metamorphism [3–5]. The distribution and enrichment mechanism of Se in coal and its environmental and health effects are of great interest [6-10]. Selenium is a micronutrient that is essential for the life activities of humans, animals and plants [11,12]. The right amount of selenium can not only promote the metabolic growth of crops and improve crop yield and quality, but it also has immune-enhancing, anticancer and antiaging effects on humans and animals [13,14]. Therefore, it is known as the "longevity element" and "king of anti-cancer" [15]. Humans and animals with a selenium deficiency will show abnormal symptoms such as Keshan disease macrosomia and liver disease [16,17]. Meanwhile, there are two sides to the biological effect of selenium, i.e., it can become an environmental toxin in excess [18,19]. It will affect the growth and development of crops and eventually act in the food chain, and this will affect human and animal health and even cause selenium toxicity with symptoms such as hair loss, discolored and ulcerated nails, lameness, adenomas, cirrhosis of the liver and even cancer [20,21]. Most of the Se in coal is emitted into the atmosphere with coal-fired power generation. Selenium released from coal combustion is the most important anthropogenic source of selenium in the atmosphere [22,23]. In the last century, residents of western Hubei and southern Shaanxi in China burned large amounts of selenium-rich "stone coal" for heating, drying maize and chili and fumigating soil for fertilizer, which led to excessive selenium levels in indoor air, outdoor soil, edible staple/side foods and drinking water, which caused the "soot-type selenium poisoning" endemic disease [24]. Therefore, the study of Se concentrations and distribution characteristics in coal is of great significance for environmental protection and health in China, where coal consumption accounts for more than half of China's energy consumption.

As of today, scholars at home and abroad have carried out fairly systematic studies on the concentration, distribution and occurrence mechanisms of Se in coal. It is generally believed that the enrichment of Se in coal is significantly correlated with sulfur [8,9,24,25]. The coal with high selenium concentrations in the USA, Russia, Uzbekistan, Bulgaria, Greece, Turkey and China are all high-sulfur coals, which further validates the correlation between selenium and sulfur [26–28]. Overall, Se can not only exist in inorganic sulfur minerals as inorganic selenium but also coexist with organic sulfur in the form of organoselenium compounds [29]. Systematic evidence from coal petrography, scanning electron microscopy and electron probe microanalysis further indicates that Se mainly occurs in sulfide minerals such as pyrite (FeS<sub>2</sub>), galena (PbS) and sphalerite (ZnS) in the homogeneous form in coal [30–32]. Among them, the correlation between pyrite and selenium is particularly significant [28,33], as sulfur and selenium share a chemical affinity and substitutability in pyrite [32,34].

The coal float-and-sink analysis is a physical coal-sorting method that uses gravity separation, which is effective when sorting coals with high inorganic sulfur (e.g., pyrite) but not when sorting coals with high organic sulfur [35–37]. Sulfide minerals such as pyrite tend to be enriched in floating coals of relatively large densimetric fractions because of their high density. Therefore, the distribution of Se concentrations and reserve mechanisms in floating coals of densimetric fractions may differ significantly [38]. It is promising that the float-and-sink analyses on coal will reveal the distribution of Se concentrations in floating coals of densimetric fractions, the mechanism of Se reserves and the correlation between Se and forms of sulfur [39,40]. So far, little research has been carried out to study selenium partition in floating coals of densimetric fractions using coal float-and-sink analyses. However, previous studies have mainly focused on smaller densimetric fractions of floating coals, meaning they have failed to cover the larger densimetric fractions of floating coal enriched in pyrite. In addition, research has rarely focused on the correlation between Se and the form and ash of sulfur in floating coals of densimetric fractions. To this end, a certain number of coal samples were collected from all over China to determine the Se and sulfur concentrations in coal. Then, representative coal samples were selected to determine the forms of sulfur to determine the distribution characteristics of organic

and inorganic sulfur. A total of 10 representative coal samples were selected for floatand-sink analyses to study the distribution of Se in floating coals of densimetric fractions and to reveal the correlation between Se and forms of sulfur in coal. This project will provide theoretical support to clarify the mechanism of Se distribution in floating coals of densimetric fractions.

## 2. Materials and Methods

## 2.1. Sample Collection

A total of 138 coal samples from borehole were collected from 14 provinces, including Inner Mongolia, Xinjiang, Ningxia, Gansu, Shanxi, Shaanxi, Henan, Shandong, Anhui, Jiangsu, Jiangxi, Fujian, Guizhou and Chongqing. This study focuses on the distribution law of selenium in floating coal of different density grades. In order to pick qualified flotation coal samples, the sample collection number was not proportional to the distribution weight of the coal resource reserves in the provinces of China because the Se concentrations of Chinese coal have the characteristic of "low in the north and high in the south" in terms of geographical distribution. The samples were dried to air dryness, crushed and split step by step and were finally prepared as 0.2 mm analytical samples to test the Se and sulfur concentrations in the coal. Tests on forms of sulfur were conducted on 81 coal samples to analyze the correlation between Se and inorganic and organic sulfur in coal.

A total of 10 coal samples with Se concentrations greater than 2.0  $\mu$ g/g were selected while considering the ash, sulfur and coal type for the float-and-sink analysis. To enhance the representativeness of the samples, the coal type, sulfur content and ash content in the coal were taken into consideration during sampling. Among the 10 coal samples, in terms of the type of coal, there were 8 gas coals (QM), 1 gas fertilizer coal (QF) and 1 1/3 coking coal (1/3 JM); in terms of the sulfur content in the coal, there were 5 extra-low-sulfur coals, 1 low-sulfur coal, 2 medium–high-sulfur coals and 2 high-sulfur coals; in terms of the ash content in the coal, there were 2 high ash coals, 3 medium–high ash coals, 1 medium ash coal and 4 low–moderate ash coals. The sample information is shown in Table 1.

Table 1. Research content and sample distribution.

Research Content	Number of Samples	The Distribution of Samples
The content of selenium and sulfur in coal.	138	Inner Mongolia (17), Xinjiang (13), Ningxia (4), Gansu (24), Shanxi (4), Shaanxi (6), Henan (8), Shandong (9), Anhui (9), Jiangsu (8), Jiangxi (3), Fujian (2), Guizhou (28), Chongqing (1) and other (2).
Forms of sulfur in coal, the correlation between selenium in coal and different forms of sulfur.	81	Inner Mongolia (7), Xinjiang (10), Ningxia (3), Shanxi (4), Shaanxi (6), Henan (8), Shandong (9), Anhui (9), Jiangsu (8), Guizhou (15) and others (2).
The distribution law of selenium and sulfur in floating coal was studied with floating and sinking experiments.	10	Anhui (7), Shandong (1), Jiangsu (1) and Guizhou (1).

#### 2.2. Instruments and Methods for Tests

All the tests were conducted in the Jiangsu Design Institute of Geology for Mineral Resources (the Testing Center of China National Administration of Coal Geology (CNACG)), China. The test instruments were in the best analytical condition. The chemical reagents were all analytically pure. The experimental water was deionized. The ash yields in this paper were based on D3175-17 (2017) in the ASTM standards [41], and the sulfur forms and total sulfur in the coal were based on D3167-02 and D2492-02 in the ASTM standards [42,43].

The AFS-8330 atomic fluorescence photometer developed by Beijing Jitian Instrument Co., Ltd., Beijing, China, was used for Se concentration (Se d) testing, of which the wavelength was 196.1 nm and the lamp was a selenium hollow cathode lamp. We weighed 1.00 g of the coal sample, mixed it evenly with 1.5 g of an Eschka reagent (magnesium oxide: anhydrous sodium carbonate mass ratio 1:1) and left it in a muffle furnace at 800 °C for 3 h. After dissolving the hydrochloric acid with a relative density of 1.18, the Se concentration in the coal was determined with a blank test and standard curve of Se as a reference.

The coulometric sulfur analyzer was used to measure the total sulfur concentration in the coal (St, d). The instrument was capable of heating up to 1200 °C or more. The platinum electrode response time was less than 1 s. The electromagnetic stirrer speed was about 500 r/min and is continuously adjustable. The Coulomb integrator electrolytic current 0~350 mA range integration linearity error was less than 0.1%. The electromagnetic pump supply capacity was 1500 mL/min. We weighed 0.05 g of the coal sample and covered it with a thin layer of tungsten trioxide. The pumping flow rate was 1000 mL/min. The coal sample was automatically sent to the constant temperature zone of  $1150 \pm 10$  °C in the tube furnace for determination. The forms of sulfur in the coal were divided into sulfate sulfur (Ss), iron sulfide sulfur (Sp) and organic sulfur (So). Among them, sulfate sulfur (Ss) was determined by boiling the coal sample with dilute hydrochloric acid to leach out the sulfate in the coal to produce barium sulfate precipitate. The sulfate sulfur concentrations in the coal were calculated according to the mass of barium sulfate. The determination of iron sulfide sulfur (Sp) was performed by leaching the nonsulfur iron ore from the coal with dilute hydrochloric acid. After leaching, the coal sample was dissolved with dilute nitric acid to titrate the iron in the nitric acid leachate with potassium dichromate. The iron sulfide sulfur concentrations of the coal were then calculated as the mass of the iron. The organic sulfur (So) was equal to the total sulfur minus the sulfate sulfur (Ss) and the iron sulfide sulfur (Sp), i.e., So = St - (Ss + Sp).

The ash content of the coal was measured using a balance and a muffle furnace. We weighed 1 g of the coal sample into the muffle furnace. Then, we heated it to  $815 \pm 10$  °C at a certain rate. We ashed and cauterized the sample until the mass was constant. The mass fraction of the residue to the mass of the coal sample was taken as the ash content of the coal sample. The coal samples to be tested were initially dried to an air-dry state with the test mentioned above. When measuring selenium, sulfur and various forms of sulfur, the air-drying base moisture of the coal was measured synchronously.

#### 2.3. Float-and-Sink Analyses

Pyrite (FeS<sub>2</sub>) is a common mineral in coal, with a specific gravity of 4.9–5.2, which is much heavier than that of coal. Sulfur and Se in coal tend to be codistributed in pyrite, so the float-and-sink analysis was designed to study the reserve pattern of Se and sulfur in the coal of densimetric fractions. The Se concentrations of the Chinese coal were characterized by "low in the north and high in the south". With selenium as the preferred index (Se d >2.00  $\mu$ g/g) and sulfur as the auxiliary index, 10 coal samples were selected for the float-and-sink analyses, including 1 from Xinwen, Shandong, 1 from Xuzhou, Jiangsu, 1 from Huaibei, Anhui, 6 from Huainan, Anhui and 1 from Kaiyang, Guizhou. They were also analyzed and tested for ash, sulfur, selenium and forms of sulfur. The test data are shown in Table 2.

The flotation solution used in the float-and-sink analysis was composed of gasoline, tetrachloroethylene (C<sub>2</sub>Cl<sub>4</sub>) and tribromomethane (CHBr<sub>3</sub>). The gasoline was No. 120 solvent gasoline, of which the main components were aliphatic hydrocarbon compounds, which are colorless and transparent and have a density  $\leq 0.730$  g/cm<sup>3</sup> and a relative density of 0.99; tetrachloroethylene (C<sub>2</sub>Cl<sub>4</sub>), which is a colorless transparent liquid of analytical purity and has a density (20 °C) of 1.621–1.624 g/mL; and tribromomethane (CHBr<sub>3</sub>), which has a density (20 °C) of 2.087–2.093 g/mL and is analytically pure. The flotation solution is commonly used when conducting flotation experiments on coal in China, and it was prepared according to China's "Method for float and sink analysis of coal" (GB/T478-2008) standard. Previous studies have indicated that some organic compounds and heavy metals (e.g., Copper, Zinc) in coal may be leached out by the flotation solution during coal flotation [44,45]. Since part of selenium is bonded to the organic matter in coal, the organic Se in coal could also be leached out by the flotation solution alongside the leaching of organic matter. However, a study on the effluents of the Washereis, which use similar

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flotation agents (e.g., pine oil, diesel oil) to wash Se-bearing coals, discovered that the Se concentrations were all below the detectable limit [45]. Moreover, the mass losses of the floating coal that were determined with the 11flotation experiments were all very small in this study (averaging 1.02%, standard deviation 0.23%) and were far below the mass loss requirement of 2% according to China's "Method for float and sink analysis of coal" standard. The mass loss data of flotation in this study could imply that the leach of organic matter and organic Se during flotation should be very limited. In addition, the research focus of this paper is to reveal the distribution of Se in floating coals at different densimetric fractions, and a small dissolution of Se during coal flotation imposes very limited influence on the distribution of Se in floating coals.

**Table 2.** Ash (%), selenium ( $\mu$ g/g), total sulfur (%) and morphological sulfur (%) content and proportion of form sulfur (%) in 10 coal samples.

Samples	A <sub>d</sub>	Se <sub>d</sub>	S <sub>t, d</sub>	S <sub>p, d</sub>	S <sub>s, d</sub>	S <sub>o, d</sub>	P/T	S/T	O/T
1	23.02	5.14	0.14	0.02	0.00	0.12	14.29	0.00	85.71
2	51.92	4.28	0.23	0.05	0.00	0.18	21.74	0.00	78.26
3	13.44	6.10	3.62	2.95	0.22	0.45	81.49	6.08	12.43
4	42.04	3.94	0.42	0.14	0.02	0.26	33.33	4.76	61.91
5	31.87	5.96	0.16	0.02	0.00	0.14	12.50	0.00	87.50
6	39.27	4.70	2.12	1.47	0.08	0.57	69.34	3.77	26.89
7	18.23	4.90	0.37	0.06	0.02	0.29	16.22	5.40	78.38
8	16.85	8.32	2.94	1.82	0.05	1.06	61.90	1.70	36.05
9	10.17	3.97	0.59	0.17	0.03	0.39	28.81	5.08	66.10
10	30.30	2.46	3.97	2.46	0.04	1.47	61.96	1.01	37.03

A, ash yield; Se, selenium; St, total sulfur; Ss, sulfate sulfur; Sp, pyritic sulfur; So, organic sulfur; d, dry basis; P/T, 100pyritic sulfur/total sulfur; S/T, 100sulfate sulfur/total sulfur; O/T, 100organic sulfur/total sulfur.

The 10 coal samples selected in this study were all bituminous coals, with a bulk density of about 1.4 g/cm<sup>3</sup>. The Test Method for the Floatation and Sedimentation of Coal (GB/T478-2008) also documented that the minimum density level of the coal floation test was 1.4 g/cm<sup>3</sup>. To make up for the shortcomings of previous studies, five densimetric fractions of 1.40 g/cm<sup>3</sup>, 1.50 g/cm<sup>3</sup>, 1.60 g/cm<sup>3</sup>, 1.80 g/cm<sup>3</sup> and 2.00 g/cm<sup>3</sup> were designed for the float-and-sink analysis, and the densities of the floating and sinking solutions were measured via densitometry. The ratios of the three reagents for each densimetric fraction are shown in Table 3.

**Table 3.** The proportion of gasoline (%), tetrachloroethylene ( $C_2Cl_4$ ) and bromomethane (CHBr3) reagents under different density grades (%).

Composition of Floating Liquid Reagents	1.40 g/cm <sup>3</sup>	1.50 g/cm <sup>3</sup>	1.60 g/cm <sup>3</sup>	1.80 g/cm <sup>3</sup>	2.00 g/cm <sup>3</sup>
gasoline	34.92	19.05	0.00	0.00	0.00
$C_2Cl_4$	65.08	80.95	100.00	61.70	19.15
CHBr <sub>3</sub>	0.00	0.00	0.00	38.30	80.85

A total of 10 pieces of coal samples were made into about 3 mm of coal powder. About 500 g of the coal samples were selected separately, and in the order of  $1.40 \text{ g/cm}^3$ ,  $1.50 \text{ g/cm}^3$ ,  $1.60 \text{ g/cm}^3$ ,  $1.80 \text{ g/cm}^3$  and  $2.00 \text{ g/cm}^3$ , six floating subsamples of  $>1.40 \text{ g/cm}^3$ ,  $1.40-1.50 \text{ g/cm}^3$ ,  $1.50-1.60 \text{ g/cm}^3$ ,  $1.60-1.80 \text{ g/cm}^3$ ,  $1.80-2.00 \text{ g/cm}^3$  and  $>2.00 \text{ g/cm}^3$  were floated in turn. The mass and percentage of each densimetric fraction coal sample were calculated for each sample, and finally, 60 subsamples of 10 floating coal samples were obtained. The test was carried out after drying.

# 3. Results and Discussion

## 3.1. Distribution and Main Control Factors of Se in Chinese Coals

The coal samples taken in this study were all borehole samples. The measured Se concentrations of 138 coal samples are shown in Table 4, where the maximum value was 12.97 µg/g, the minimum value was 0.00 µg/g and the arithmetic mean was 2.26 µg/g, which lies in the range of 2 µg/g to 3.86 µg/g [24,35]. Bai et al., (2003) weighted coal from coal-proven reserves and found that the average concentration was 2.82 µg/g. Additionally, they classified Chinese coals into four classes: extra-low selenium coal (Se d ≤ 0.50 µg/g), low selenium coal (Se d = 0.50–2.00 µg/g), medium selenium coal (Se d = 2.00–10.00 µg/g) and high selenium coal (Se d > 10.00 µg/g) [35].

Sample Location	Minimum	Maximum	Average	Number of Samples	Standard Deviation
Inner Mongolia	0.01	4.50	0.88	17	1.47
Xinjiang	0.00	0.26	0.09	13	0.09
Gansu	0.07	0.44	0.19	24	0.34
Ningxia	0.89	2.96	1.95	4	0.75
Shanxi	2.05	5.02	3.74	4	1.09
Shandong	1.06	12.97	5.66	9	3.63
Henan	2.11	9.32	4.38	8	2.79
Anhui	2.29	8.55	5.32	9	2.12
Shaanxi	0.01	0.61	0.26	6	0.21
Jiangsu	2.18	3.97	2.94	8	0.64
Jiangxi	0.16	0.71	0.50	3	0.24
Chongqing	0.42	0.42	0.42	1	-
Fujian	0.10	0.25	0.18	2	0.075
Guizhou	0.53	9.91	3.50	28	1.93
Others	4.10	5.49	4.80	2	0.70
This study	0.00	12.97	2.26	138	2.56

**Table 4.** Contents of selenium in coals from various provinces  $(\mu g/g)$ .

After comparing the weighted average with the research results of Chen et al. (2002) and Bai et al. (2003) [24,35], it was found that the average concentration of selenium in Chinese coal was 2.82  $\mu$ g/g, which is in full agreement with the weighted average concentrations of 2.82  $\mu$ g/g of coal proven reserves in different coal gathering areas found by Bai et al. (2003) [35]. The coal samples and quantities taken by each study varied greatly, and the sample uniformity and representativeness were also different. Especially, the distribution of the coal resources in China was not uniform, and the geological period and thickness of the coal formation were very variable.

Since the type, quantities, homogeneity and representativeness of the coal samples used in each study varied greatly, it is reasonable that the concentrations of Se in the Chinese coal used in different studies were not completely consistent. For example, Dai et al., (2006) calculated that the average concentration of Se in Chinese coal was 2.47  $\mu$ g/g [46], Wang et al., (2012) concluded that the average concentration of Se in Chinese coal was 3.91  $\mu$ g/g [47] and Zhang et al., (2007) considered that the average concentrations of Se in Chinese coal was 5.60  $\mu$ g/g and divided the Se in Chinese coal into the low Se fraction (<2  $\mu$ g/g), which includes the coal in Meng Liaoxin; the medium–low fraction (2–5  $\mu$ g/g), which includes the coal in Jilin Shaanxi, Guizhou, Yunnan, Sichuan, Shandong, Shanxi and Hunan; and the high Se fraction (>5  $\mu$ g/g), which includes the coal in Chinese to coal in Chongqing, Anhui, Jiangsu and Hubei [48]. Combined with previous studies, it is reasonable to conclude that the average Se concentration of Chinese coal is 2–3  $\mu$ g/g.

In terms of the Se concentrations in the 138 coal samples, the highest was found in the samples from Shandong, which had an average concentration of 5.66  $\mu$ g/g, followed by the samples from Anhui at 5.32  $\mu$ g/g, Henan at 4.38  $\mu$ g/g, Shanxi at 3.74  $\mu$ g/g and Guizhou at 3.50  $\mu$ g/g. The lowest concentration was 0.09  $\mu$ g/g in the coal from Xinjiang, followed by the coal from Fujian at 0.18  $\mu$ g/g and the coal from Gansu at 0.19  $\mu$ g/g. Overall, the provinces with coal with high Se concentrations were distributed in East China and

Guizhou. The Se concentrations in the northern coals, such as those found in Xinjiang, Inner Mongolia and Gansu, were lower. The statistical analysis on the Se and sulfur concentrations in the coal of the above-mentioned provinces in China are shown in Table 4. In terms of the perspective of geographical distribution, the coal reserves in China showed the phenomenon of "more in the north and less in the south", but the Se concentrations in the coal showed the distribution characteristics of "low in the north and high in the south".

In addition to the influence of coal-forming plants and the environment, the Se concentrations in coal are also influenced by magmatic-hydrothermal activity, tectonic action and groundwater activity [3,49–55]. It is generally believed that the coal-forming environment and magmatic-hydrothermal effects are two dominant factors responsible for the "low in the north and high in the south" distribution of Se in Chinese coal. The Se concentrations of marine and land-sea interaction coal-forming environments are higher than that in terrestrial coal. The seawater can change the pH of peat bog, which is favorable to the formation of sulfide minerals, which thus favors the enrichment of selenium [3,5,9]. The coal in North and East China was mostly influenced by seawater and had a high Se concentration. The Late Permian coal-bearing rock series in Guizhou was formed during a large-scale transgression, and the sedimentary facies from west to east changed from continental facies to marine facies, while the continental coal-forming facies is common in the northwest and northeast of Guizhou, so the Se concentrations are lower [24,56]. Moreover, sulfide minerals from volcanic activity may be a key source of Se in coal. The frequent magmatic activity in southeastern China leads to relatively high Se concentrations in the coal from this region [3,48,49].

# 3.2. Distribution Characteristics of Se in Floating Coal

## 3.2.1. Distribution of Se in Floating Coals

In order to reveal the distribution of selenium in densimetric fractions more clearly, the sulfur yield (V<sub>S</sub>) and selenium yield (V<sub>Se</sub>) were defined in this study and then calculated as the cumulative yield of sulfur and selenium ( $\sum V_S$ ,  $\sum V_{Se}$ ) in each float densimetric fraction accordingly. The sulfur yield (V<sub>S</sub>) is the percentage of sulfur concentrations in a subsample of a certain densimetric fraction of the total sample coal, as shown in equation (1). The Se yield (V<sub>Se</sub>) is the percentage of Se in a density subsample of the total sample coal, as shown in Equation (2). The cumulative yield ( $\sum V_S$ ,  $\sum V_{Se}$ ) represents the algebraic sum of the yields of sulfur and selenium at densimetric fractions, respectively. The 3# float–sink sample was high-sulfur coal, and a subsample of the >2.00 g/cm<sup>3</sup> densimetric fraction showed the rapid enrichment of selenium and sulfur. Accordingly, a 2.10 g/cm<sup>3</sup> densimetric fraction was added in the float-and-sink analyses to deepen the study (3#\*). A summary of the float-and-sink analysis data is shown in Table 5.

$$V_{\rm S} = {\rm Mn} \times {\rm Sn} / \sum {\rm Mi} \times {\rm Si}$$
<sup>(1)</sup>

Samples	DFL	QFC	PTS	S <sub>t,d</sub>	Se,d	SY	CYS	SEY	CYSE	A <sub>d</sub>
	≤1.40	182	32.50	0.22	4.77	39.86	39.86	29.29	29.29	7.49
	1.40 - 1.50	181	32.30	0.20	6.01	36.01	75.87	36.70	65.99	18.43
1.1	1.50 - 1.60	86	15.30	0.18	6.43	15.38	91.24	18.66	84.65	30.81
1#	1.60 - 1.80	49	8.70	0.12	5.44	5.84	97.09	8.99	93.64	38.78
	1.80-2.00	28	5.00	0.08	4.12	2.23	99.32	3.89	97.53	53.67
	>2.00	34	6.10	0.02	2.15	0.68	100.00	2.47	100.00	62.82
	$\leq 1.40$	84	17.00	0.52	5.64	30.26	30.26	23.03	23.03	7.17
	1.40 - 1.50	40	8.10	0.44	7.96	12.21	42.46	15.48	38.51	16.39
0.11	1.50 - 1.60	20	4.00	0.40	8.91	5.55	48.01	8.66	47.18	26.36
2#	1.60 - 1.80	23	4.70	0.36	9.48	5.74	53.75	10.60	57.78	39.52
	1.80-2.00	34	7.00	0.23	5.55	5.46	59.21	9.17	66.95	58.15
	>2.00	293	59.20	0.20	2.32	40.79	100.00	33.05	100.00	73.19

Table 5. Content and distribution of ash, total sulfur and selenium of float-sink experiments.

Table 5. Cont.

Samples	DFL	QFC	PTS	S <sub>t,d</sub>	Se,d	SY	CYS	SEY	CYSE	A <sub>d</sub>
	<1.40	372	66.90	0.67	0.82	12.54	12.54	16.21	16.21	nd
	1.40 - 1.50	85	15.30	1.01	2.56	4.34	16.88	11.56	27.78	nd
	1.50-1.60	23	4.10	1.63	4.13	1.90	18.78	5.05	32.82	nd
3#	1.60-1.80	19	3.40	2.10	6.00	2.02	20.80	6.06	38.88	nd
	1.80-2.00	6	1.10	3.01	8.07	0.92	21.72	2.57	41.46	nd
	>2.00	51	9.20	30.28	21.60	78.28	100.00	58.54	100.00	nd
	≤1.40	135	22.80	0.45	3.72	25.16	25.16	20.23	20.23	8.00
	1.40 - 1.50	63	10.60	0.52	6.11	13.57	38.72	15.51	35.74	18.93
	1.50-1.60	70	11.80	0.46	7.04	13.34	52.06	19.85	55.60	29.17
4#	1.60-1.80	96	16.20	0.54	5.47	21.46	73.53	21.16	76.75	42.62
	1.80-2.00	56	9.40	0.84	4.28	19.26	92.79	9.66	86.41	55.41
	>2.00	173	29.20	0.10	1.95	7.21	100.00	13.59	100.00	79.09
	$\leq 1.40$	171	29.70	0.14	3.64	34.20	34.20	25.01	25.01	9.39
	1.40 - 1.50	106	18.40	0.17	5.54	25.75	59.95	23.60	48.61	20.48
<b>F</b> #	1.50 - 1.60	81	14.10	0.15	6.91	17.34	77.29	22.49	71.11	28.51
5#	1.60 - 1.80	111	19.30	0.10	4.75	15.87	93.16	21.19	92.29	42.27
	1.80-2.00	27	4.70	0.06	3.62	2.32	95.48	3.93	96.22	58.35
	>2.00	79	13.70	0.04	1.19	4.52	100.00	3.78	100.00	78.34
	$\leq 1.40$	103	22.00	0.76	2.40	8.57	8.57	15.40	15.40	7.35
	1.40 - 1.50	85	18.20	1.04	3.80	9.71	18.28	20.13	35.53	16.55
6#	1.50 - 1.60	50	10.60	1.43	5.48	7.83	26.11	17.07	52.61	25.93
0#	1.60 - 1.80	50	10.60	1.61	4.40	8.87	34.98	13.71	66.32	40.41
	1.80-2.00	39	8.30	1.36	3.70	5.83	40.82	8.99	75.31	56.15
	>2.00	141	30.10	3.82	2.81	59.18	100.00	24.69	100.00	78.20
	$\leq 1.40$	343	63.10	0.34	2.77	68.78	68.78	61.27	61.27	9.04
	1.40 - 1.50	91	16.80	0.32	4.59	17.15	85.93	22.21	83.48	17.02
	1.50-1.60	39	7.20	0.29	3.67	6.66	92.59	7.61	91.09	22.17
7#	1.60-1.80	27	5.00	0.26	3.64	4.14	96.72	5.23	96.31	34.10
	1.80-2.00	9	1.60	0.24	3.59	1.27	98.00	1.72	98.03	45.93
	>2.00	34	6.30	0.10	1.09	2.00	100.00	1.97	100.00	68.15
	1.4d	75	24.3	1.64	6.95	15.69	15.69	16.63	16.63	nd
	1.5d	49	15.8	1.66	8.64	10.36	26.05	13.51	30.14	nd
0#	1.6d	59	19.1	1.79	7.73	13.48	39.53	14.57	44.71	nd
0#	1.8d	81	26.2	1.50	6.65	15.47	55.00	17.20	61.91	nd
	2.0d	15	4.9	3.86	17.48	7.39	62.39	8.37	70.28	nd
	>2.0d	30	9.7	9.83	31.04	37.61	100.00	29.72	100.00	nd
	1.4d	396	77.5	0.61	5.14	75.59	75.59	75.01	75.01	nd
	1.5d	62	12.1	0.59	5.68	11.45	87.04	12.97	87.98	nd
Q#	1.6d	22	4.3	0.63	5.53	4.34	91.38	4.48	92.46	nd
211	1.8d	13	2.5	0.69	5.11	2.81	94.19	2.45	94.91	nd
	2.0d	9	1.8	0.41	4.76	1.15	95.34	1.58	96.49	nd
	>2.0d	9	1.8	1.64	10.58	4.66	100	3.51	100.00	nd
	1.4d	276	48.5	2.75	1.32	31.87	31.87	25.10	25.10	nd
	1.5d	22	3.9	2.81	2.41	2.60	34.47	3.66	28.76	nd
10#	1.6d	13	2.3	2.87	2.75	1.57	36.04	2.46	31.22	nd
100	1.8d	16	2.8	2.69	2.91	1.81	37.85	3.21	34.43	nd
	2.0d	7	1.2	3.19	3.61	0.94	38.78	1.74	36.17	nd
	>2.0d	235	41.3	6.20	3.94	61.22	100	63.83	100.00	nd
	1.4d	318	71.8	0.65	1.72	14.52	14.52	20.33	20.33	nd
	1.5d	42	9.5	0.97	3.49	2.87	17.39	5.46	25.79	nd
	1.6d	24	5.4	1.45	5.63	2.46	19.85	5.03	30.82	nd
3#*	1.8d	12	2.7	2.54	9.33	2.15	22.01	4.17	34.98	nd
	2.0d	8	1.8	1.92	6.73	1.08	23.09	2.00	36.98	nd
	2.1d	4	0.9	6.59	12.27	1.86	24.95	1.83	38.81	nd
	>2.1d	35	7.9	30.39	47.00	75.05	100.00	61.19	100.00	nd

DFL, density of floating liquid (g/cm<sup>3</sup>); QFC, quality of floating coal (g); PTS, proportion of the total sample; SY, sulfur yield (%); CYS, cumulative yield of sulfur (%); SEY, selenium yield (%); CYSE, cumulative yield of selenium (%); nd, no date.

In the Formula (1),

V<sub>S</sub>—sulfur yield, %;

Mn—mass of floating coal at a certain densimetric fraction, g;

Sn—percent sulfur concentration at a certain densimetric fraction, %; i is taken as 1, 2, 3, 4, 5 or 6.

$$V_{Se} = Mn \times Sen / \sum Mi \times Sei$$
 (2)

In the Formula (2),

V<sub>Se</sub>—selenium yield, %;

Mn—mass of floating coal of a certain densimetric fraction, g; Sen—Se concentration at a certain densimetric fraction,  $\mu g/g$ ; i is taken as 1, 2, 3, 4, 5 or 6.

As shown in Table 5, the Se concentrations were not uniformly distributed in the floating coals of different densimetric fractions, but a certain regularity can be discovered as follows. The samples of 3#, 8# and 10# were high-sulfur coals, and the Se concentrations of each densimetric fraction showed a "linear growth" distribution, with the lowest Se concentration in <1.40 g/cm<sup>3</sup> densimetric fraction coals and the highest Se concentration in >2.00 g/cm<sup>3</sup> densimetric fraction coals. The Se concentrations in the floating coal gradually increased with the increase in the densimetric fraction. The Se concentrations of the 3# and 8# coal samples were higher, and the Se concentrations in the >2.00 g/cm<sup>3</sup> densimetric fraction coals increased sharply (Figure 1a). The 3# and 8# coal samples were high in total sulfur and inorganic sulfur primarily in the form of pyrite sulfur (Table 2). Pyrite has a high specific gravity and tends to be locally enriched in floating coals with large densimetric fractions, and selenium and sulfur are in the subsistent state of isomorphism in pyrite, so selenium is enriched together with pyrite in the heaviest densimetric fraction of floating coal with Se concentrations reaching Se =  $21.60 \mu g/g$  and  $31.04 \mu g/g$ . In this study, parallel float-and-sink analyses were carried out on the 3# coal samples with an additional 2.1 g/cm<sup>3</sup> densimetric fraction. The parallel float-and-sink analysis indicated that the sulfur and selenium were more enriched in the  $2.1 \text{ g/cm}^3$  densimetric fraction coal sample, with St, d and Se reaching 30.39% and Se =  $47.00 \mu g/g$  (Figure 1a).



**Figure 1.** Distribution of Se concentrations in floating coals of densimetric fractions, where (**a**) is medium–high-sulfur coal and (**b**) is medium–low-sulfur coal.

These findings suggest that selenium and sulfur are enriched in the coal in the form of pyrite [25,57–59], and the enrichment degree of sulfur and selenium increases with an increasing densimetric fraction. The Se concentrations in the 10# coal sample increased slowly with the raising densimetric fraction (>2.00g/cm<sup>3</sup> densimetric fraction coal) because the Se concentration was low (Se = 2.46  $\mu$ g/g). Although it is not as obvious as the 3# and 8# warp tail, the Se concentration of the densimetric fraction > 2.00 g/cm<sup>3</sup> was also the largest.

The Se concentrations of each densimetric fraction of the 1#, 2#, 4#, 5#, 6# and 7# coal samples showed a "parabolic-like" distribution (Figure 1b). The middle densimetric fraction was the richest in selenium content, and the two ends had much less selenium content. The four coal samples of 1#, 4#, 5# and 6# had the highest Se concentration of 1.50–1.60 g/cm<sup>3</sup> in the densimetric fraction. The 7# coal sample showed the highest Se concentration of 1.40–1.50 g/cm<sup>3</sup> in the densimetric fraction. The 7# coal sample showed the highest Se concentration of 1.60–1.80 g/cm<sup>3</sup> in the densimetric fraction. The 2# coal sample showed the highest Se concentration of 1.60–1.80 g/cm<sup>3</sup> in the densimetric fraction. The six medium–low-sulfur coal samples all showed the lowest Se concentration of >2.00 g/cm<sup>3</sup> d in the densimetric fraction, and the next two lowest densimetric fractions had a Se concentration of 1.80–2.00 g/cm<sup>3</sup> and  $\leq$ 1.40 g/cm<sup>3</sup>. The sulfur abundance of the six coals with a "parabolic-like" distribution of selenium abundance was less than 3.00%, and thecoal 7#, which had the lowest ash content, showed the highest Se concentration in the 1.40–1.50 g/cm<sup>3</sup> densimetric fraction. Additionally, the densimetric fraction with the highest Se concentration shifted to 1.50–1.60 g/cm<sup>3</sup> and 1.60–1.80 g/cm<sup>3</sup> with the increasing ash content.

After reordering the six coal samples according to the ash content, it was discovered that the densimetric fraction with the highest Se concentration gradually increased with the growing ash content. The densimetric fractions with the highest Se concentration in the coal samples of 1#, 5#, 6# and 4# all had Se concentrations of  $1.50-1.60 \text{ g/cm}^3$ , and the floating density had an interval range of  $0.10 \text{ g/cm}^3$ . Combined with the trend analysis of the densimetric fraction before and after the fractions with the highest Se concentration, it is obvious that the densimetric fraction with the highest Se concentration in the coal gradually shifted backward with increasing ash content (Figure 2). Among the six coal samples, the 1#, 2#, 4#, 5# and 7# coals were extra-low-sulfur coals, and organic sulfur accounted for 78.35% on average, while iron sulfide sulfur accounted for 19.62% on average. Since it was difficult to separate the organic sulfur in the coal by floating and sinking, and because the selenium tended to accumulate in the pyrite because of the isomorphism of the selenium and sulfur, there was no warping phenomenon presented by the high-sulfur coal after the float-and-sink analysis [60]. Typically, the more ash content in the coal, the more minerals such as pyrite are present, and the more selenium is present to be enriched in minerals, which accordingly results in a high Se concentration [61-64]. Because the content of inorganic sulfur is low in general, minerals such as pyrite are floated out in the intermediate densimetric fraction, the selenium is enriched in the intermediate densimetric fraction floating coal and the densimetric fraction with the highest Se concentration increases with growing ash content.

The 9# sample was a low-sulfur and low-ash coal, the Se content in the raw coal was not high (Se =  $3.97 \ \mu g/g$ ) and the sortability of the Se concentration in each densimetric fraction was not obvious, except for the >2.00 g/cm<sup>3</sup> densimetric fraction coal with a significantly higher Se concentration.

3.2.2. Analysis of Selenium and Sulfur Yields and Cumulative Yields of Floating and Sinking Coal Samples

As shown in Table 5, the yield and cumulative yield of the selenium and sulfur in each densimetric fraction of the 10 floating coal samples were calculated, and there seemed to be no rule to follow based on the analysis alone (Figure 3). However, if the yield and cumulative yield of Se are compared with the yield and cumulative yield of sulfur (Figures 4 and 5, respectively), it can be found that the trend of the yield and cumulative yield of Se and sulfur in each densimetric fraction coal is highly consistent and highly positively correlated, except for the abnormal data of the individual floating coals.

## 3.2.3. Correlation between Ash and Selenium in Floating and Sinking Coal Samples

As shown in Table 5, 36 subsamples from six non-high-sulfur floating coal samples of 1#, 2#, 4#, 5#, 6# and 7# were selected for ash determination. The correlation analysis found that the ash content and Se concentrations in the floating coal of each densimetric fraction of the same raw coal were positively correlated. The correlation coefficient ranged



between 0.6503 and 0.9670, averaging 0.8147. The correlation results are shown in Table 6 and Figure 6.

Figure 2. Effect of ash on the variation in Se concentrations in coals of densimetric fractions.







Figure 4. Correlation between Se yield and sulfur yield in floating coal of densimetric fractions.



**Figure 5.** Correlation between cumulative Se yield and cumulative sulfur yield in floating coal of densimetric fractions.

Samples	A <sub>d</sub>	Se,d	S <sub>t,d</sub>	Polynomial Correlation Function	Correlation Coefficient
1#	23.02	5.14	0.14	$y = -0.002x^2 + 0.0904x + 4.5603$	$R^2 = 0.6651$
2#	51.92	4.28	0.23	$y = -0.0046x^2 + 0.3127x + 3.8746$	$R^2 = 0.9670$
4#	42.04	3.94	0.42	$y = -0.0023x^2 + 0.1577x + 3.3365$	$R^2 = 0.8218$
5#	31.87	5.96	0.16	$y = -0.0024x^2 + 0.1607x + 2.9733$	$R^2 = 0.8351$
6#	39.27	4.70	2.12	$y = -0.0016x^2 + 0.1326x + 2.0021$	$R^2 = 0.6503$
7#	18.23	4.90	0.37	$y = -0.0019x^2 + 0.1051x + 2.6543$	$R^2 = 0.9489$

Table 6. Correlation between ash and selenium in 6 samples of float-sink coal.



Figure 6. Correlation analysis of ash and selenium in floating coal.

In summary, selenium was unevenly distributed in the floating coal. The Se concentrations of the high-sulfur coal showed a "linear growth" distribution in each densimetric fraction, the Se concentrations increased with the increasing densimetric fraction and the last densimetric fraction increased sharply, which gave rise to the tail-warping phenomenon. The Se concentrations of the other coal samples showed a "parabolic-like" distribution, generally with high Se concentrations in the middle densimetric fraction, and the densimetric fraction with the largest Se concentration gradually moved backward with the increasing ash content of the raw coal.

The dominant factor responsible for the distribution mechanism of selenium in coal is the sulfur content, and typically Se is abnormally enriched in the largest floating and sinking densimetric fraction of coal. Selenium and sulfur are isomorphous, and under certain geological conditions, some of the sulfur was replaced by selenium and was stably preserved in the sulfur minerals of coal over long geological periods [63–66]. For high-sulfur coal, the higher the sulfur concentrations in the floating coal, the higher the selenium [25,48,57–59]. The iron sulfide sulfur content of the three high-sulfur coals used in the float-and-sink analysis was very high. For coal 3# (St, d = 3.62%, Sp, d = 2.90%, Se d =  $6.10 \,\mu g/g$ ), the Se concentrations of the floating coal in each densimetric fraction gradually increased from 0.82  $\mu$ g/g  $\rightarrow$  2.56  $\mu$ g/g  $\rightarrow$  4.13  $\mu$ g/g  $\rightarrow$  6.00  $\mu$ g/g  $\rightarrow$  8.07  $\mu$ g/g  $\rightarrow$  21.60 µg/g, and the last fraction sharply increased to 3.54 times the selenium abundance of the original coal. For coal 8# (St, d = 2.94%, Sp, d = 1.82% and Se d = 8.32  $\mu$ g/g), the Se concentrations of the floating coal in each densimetric fraction increased gradually from  $6.95 \ \mu g/g \rightarrow 8.64 \ \mu g/g \rightarrow 7.73 \ \mu g/g \rightarrow 6.65 \ \mu g/g \rightarrow 17.48 \ \mu g/g \rightarrow 31.04 \ \mu g/g$  in general, and the last fraction increased sharply to 3.73 times the selenium abundance of the original coal selenium. Coal 10# was a high-sulfur coal (St, d = 3.97%, Sp, d = 2.46%); however, because of its small Se concentration (Se d =  $6.10 \,\mu g/g$ ), the overall Se concentrations of the floating coal in each densimetric fraction also tended to increase gradually. The Se concentration of the last stage was 1.47 times higher than that of the original coal.

The secondary factor affecting the Se concentration of floating coal is the ash content of coal. Coal is an energy source made of plant fossils with a long formation history, and it is produced in a complex coal-forming geological environment. The origin of selenium in coal is also very complex; the primary source of selenium is coal-forming plants, and the paleogeographic environment during the coal-forming period, underground magmatic rock activity, large-area seawater intrusions, groundwater and fault structures are all also important sources of selenium. The six "parabolic-like" floating and sinking coal samples are all located in the Yangzi plate of China, and all of them have experienced extensive seawater intrusions in geological history. During its long geological history, the selenium in the coal is stored in the minerals of the coal in the form of selenides and selenates. These minerals are also important contributors to the ash content of coal, so there is a correlation between selenium and ash content [48,49,62,65]. Figures 2 and 6 can also verify the correlation between selenium and the ash content.

## 3.3. Correlation Analysis of Se and Sulfur in Coal

## 3.3.1. Relationship between Se and Total Sulfur in Coal

Selenium can very easily replace sulfur in sulfide minerals and enter into the crystals of sulfide minerals because selenium and sulfur have a similar covalent radius and electronegativity [59,66]. Thus, pyrite is the main carrier of selenium enrichment in coal. It was indicated by Zhang et al.'s study that in 29 coal samples from the Huabei coalfield and 21 samples from the Yanzhou mine in Shandong province, the organic selenium and inorganic selenium almost shared the same concentrations in the low-sulfur coal; however, selenium mainly occurred in pyrite in high-sulfur coals [48]. Zhang et al., (2007) insisted that there exists a close positive correlation between the existing form of selenium in coal and the sulfur content in coal [48]. Liam et al., (2018) concluded that selenium in coal has a significant positive correlation with sulfur and iron and a negative correlation with the total organic carbon [28]. It was further shown that pyrite is the key carrier of selenium enrichment in coal [28,33,34].

Since the sulfate sulfur (Ss, d) content in the coal was very low, this study investigated the correlation between selenium and total sulfur, pyrite sulfur (Sp, d) and organic sulfur (So, d) in 81 coal samples. The results showed that there existed no obvious correlation between selenium in the coal and the total sulfur, pyrite sulfur (Sp, d) and organic sulfur (So, d) (Figure 7), which is different from the results obtained by most scholars. The difference in conclusions is mainly attributed to the fact that previous studies chose a particular mining area or coal basin as their research area, but the coal samples in this study came from 14 major coal-producing provinces in China, of which there are great differences in terms of the coal-forming environment, coal-forming age, type of coal rock, horizons, sulfur concentration (0.06%–5.76%) and selenium concentration (0.00– $12.97 \mu g/g$ ) [3,49,51,53–55].



**Figure 7.** Scatter plot of Se in coal with total sulfur (**a**), pyrite sulfur (**b**) and organic sulfur (**c**).

To this end, selenium and sulfur were tested on 10 subsamples of each densimetric fraction of floating and sinking coal samples, of which the coal-forming environment, coal-forming age, type of coal rock, etc., were all the same. The analysis of the different densimetric fractions of the individual floating coal samples showed that the correlation between selenium and sulfur was significant. The data are shown in Table 5, and the correlation results are shown in Figure 8 and Table 7.



Figure 8. Correlation analysis of selenium and sulfur of floating coal.

Table 7. Correlation between selenium and sulfur in 10 samples of float-sink coal
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Samples	A <sub>d</sub>	Se,d	S <sub>t.d</sub>	Polynomial Correlation Function	Correlation Coefficient
1#	23.02	5.14	0.14	$y = -188.57x^2 + 62.485x + 0.7455$	$R^2 = 0.9184$
2#	51.92	4.28	0.23	$y = -193.53x^2 + 148.25x - 19.193$	$R^2 = 0.9638$
3#	13.44	6.10	3.62	$y = 5.5575\ln(x) + 2.2484$	$R^2 = 0.9934$
4#	42.04	3.94	0.42	$y = -17.892x^2 + 20.069x + 0.0584$	$R^2 = 0.6615$
5#	31.87	5.96	0.16	$y = -262.49x^2 + 84.752x - 1.294$	$R^2 = 0.6859$
6#	39.27	4.70	2.12	$y = -1.1606x^2 + 5.3824x - 0.8236$	$R^2 = 0.7205$
7#	18.23	4.90	0.37	$y = -65.75x^2 + 40.389x - 2.3231$	$R^2 = 0.8889$
8#	16.85	8.32	2.94	$y = -0.2706x^2 + 5.9817x - 1.6123$	$R^2 = 0.9964$
9#	10.17	3.97	0.59	$y = 2.6135x^2 - 0.7686x + 4.7847$	$R^2 = 0.9826$
10#	30.30	2.46	3.97	$y = -0.7642x^2 + 7.3198x - 12.065$	$R^2 = 0.6224$

The correlation between the Se and sulfur in each densimetric fraction of the 10 floating coal samples is very obvious. However, the correlation coefficients ranged from 0.6224 to 0.9964, and averaged 0.8434.

Further analysis of the 10 floating coal samples found that the 2# coal sample was an abnormal sample because of its unusually high ash content (Ad = 51.92%); among the remaining nine floating coal samples, the coal samples with lower correlation coefficients of selenium and sulfur were the coal samples with large ash in Area A (except for coal sample 2#), while the coal samples with higher correlation coefficients of selenium and sulfur were the coal samples with low ash in Area B (Figure 9).

Area A contained the 4#, 5#, 6# and 10# floating coal samples with a somewhat lower correlation between selenium and sulfur. The corresponding correlation coefficients were 0.6615, 0.6589, 0.7205 and 0.6224, respectively, averaging 0.6658. The corresponding ash content of the raw coal was 42.02%, 31.87%, 39.27% and 30.30%, respectively, averaging 35.87%. Area B contained the 1#, 3#, 7#, 8# and 9# floating coal samples with a very significant correlation between selenium and sulfur. The corresponding correlation coefficients were 0.9184, 0.9638, 0.8889, 0.9964 and 0.9826, respectively, averaging 0.9500. The corresponding ash content of the raw coal was 23.02%, 13.44%, 18.23%, 16.85% and 10.17%, respectively, averaging 16.34%. It follows that the ash content of the raw coal is

an important factor affecting the correlation between selenium and sulfur in the floating coal of various densimetric fractions. Coal is an energy source made of plant fossils, so when the ash content is high, the content of various mineral components is also high. The occurrence form of selenium and sulfur would be more complex, and the correlation is poor after floating and sinking. By contrast, when the ash content is low, the content of various mineral components is also low, and the occurrence form of selenium and sulfur would be relatively simple. Then, the distribution of each density level during floating and sinking would be more regular, and the positive correlation between selenium and sulfur would be better. It can be found that the ash yield of raw coal is an important factor that influences the correlation between Se and sulfur in floating coals of all densimetric fractions [48,49,62,65].



Figure 9. Correlation analysis of ash in coal with selenium and sulfur.

3.3.2. Relationship between Se and Forms of Sulfur in Coal

Sulfur occurs in three forms in coal: pyrite sulfur (Sp, d), sulfate sulfur (Ss, d) and organic sulfur (So, d). In order to discover which form of sulfur is more closely related to Se in coal, 81 coal samples were selected to test the occurrence forms of sulfur. The comprehensive analysis of selenium with the total sulfur and forms of sulfur is shown in Figure 10. Because the 81 coal samples came from different regions with different coal types and sedimentary environments, the content of sulfur and Se in coal varies greatly, and the two are not comparable. However, from the overall view of Figure 10, the Se content was proportional to the sulfur content in the coal, and a more positive correlation was observed between selenium and pyrite sulfur while a less positive correlation was observed between selenium and organic sulfur.

The levels of organic sulfur in the samples distributed in the four regions with significant correlations are all very low, while the levels of organic sulfur in the samples distributed in other regions are higher. The presence of higher organic sulfur leads to a decrease in the proportion of pyrite sulfur in coal, and the probability of a sulfur–selenium isomorphism is reduced greatly. So, the stable occurrence of Se in coal and the positive correlation between Se and sulfur was affected. It can be found that the Se in the coal had a certain positive correlation with sulfur, and the correlation was more positive between the Se and pyrite sulfur.

To further reveal the intrinsic correlation link between selenium and sulfur, an analysis on the forms of sulfur was carried out on four floating coal subsamples (3#, 6#, 8# and 10#)



with a high sulfur concentration (Table 8). The correlation analysis is shown in Figure 11 and Table 9.

Sample No

Figure 10. Combined analysis graph of selenium with total sulfur and forms of sulfur.

Samples	DFL	PTP	Se <sub>,d</sub>	$\mathbf{S}_{t,d}$	S <sub>p,d</sub>	S <sub>s,d</sub>	S <sub>o,d</sub>
	1.4d	71.8	1.72	0.65	0.08	0.01	0.56
	1.5d	9.5	3.49	0.97	0.46	0.01	0.49
	1.6d	5.4	5.63	1.45	1.02	0.00	0.43
3#	1.8d	2.7	9.33	2.54	2.06	0.01	0.47
	2.0d	1.8	6.73	2.28	2.16	0.04	0.08
	2.1d	0.9	12.27	6.59	nd	nd	nd
	>2.1d	7.9	47.00	30.39	28.09	0.16	2.14
	1.4d	22.0	2.40	0.76	0.24	0.01	0.50
	1.5d	18.2	3.80	1.04	0.46	0.01	0.57
6#	1.6d	10.6	4.88	1.43	0.86	0.00	0.57
0#	1.8d	10.6	4.40	1.61	1.08	0.01	0.52
	2.0d	8.3	3.70	1.36	1.07	0.01	0.28
	>2.0d	30.1	3.93	3.82	3.39	0.02	0.41
	1.4d	24.3	6.95	1.64	1.04	0.03	0.57
	1.5d	15.8	8.64	1.66	1.09	0.06	0.50
0	1.6d	19.1	7.73	1.79	1.11	0.09	0.58
0	1.8d	26.2	6.65	1.50	0.86	0.15	0.49
	2.0d	4.9	17.48	3.86	3.12	0.44	0.30
	>2.0d	9.7	31.04	9.83	8.45	0.94	0.44
	1.4d	48.5	1.32	2.75	0.56	0.00	2.19
	1.5d	3.9	2.41	2.81	0.96	0.01	1.85
10#	1.6d	2.3	2.75	2.87	1.21	0.02	1.64
10#	1.8d	2.8	2.91	2.69	1.31	0.02	1.35
	2.0d	1.2	3.61	3.19	nd	nd	nd
	>2.0d	41.3	3.94	6.20	6.01	0.07	0.12

Table 8. Correlation between selenium and morphological sulfur in float-sink coal.



**Figure 11.** Correlation analysis of Se in floating coal with total sulfur, pyrite sulfur, sulfate sulfur and organic sulfur, where (**a**) is the correlation analysis between Se and forms of sulfur in 3#; (**b**) is the correlation analysis between Se and forms of sulfur in 6#; (**c**) is the correlation analysis between Se and forms of sulfur in 10#; (**e**) is the correlation analysis between Se and forms of sulfur in 3#, 8# and 10#; and (**f**) is the correlation analysis between Se and forms of sulfur in 3#, 6#, 8# and 10#.

The 3# coal was a high-sulfur coal from Huainan, Anhui Province, with a selenium content of 6.10  $\mu$ g/g and sulfur content 3.62%; the 6# coal was a medium–high-sulfur coal from Huainan, Anhui Province, with a selenium content of 4.70  $\mu$ g/g and sulfur content of 2.12%; the 8# coal was a high-sulfur coal from Kaiyang, Guizhou Province, with a selenium content of 8.32  $\mu$ g/g and sulfur content of 2.94%; and the 10# coal was a high-sulfur coal from Xinwen, Shandong Province, with a selenium content of 2.46  $\mu$ g/g and sulfur content of 3.97%. As shown in Figure 11 and Table 9, a significant positive correlation was observed between selenium and THE total sulfur, pyrite sulfur, sulfate sulfur and organic sulfur for THE 3#, 8# and 10# high-sulfur coals. Additionally, the most positive correlation was observed between the 3# and 8# high-sulfur coals. Among the four correlations, selenium was the most correlated with pyrite sulfur, followed by total sulfur, organic sulfur and sulfate sulfur, respectively.

Samples	CF-Se-S <sub>t,d</sub>	<b>R</b> <sup>2</sup>	CF-Se-S <sub>p,d</sub>	<b>R</b> <sup>2</sup>	CF-Se-S <sub>s,d</sub>	<b>R</b> <sup>2</sup>	CF-Se-S <sub>o,d</sub>	<b>R</b> <sup>2</sup>
3#	$y = 0.0049x^2 + 0.4307x - 0.6722$	0.9948	$y = 0.0085x^2 + 0.2039x - 0.2446$	0.9991	y = 0.0035x - 0.0041	0.9421	$y = 0.0017x^2 - 0.0457x + 0.5936$	0.9583
6#	$y = -0.0664x^2 + 0.3455x + 1.3483$	0.0372	$y = -0.1111x^2 + 0.678x + 0.3039$	0.0477	$y = 0.0471x^2 - 0.3471x + 1.0531$	0.3086	$y = -0.0024x^2 + 0.0146x - 0.0088$	0.6924
8#	$y = 0.0094x^2 - 0.0154x + 1.2317$	0.9993	$y = 0.0079x^2 + 0.0113x + 0.4975$	0.9995	$y = 0.0013x^2 - 0.0542x + 0.8651$	0.8061	$y = 0.0002x^2 + 0.0274x - 0.1309$	0.9787
10#	$y = 0.951x^2 - 4.0556x + 6.6041$	0.7496	$y = 1.3424x^2 - 5.0328x + 4.9314$	0.9875	$y = 0.0118x^2 - 0.0354x + 0.0265$	0.9952	$y = -0.3047x^2 + 0.8094x + 1.6526$	0.9965
3# 8# 10#	$y = 0.0175x^2 - 0.2599x + 3.2321$	0.9439	$y = 0.0171x^2 - 0.2691x + 2.1734$	0.9529	$y = -0.0009x^2 + 0.0529x - 0.1848$	0.6755	$y = 0.0034x^2 - 0.1444x + 1.452$	0.5283
3# 6# 8# 10#	$y = 0.0168x^2 - 0.2213x + 2.8133$	0.9359	$y = 0.0169x^2 - 0.2568x + 2.0338$	0.9461	$y = -0.0009x^2 + 0.05x - 0.164$	0.6734	y = 0.0029x <sup>2</sup> - 0.116x + 1.1722	0.4194
10 raw coal mixed samples	$y = 0.276x^2 - 2.9024x + 8.5212$	0.3761	$y = 0.1591x^2 - 1.6205x + 4.743$	0.2426	$y = -0.0025x^2 + 0.0387x - 0.0723$	0.0897	y = -0.0176x + 0.6218	0.0043

Table 9. Correlation between selenium and total sulfur and form sulfur in float-sink coal.

CF-Se-S<sub>t,d</sub>, correlation function between selenium and total sulfur; CF-Se-S<sub>p,d</sub>, correlation function between selenium and pyrite sulfur; CF-Se-S<sub>s,d</sub>, correlation function between selenium and sulfate sulfur; CF-Se-S<sub>o,d</sub>, correlation function between selenium and organic sulfur; R<sup>2</sup>, correlation coefficient.

The 10# coal was rich in sulfur but only had a Se concentration of 2.46  $\mu$ g/g. The correlation between Selenium and total sulfur, pyrite sulfur, sulfate sulfur and organic sulfur was also observed in the 10# coal, but the coefficients were different from those of the 3# and 8# coal. Selenium was positively correlated with the total sulfur, pyrite sulfur and sulfate sulfur. Among them, selenium showed the most significant positive correlation with sulfate sulfur (R<sup>2</sup> = 0.9952), followed by pyrite sulfur (R<sup>2</sup> = 0.9875) and the total sulfur (R<sup>2</sup> = 0.7496). Selenium was significantly and negatively correlated with organic sulfur, with a negative correlation coefficient of 0.9965. The 6# coal was a medium–high-sulfur coal, and selenium showed no correlation with the total sulfur, pyrite sulfur and sulfate sulfur, and a negative correlation with organic sulfur (R<sup>2</sup> = 0.6924).

If all the 17 floating coal subsamples of the three high-sulfur coals (3#, 8# and 10#) were combined for the correlation analysis, selenium still had a strong positive correlation with the total sulfur and pyrite sulfur, with the coefficient being 0.9439 and 0.9529, respectively. However, selenium was not significantly correlated with sulfate sulfur and organic sulfur. If all 23 subsamples of the four floating coals 3#, 6#, 8# and 10# were combined for the correlation analysis, selenium still had a strong positive correlation with the total sulfur and pyrite sulfur, with the coefficient being 0.9359 and 0.9461, respectively. Selenium also showed an insignificant correlation with sulfate sulfur and organic sulfur.

To further study the correlation between Se and pyrite, a part of the 138 raw coal samples with an obviously different Se abundance (Se, d, 0.72–12.97  $\mu$ g/g) and the 3# floating coal with a density grade >2.0 (Se, d = 21.6  $\mu$ g/g) were selected to conduct a coal petrology analysis using a LEICA multifunctional optical microscope. The Se abundance of the raw coal samples with generally similar total organic matter (80%–90%) varied greatly from 0.72 $\mu$ g/g to 12.97  $\mu$ g/g, implying that the organic matter was not very correlated with Se. Overall, the more pyrite content in the raw coal samples, the higher the Se abundance. Especially for the 3# floating coal with a density grade >2.0, the extremely Se-rich floating coal was also enriched with extensive bulk and granular pyrite. The mass pyrite was observed under a microscope, which had a massive form and different grain sizes and shapes (Figure 12). Accordingly, the enrichment of pyrite during flotation was probably responsible for the enrichment of Se. Although Se was closely correlated with pyrite in the coal, the Se abundance was not strictly proportional to the pyrite content (Table 10), which may be attributed to the following reasons: (1) The occurrence (e.g., whether it is

massive, small and granular, a berry ball, filled within a cell cavity or fissure) and genesis of pyrite (e.g., biogenetic, nonbiogenetic) is very complicated in coal [67]. (2) The occurrence (e.g., whether it is water soluble, exchangeable, alkali soluble, elemental, acid soluble, sulfur/selenide binding and a residue) and genesis (e.g., biogenetic, nonbiogenetic) of Se is also very complicated in coal [68]. (3) The total Se abundance is not strictly proportional to the total pyrite content, probably because certain occurrences of pyrites are responsible for the dominant Se; in other words, Se is not uniformly distributed in pyrite. Our further microanalysis on the 3# floating coal with a density grade >2.0 using the field emission electron probe microanalyzer (SHIMADZU, EPMA-8050G) discovered the local enrichment of selenium in the pyrite particles, but the enrichment regularity of selenium in pyrite was not discovered yet, which further validates the correlation between selenium and pyrite sulfur proposed by previous studies [28,30,31] as well as the uneven distribution of Se in pyrite. The preliminary SHIMADZU analysis still needs to be studied with different occurrence of Se and pyrite.



Figure 12. LEICA multifunctional optical microscope analysis of 3# floating coal.

Fable 10. Coal petrograph	y characteristics and	l corresponding Se abundance.
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	Se Abundance (µg/g)	<b>Coal Petrography Composition (%)</b>				
Sample		Total Organic Matter	Clay	Sulfide	Carbonate	Microscope Features of Sulfide
21MT173-001	2.50	90.31	7.49	1.32	0.44	Pyrite is massive, small granular, a berry ball or filled within a cell cavity
21MT173-002	6.98	82.07	16.14	1.79	-	Pyrite is massive, small granular or filled within cell a cavity
21MT173-003	7.12	80.00	16.89	3.11	-	Pyrite is massive, small granular or filled within a fissure
21MT173-006	9.53	86.36	11.98	0.83	0.83	Pyrite is massive or small granular
21MT173-007	12.97	84.96	9.29	4.42	1.33	Pyrite is filled within a fissure or cell cavity
21MT209-002	1.98	67.40	31.30	0.87	-	Pyrite is occasionally observed under a microscope and is massive, small granular or a berry ball
21MT209-003	0.72	90.04	7.66	-	-	Not observed
21MT209-004	5.49	90.54	6.58	2.88	-	Pyrite is small granular or massive
21MT264-001	4.50	87.20	8.00	-	4.40	Pyrite is occasionally observed under microscope, but it is below the detection limit
21MT264-002	3.37	91.98	6.20	-	1.46	Not observed
21MT379-002	5.02	92.37	4.96	1.15	0.76	Pyrite is small granular or filled within the cell cavity
21MT104-003	21.60	8.90	0.85	88.13	2.12	Mass pyrite is observed under the microscope and is massive with a different grain size and shape

## 4. Conclusions

- 1. In this study, Se concentration tests of 138 coal samples showed that the average Se concentration of Chinese coal is 2.26  $\mu$ g/g, which is consistent with the average Se concentration of 2 to 3  $\mu$ g/g found by previous studies. The geographical distribution of Se concentration in China has the characteristics of "low in the northwest and high in the southeast". In particular, the coal in Anhui, Shandong, Jiangsu and Henan in the east of China are generally high in selenium content, which may be attributed to the marine facies and the marine–continental interaction coal-forming environment in the region, as well as the impact of the late transgression and the late magmatic hydrothermal intrusion.
- 2. The distribution characteristics of selenium in floating coal and the corresponding dominant factors were revealed in this study. The selenium concentration in the highsulfur floating coal increased slowly with a growing density when the density grades were  $<2.00 \text{ g/cm}^3$  and increased sharply when the density grades were  $>2.00 \text{ g/cm}^3$ and  $>2.10 \text{ g/cm}^3$ , with an overall "linear growth" distribution. The selenium concentration in the medium-low-sulfur floating coal was high at the middle density grade and low at both ends, with an overall "similar parabola" distribution. Thereby, the sulfur content in the coal was the dominant factor responsible for the distribution of selenium in the floating coal since the occurrence of selenium was closely related to the forms of sulfur in the floating coal. For the high-sulfur floating coals, the selenium concentration increased with the growing ash content and sulfur content; for the medium-low-sulfur floating coals, the densimetric fraction with the highest Se concentration gradually moved backward from  $1.40 \text{ g/cm}^3$  to  $1.80 \text{ g/cm}^3$  with increasing ash content. Thus, ash content is the other dominant factor responsible for the distribution of selenium in floating coal, which may be attributed to the fact that selenium-related minerals (etc., pyrite, selenide, selenate) are both the dominant source of selenium and important contributors of ash content in coal.
- 3. The correlation between selenium and forms of sulfur in coal was analyzed in this study. The selenium in high-sulfur floating coal was highly correlated with the total sulfur, pyrite sulfur and organic sulfur, among which pyrite sulfur had the best correlation with selenium, followed by the total sulfur and organic sulfur. Selenium had a significant positive correlation with the total sulfur and pyrite sulfur in the floating coal. There also existed a good correlation between selenium and organic sulfur in the high-sulfur floating coal, but for the high-selenium floating coals, the correlation was significantly positive; for the low-selenium floating coals, the correlation was significantly negative. This can probably be attributed to the fact that inorganic sulfur accounts for a large proportion of high-sulfur coal with high selenium content, and selenium mostly occurs in inorganic pyrite.

Author Contributions: Conceptualization, G.Z. and Q.F.; investigation, H.Z. and X.W.; methodology, G.Z.; data analysis, G.Z. and H.Z.; experiment, G.Z., N.Z., M.W. (Mingzhong Wen), Y.D. and Z.Y.; writing, G.Z., H.Z. and M.W. (Meng Wu). All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was supported by the Special Science and Technology Fund of China, Coal Geology Bureau (ZMKJ-2022-JBGS01).

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank Wenfeng Wang for his advice, which greatly improved the expression of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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