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Review

Fluorine in Chinese Coal: A Review of Distribution, Abundance, Modes of Occurrence, Genetic Factors and Environmental Effects

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Abstract: Fluorine, a hazard that is associated with coal, has resulted in serious environmental issues during the production and utilization of coal. In this paper, we provide a detailed review of fluorine in Chinese coal, including the distribution, concentration, modes of occurrence, genetic factors, and environmental effects. The average concentration of fluorine in Chinese coal is 130.0 mg/kg, which is slightly higher than coal worldwide (88.0 mg/kg). The enrichment of fluorine in Chinese coal varies across different coal deposit regions, and it is especially high in Inner Mongolia (Junger coalfield, Daqingshan coalfield) and southwest China (coal mining regions in Yunnan, Guizhou province). The fluorine distribution is uneven, with a relatively high content in southwest coal (including Yunnan, Guizhou, Chongqing, and Sichuan provinces), very high content in the coal of North China (Inner Mongolia) and South China (Guangxi), and is occasionally found in the northwest (Qinghai). Fluorine occurs in various forms in coal, such as independent minerals (fluorine exists as fluorapatite or fluorite in coal from Muli of Qinghai, Taoshuping of Yunnan, Guiding of Guizhou, and Daqingshan of Inner Mongolia), adsorption on minerals (fluorine in coal from Nantong, Songzao of Chongqing, Guxu of Sichuan, and Shengli, Daqingshan, and Junger from Inner Mongolia), substitution in minerals (Wuda coal, Inner Mongolia), and a water-soluble form (Haerwusu coal, Inner Mongolia). The enrichment of fluorine is mainly attributed to the weathering of source rock and hydrothermal fluids; in addition to that, volcanic ash, marine water influence, and groundwater affect the fluorine enrichment in some cases. Some environmental and human health problems are related to fluorine in coal, such as damage to the surrounding environment and husbandry (poisoning of livestock) during the coal combustion process, and many people have suffered from fluorosis due to the burning of coal (endemic fluorosis in southwest China).

Keywords: fluorine; geochemistry; environmental effects; coals; China

1. Introduction

Coal is the most important fossil fuel for China, and it is a reliable long-term fuel source. For many years, coal made up more than 60% of the country's total primary energy consumption and about 65% of the country's chemical materials are derived from coal products. The National Energy Administration of China (NEAC) has predicted that coal will account for 50% of primary energy consumption in China until 2050. Large quantities of pollutants are produced with the utilization of coal in China, not only in the form of gas emissions, but also as ash residues. Trace elements in coal can provide useful information from an environmental point of view for the possible control of toxic trace element pollution during the coal combustion and utilization process [1].

Fluorine is one of the abundant and harmful trace elements in coal. In general, fluorine is enriched in Chinese coal and widely distributed, particularly in southwestern (SW) and northern China. With the large amount of domestic coal consumption and commercial coal use, fluorine-related environmental pollution is very serious [2–4], such as endemic fluorosis resulted from domestic use in SW China. Many studies have focused on the geochemistry of fluorine in coal [5,6], including abundance, distribution, modes of occurrence, and genetic factors, providing more details about the fluorine in Chinese coals [7–12].

Based on previous research, this study summarizes the fluorine in coal from the main coal deposit basins (coalfield, coal production region) (Figure 1), including its abundance, enrichment, and modes of occurrence. In addition, fluorine genetic factors and its environmental effects are discussed. All of these could provide valuable suggestions for the utilization of clean coal and prevention of pollution.

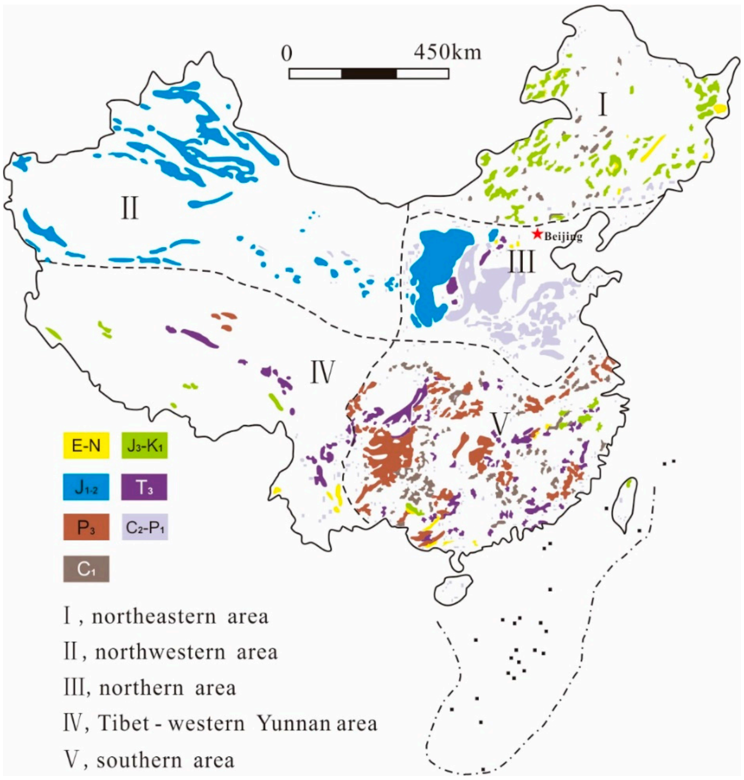

Figure 1. Coal-distribution areas in China, modified from Dai et al. [13].

2. Fluorine in Chinese Coal

2.1. Abundance of Fluorine in Coal

Swaine [14] reported the average value of fluorine (F) in coal worldwide was 150.0 mg/kg, and Lu [15] found that in China there was on average 217 mg/kg in coking coal and 193 mg/kg in anthracite, Qi et al. [16] reviewed data on coal from 96 districts of China, suggesting that the F concentration varied from 17.0 to 1226.0 mg/kg, with an average of 202.0 mg/kg.

Between the years of 2002 to 2004, the Chen et al. [7], Bai and Tang and Huang [8] found F contents of 140.0 mg/kg (based on 581 samples), 212.45 mg/kg (based on 1081 samples), and 186.0 mg/kg (based on 1069 samples), respectively. Ren et al. [9] and Tang et al. [10] later investigated fluorine content, finding averages of 131.29 mg/kg (746 samples) and 139.51 mg/kg (108 samples). During the same period, other reports discussed the fluorine concentration in Chinese coal, reporting averages of 82 mg/kg [11] and 130.00 mg/kg [12]. In 2012, a geochemical review of trace elements [13] reported the F value to be 130.0 mg/kg in Chinese coal, which was higher than the average worldwide (88 mg/kg) [14], the report was based on more data and included wider areas than previous studies, we prefer accept this value (130.00 mg/kg) as the mean F value in Chinese coals. According to reports in recent years, the F content is higher than 130.0 mg/kg in many coal-deposits of China (Table 1), especially in SW and North China [15–18].

Table 1. Fluorine in Chinese coal (average of 130 mg/kg).

Studied Area	Period	Formation	F Content	Sample Numbers	Reference
Songzao, Chongqing	P_2	Longtan Form.	326–536/440	24	Zhao et al. [19]
Nantong, Chongqing	P_2	Longtan Form.	239–692/429	26	Chen et al. [20]
Luquan, Yunnan	D_2	Haikou Form.	85–235/181	8	Dai et al. [21]
Lincang, Yunnan	N	Bangmai Form.	104–654/369	57	Dai et al. [22]
Songshao, Yunnan	P_1	Liangshan Form.	82–293/154	12	Wang [23]
Zhijin, Guizhou	P_2	Longtan Form.	500	19	Dai et al. [24]
Guiding, Guizhou	P_2	Wujiaping Form.	1296–3575/2076	13	Dai et al. [25]
Huayingshan, Sichuan	P_2	Longtan Form.	82–940/145	12	Dai et al. [26]
Changhe, Sichuan	T_3	Xujiahe Form.	129.1–210.5/142.2	10	Wang et al. [27]
Enshi, Hubei	P_2	Longtan Form.	249–889/717.3	-	Zheng et al. [28]
Fusui, Gunagxi	P_2	Heshan Form.	116–538/329	19	Dai et al. [29]
Heshan, Guangxi	P_2	Heshan Form.	319–2230/1728.3	-	Lu [15]
Heshan, Guangxi	P_2	Heshan Form.	821–2791/1179	14	Dai et al. [30]
Hechi, Guangxi	P_2	Longtan Form.	227–1907/614	-	Zheng et al. [28]
Xinde, Yunnan	P_2	Xuanwei Form.	46–106/60.9	10	Dai et al. [31]
Dafang, Guizhou	P_2	Longtan Form.	44.9–321	71	Dai et al. [32]
Xingren, Guizhou	P_2	Longtan Form.	52–144	9	Dai et al. [33]
Yishan, Guangxi	P_2	Heshan Form.	301–2334/1309	48	Dai et al. [34]
Moxinpo, Chongqing	P_2	Longtan Form.	813–1082/924	38	Dai et al. [35]
Songzao, Chongqing	P_2	Longtan Form.	96.9–584/246	10	Dai et al. [36]
Yueliangtian, Guizhou	P_2	Longtan Form.	11–71.7/20.7	12	Wang et al. [37]
Dafang, Guizhou	P_2	Longtan Form.	44.6–321	-	Dai et al. [32]
Xingren, Guizhou	P_2	Longtan Form.	52–144/89	9	Dai et al. [33]
Xiaoxian, Anhui	C-P	-	86–254/158.3	-	Ren et al. [9]
Huaibei, Anhui	C-P	-	77.1–2665.9/156.1	-	Chen and Tang [7]
Huainan, Anhui	C-P	-	101–255/193	-	Chen and Tang [7]
Fengfeng, Hebei	C-P	-	110–200/155	-	Ren et al. [9]
Kailuan, Hebei	C-P	-	48–859/188	-	Ren et al. [9]
Pingdingshan, Henan	C_2	Taiyuan Form.	325–1470/637	-	Chen and Tang [7]
Luxi, Shandong	P_1	Shanxi Form.	20–241/130	45	Wang et al. [38]
Pingshuo, Shanxi	C_2	Taiyuan Form.	11–384/167	10	Yang et al. [39]
Huozhou, Shanxi	P_1	Shanxi Form.	74–1050/373	-	Chen and Tang [7]
Chuancaogedan, I.M.	P_1	Shanxi Form.	124.3–385.3/218.4	15	Yang et al. [40]
Handan-Fengfeng, Hebei	P_1	Shanxi Form.	62.2–1212.1/429.8	12	Dai and Ren [41]
Hailiushu, I.M.	C_2	Shuanmazhuang Form.	78.2–476/179	19	Dai et al. [42]
Adaohai, I.M.	C_2	Shuanmazhuang Form.	87.6–824/207	48	Dai et al. [43]
Wulantuga, I.M.	K_1	Shengli Form.	158–1104/336	13	Dai et al. [44]
Guanbanwusu, I.M.	C_2	Taiyuan Form.	127–1286/434	50	Dai et al. [45]
Haerwusu, I.M.	C_2	Taiyuan Form.	135–611/286	29	Wang et al. [46]
Heidaigou, I.M.	C_2	Taiyuan Form.	135–611/286	29	Dai et al. [47]
Qitaihe, Heilongjinag	J–K	-	143–192/172	-	Ren et al. [9]
Jixi, Heilongjiang	J–K	-	55–324/188	-	Ren et al. [9]
Yili, Xinjiang	J	Sangonghe Form.	38–860/311.4	64	Dai et al. [48]
Muli, Qinghai	J	Muli Form.	60–441/253	22	Dai et al. [49]

Abbreviation: I.M.—Inner Mongolia; P_1—early Permian; P_2—late Permian; D_2—late Devonian; N—Neogene; T_3—late Triassic; C-P—Carboniferous to Permian; C_2—late Carboniferous; K_1—early Cretaceous; J–K—Jurassic to Cretaceous; J—Jurassic.

2.2. Enrichment of Fluorine in Coal

The enrichment factor (EF) and concentration coefficient (CC) represent the enrichment level of trace elements in coal [50], where CC > 100 indicates unusually enriched, 100 > CC > 10 indicates significantly enriched, 10 > CC > 5 indicates enriched, 5 > CC > 2 indicates slightly enriched, 2 > CC > 0.5 indicates normal enrichment, and CC < 0.5 indicates depleted enrichment. According to the standards (the global average of 88 mg/kg is used as the baseline), if the F content is higher than 176.0 mg/kg in coal, it is F-enriched coal.

The element F has an uneven distribution in coal that was deposited during different geological periods or different areas (Figure 2), and most of the F-enriched coal is found in SW China, some of coal-sediments in NW, South, and North China also have an enriched fluorine content; the highest concentration of F in coal varies from 1296 to 3575 mg/kg, with a mean of 2076 mg/kg in the Guiding coalfield, Guizhou province [25].

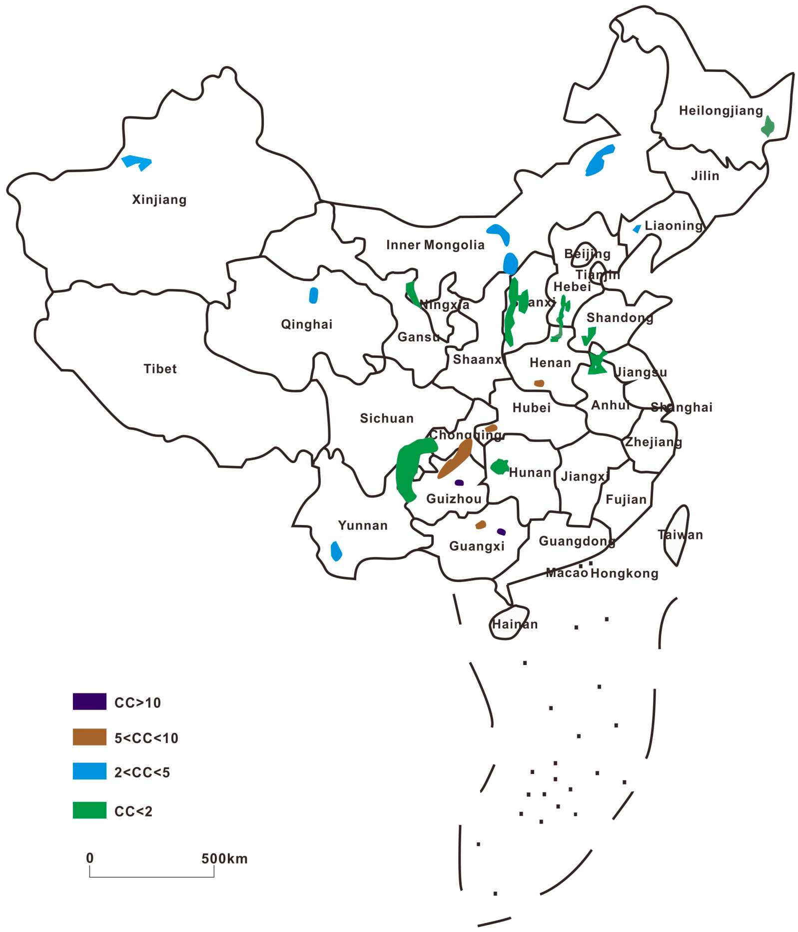

Figure 2. The fluorine enrichment distribution of Chinese coal (based on reported data [7–13]).

For coal deposited during different periods, the coal of the Paleozoic and Cenozoic contains relatively higher levels of fluorine, especially in C-P and E-N coal, while middle Jurassic coal from NE and NW China is slightly enriched (Figure 3).

As for different areas, Zheng et al. [51] reported that the F content in coal from the Longtan formation of the Permian in Fuling, Chongqing varied from 300 to 1488 mg/kg, with a mean of 866 mg/kg, far higher than average values worldwide and in China (CC ≈ 10). Soon afterwards, F-enriched coal was found in Fuyuan, Yunnan province, deposited in the late Permian era, with an average concentration of 549.7 mg/kg [52], reaching the enriched level (CC > 5). Chen and Tang [7] investigated fluorine in Chinese coal, finding that F was significantly enriched in coal of the late Permian Longtan formation coal in Laochang, Yunnan, with a mean of 1977.2 mg/kg based on 29 samples (CC > 10). In surrounding areas, F was also enriched in coal of Zhijin, Nantong, Songzao and Lingcang Dazhai coal, with respective means of 500 mg/kg, 429 mg/kg, 440 mg/kg, 369 mg/kg (CC ≥ 5) [19–22,53]. In addition, fluorine in Jurassic coal from Muli, Qinghai was slightly enriched (CC > 2), with a mean value of 253 mg/kg [49]. In other districts, the F in coal had a similar content to the averages worldwide or in China [15,17,53–55].

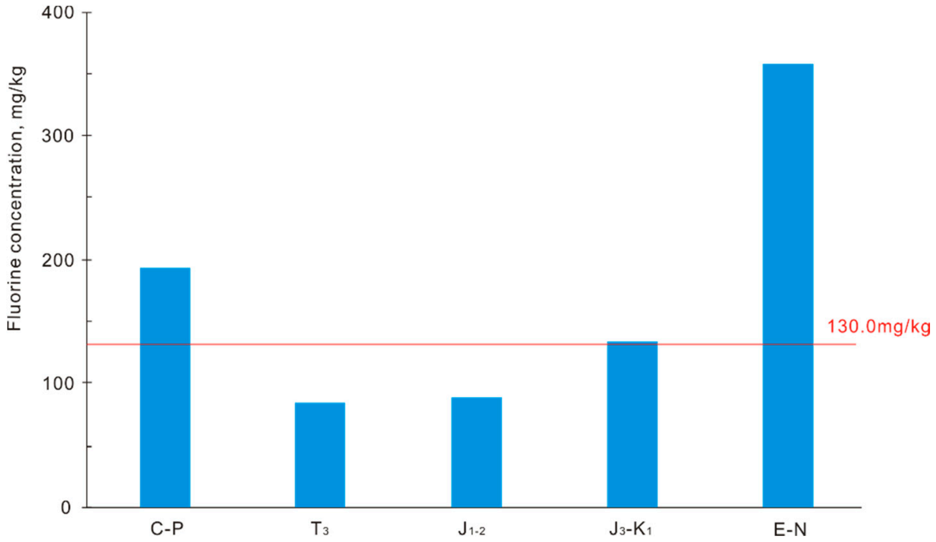

Figure 3. The fluorine content distributed in different eras of Chinese coal (1883 samples for C-P, 35 samples for T_3, 33 samples for J_{1-2}, 10 samples for J_3–K_1, 25 samples for E-N).

In South China coal, there were many instances where the F concentration was enriched or slightly enriched (10 > CC > 5), such as in Heshan, Guangxi (average 1728.3 mg/kg), Enshi, Hubei (average 717.3 mg/kg), Hechi Guangxi (average 614 mg/kg) [28], and Fusui, Guangxi (average 329 mg/kg) [29].

In other areas, including North, NE, and NW China, F in coal was enriched in some cases; for example, in Pingdingshan, Henan (average 637.0 mg/kg) (CC > 5) [7], Heidaigou (average 286.0 mg/kg) (CC > 2) [47], Guanbanwusu (average 434.0 mg/kg) (CC ≈ 5) [45], Wulantuga (average 336.0 mg/kg) (CC > 2) [44], and Adaohai (average 207.0 mg/kg) (CC > 2) [43] of Inner Mongolia. Moreover, fluorine in Junger coal was on average of 218.4 mg/kg [40], or slightly enriched (CC > 2), while F was slightly enriched in Yili coal, Xinjiang (average 311.38 mg/kg) [48], Tiefa coal, Liaoning (average 170.0 mg/kg) [56], Qitaihe, Heilongjiang (average 188.0 mg/kg) [9], and Jixi, Heilongjiang (average 172.0 mg/kg) [9].

2.3. Modes of Fluorine Occurrence in Coal

Swaine [14], Huggins and Huffman [57], and Finkelman [58] presented pioneering reports about the modes of halogens (F, Cl, Br) occurrence in coal, suggesting that F occurred in minerals with inorganic associations, such as clay and mica. A study of Bulgarian coal found evidence that F exists in kaolinite, montmorillonite, and chlorite [5]. F in Czech coal occurred with an organic affinity [59]. All of this indicates that fluorine occurs in variety of forms in coal, most of them in multiple states with mixed affinities [15,17,49,50].

As for F found in Chinese coal, many studies [19,41,47,60] argue that F indicates the following associations in coal:

(1) The mineral form. The fluorine minerals, including fluorite, fluorapatite, illite, kaolinite, and montmorillonite, always found in coal, feldspar and augite contain little fluorine in some cases [11,12]. Dai et al. [49] studied the mineralogy and geochemistry of Jurassic coal from Qinghai, discovering

that the variations in concentrations of F, P, Sr, and Ba throughout the coal seam section were broadly similar, and that F shared same geochemical characteristics with P, indicating that F primarily occurred as fluorapatite. In Taoshuping coal, Yunnan province, elemental fluorine shared a similar vertical distribution with P_2O_5 in coal seams, evidence that fluorine existed in P-containing minerals (such as fluorapatite) [52], while the F occurring in fluorapatite was verified by Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) detection in Adaohai coal of Daqingshan coalfield, Inner Mongolia [43]. The fluorine in Guiding Permian coal had a strong positive correlation with ash yield (r = 0.88), indicating an inorganic association; in addition, the correlation coefficients between F and B, Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO, V, Mn, and Fe_2O_3, Cr varied from 0.88 to 0.95, suggesting that F may exist in verdelite [25].

(2) Adsorbed on minerals. Fluorine in source rock was dissolved during the weathering process. Most of it was adsorbed on minerals, and the rest was in solution or substituted in minerals structures. According to recent reports, most of the fluorine in coal was adsorbed [24,27,28,37,42,43]. Studies on Songzao coal from Chongqing found that F, together with Ga, Sn, U, Th, Zr, Hf, and Ta, had positive correlations with Al_2O_3, suggesting that fluorine occurred in clay minerals (kaolinite and others) [19,61]. The F found in Guxu coal from the Guizhou province had a significant positive correlation with ash content and kaolinite concentration, indicating that fluorine exists in kaolinite [54]. Chen et al. [20] studied the geochemistry of coal from the Nantong coalfield, Chongqing, and detected F with similar characteristics of ash yield, SiO_2, Al_2O_3, V, Cr, Co, Ni, Cu, Ga, Sr, Mo, Cs, Ba, Tl, U, and REY in the vertical distribution. In addition, it had weak positive correlations with SiO_2, Al_2O_3, CaO, and kaolinite, suggesting that fluorine occurred in a variety of minerals. Meanwhile, in Shengli coal of Inner Mongolia, elemental F was found in illite and the illite smectite mixed layer (IS), which was verified by the strong positive correlations between F and ash yield, SiO_2, Al_2O_3, and K_2O (r > 0.95) [62]. The F in Daqingshan coal is slightly enriched (2 < CC < 5), has similar concentrations as Ga, V, Cu, Se, and Mo, and has positive correlations with ash, SiO_2, and Al_2O_3 (r = 0.93) [42], the primary minerals in coal are quartz and kaolinite [33,34,46], elemental F found in kaolinite and elemental F in Wulantuga coal was also adsorbed on clay minerals and was verified by statistical analysis (with positive correlations between F and ash, Al_2O_3, SiO_2, and K_2O) [44]. The same occurred in Guanbanwusu [45] and Haerwusu coal [46], where fluorine was found in kaolinite and boehmite.

(3) Substitution form in minerals. In the process of diagenesis, elemental F would be in its ion form occurring in a mineral crystal lattice. During the hydrolysis of phosphorus organic compounds, the generated phosphate anions may be absorbed onto Fe^- and Al^- hydroxides by the replacing of OH^- groups. As F^- can also be substituted for OH^-, it can be interpreted that the high correlation between the two elements is the result of the above pattern. F is enriched in Wuda coal, and the positive correlation coefficients of F–P_2O_5 (0.83) and F–Ca (0.71) demonstrate that F largely occurs in apatite [63]. The correlation between F and P may be the result of the mobility of both elements during diagenesis.

(4) Water-soluble form. As stated above, some of the fluorine in rock is dissolved in water during the weathering process, and few reports have discussed this. Wang et al. [46] used a sequential extraction/density separation (SE/DE) procedure to examine the modes of F occurrence in Haerwusu coal, indicating that 1.33% of fluorine occurred in its water-soluble form in coal. In addition, Lu [15] reported that fluorine in the water-soluble form existed in the water within rock pores, Huggins and Huffman [57] reported that halogens was a kind of soluble from of Cl and Br in coal moisture.

Fluorine may also occur in coal organic matter, such as inertinite [32,46].

3. Fluorine Occurs in Coal Deposits of China

Among the six major coal-forming periods in China: Late Carboniferous and Early Permian (C_2–P_1), Late Permian (P_2), Late Triassic (T_3), Early and Middle Jurassic ($J_{1–2}$), Late Jurassic and Early Cretaceous (J_3–K_1), and Paleogene and Neogene (E–N) [9], the majority of coal reserves were formed in C_2–P_1, P_2, $J_{1–2}$, and K_1, accounting for more than 98% of all the reserves. Nearly all of the elements in the periodic table, from Be to U, have been detected in coal [64,65]. In this section, fluorine concentration and distribution in coal deposited in different coalfield of China will be reported, including in north China (Junger, Daqingshan, Wuda, and Ningwu coalfields), northeast China (Shengli, Huolinhe, Qitaihe, Zhalainuoer, and Tiefa coalfields), northwest China (Yili coalfield), southwest China (Songzao, Huayingshan, Yongrong, Junlian, Guxu, Xuanwei, Lincang, Zhaotong, Guiding, Xingren, Zhijin, Nayong, and Puan coalfields), and Muli coalfield in Tibetan.

3.1. Fluorine Deposited in Coal of North China

In China, coal distribution concentrates in the north, and fluorine is generally slightly enriched in coal deposited in north China. In this section, fluorine concentration and distribution in coal from north China will be reported, mainly including the coalfield located at Inner Mongolia and Shanxi Provinces.

3.1.1. Junger Coalfield

Fluorine is slightly enriched in Junger coal (CC > 2), mainly derived from bauxite of Yinshan Old land, and occurs in kaolinite and boehmite. The Junger coalfield is located at the south-central part of Inner Mongolia, including Guanbanwusu, Haerwusu, Heidaigou, and Chuancaogedan. The main recoverable coal seams are No.5 coal in the Shanxi formation of early Permian and No.6 coal of the Taiyuan formation from late Carboniferous. Numerous studies [66–68] have reported on the petrology, mineralogy and geochemistry of Junger coal in detail.

F is enriched in Guanbanwusu coal and the content varies from 127.0 to 1286.0 mg/kg, with a mean of 434.0 mg/kg, implying an increasing trend from the bottom to the roof in the vertical distribution [45]. In the Heidaigou mine, the F concentration ranges from 54.0 to 121.0 mg/kg (average 101.0 mg/kg) in No.6 coal [66], similar to Chinese coal (130.0 mg/kg), without variation in the vertical distribution. Haerwusu mine, in nearby Heidaigou, is situated at the southern part of Junger coalfield, and elemental F is slightly enriched (286.0 mg/kg, CC > 2) with increasing from the bottom to top, more than 90% of which occurs as silicate association and an organic association [44,46]. While fluorine content in Chuancaogedan coal is 218.4 mg/kg, it is slightly enriched when compared to coal worldwide (88.0 mg/kg) [40].

3.1.2. Daqingshan Coalfield

The coalfield situated at the center of Inner Mongolia includes Adaohai, Hailiushu, Zhaogou, and more. The Permian coal seams are in the Shuangmazhaung formation and the Zahuaigou formation of C_2–P_1.

The Adaohai coal mine is located to the southeast of the coalfield where the main coal seam is CP2 coal in the upper Shuanmazhuang formation with a total thickness of 22.58 m. The results of a total sulfur and proximate analysis suggested that it was medium-low ash and low sulfur. The fluorine values ranged from 87.0 to 824.0 mg/kg (average 207.0 mg/kg), with an uneven distribution along the coal seams. Analysis revealed that F exists in fluoapatite and gorceixite [43]. In the Hailiushu mine, which is situated in the southwest of Daqingshan coalfield, and the recoverable coal seam was Cu2 coal (CP2 coal in Adaohai) with mean F concentration of 179.0 mg/kg. It has an even vertical distribution and the modes of F occurrence are mainly inorganic, according to the correlation coefficients between F and ash yield, SiO_2, and Al_2O_3 (r = 0.93) [42].

3.1.3. Other Coal Producing Districts of North China

The Wuda coalfield is located in the west of Inner Mongolia, at the western margin of Ordos basin, and it is the main coking coal production base in north China, including Wuhushan, Suhaitu, and Huangbaici Mines. The main recoverable coal seam covers the coal bearing strata in the Benxi, Taiyuan, Shanxi, lower-Shihezi, and upper-Shihezi formations of C–P tera, including No.9 coal, No.10 coal, No.12 coal, No.13 coal, and No.15 coal. According to the recent study [46], the average content of

F is 262.0 mg/kg, and it has significantly positive correlation with ash, Ca, and P_2O_5; meanwhile, fluoapatite is easily detected by SEM, where F is mainly found.

The Ningwu coalfield is situated at Ningwu basin, located in the northern Shanxi province. The coal-bearing strata include the Taiyuan and Shanxi formations. Fluorine is slightly enriched in Pingshuo (a main coal mining base of Ningwu coalfield) coal, with a mean of 167.0 mg/kg, decreasing from the middle part to the bottom and roof in the coal seam. F is adsorbed on kaolinite as indicated by a positive correlation between F and kaolinite, and between F and ash yield [39].

Apart from the areas described above, the F content is relatively high in Fengfeng coal and Kailuan coal of Hebei, and in Huozhou coal of Shanxi [7,9], while in Luxi coal of Shandong, the fluorine concentration is between 30.0 and 241.0 mg/kg (average 130.0 mg/kg) [38]. Fluorine in the coal of Huainan, Huaibei, and Yanzhou is depleted [69,70].

3.2. Fluorine Deposited in the Coal of NE China

The Shengli coalfield is located in NE Inner Mongolia, a sub-deposit within the Erlian basin, and the coal bearing strata are the Cretaceous Shengli and Xilin formations. The No.6 coal is the main recoverable coal seam [71]. The F content ranges from 158.0 to 1004.0 mg/kg, averaging on 336.0 mg/kg, slightly enriched (CC > 2). The coal in Shengli coalfield is unusually Ge-enriched, and fluorine has a similar distribution to the ash yield. Elemental F has a strongly positive correlation with ash yield, Al_2O_3, SiO_2, and K_2O, with respective correlation coefficients of 0.88, 0.86, 0.75, and 0.82, indicating that F occurs in clay minerals (kaolinite and illite) [44,62].

Meanwhile, in other coal producing areas of NE China, fluorine is also enriched (CC $\geq$ 2) in Huolinhe coal (average 140.0 mg/kg), Qitaihe coal (172.0 mg/kg), Zhalainuoer coal (117.0 mg/kg), Jixi coal (188.0 mg/kg), and Tiefa coal (170.0 mg/kg) [7,12].

3.3. Fluorine Deposited in the Coal of NW China

The Yili basin is the largest sedimentary basin in NW China, located in the Xinjiang Uygur autonomous region. The Jurassic coal-bearing strata in the Yili Basin include the early Jurassic Badaowan and Sangonghe Formations as well as the middle Jurassic Xishanyao Formation [72]. The coal is remarkably rich in U, and the F content is 311.4 mg/kg on average. Fluorine is depleted in U-rich coal [48], and has multiple associations.

3.4. Fluorine Deposited in the Coal of SW China

3.4.1. Sichuan & Chongqing Coal Producing Areas

Sichuan and Chongqing Provinces are the main coal production areas in SW China with a number of coalfields, including the Songzao, Huayingshan, Yongrong, Junlian, and Guxu coalfields.

The Guxu coalfield is located in the southwest of Sichuan province with an annual production of 1.2 Mt. The main coal strata is the Longtan Formation of the late Permian, with a total thickness of 81.81 to 99.42 m. The F concentration is 108.0 mg/kg on average in No. 25 coal from the Guxu coalfield, and it mainly occurs in clay minerals (kaolinite) [54]. The Huayingshan coalfield is situated in east Sichuan, where its main coal-bearing strata are also in the Longtan Formation, and the main recoverable coal seam is K1 coal. Fluorine is an average of 145.0 mg/kg, and F exists in kaolinite [26]. The F content ranges from 129.0 to 210.5 mg/kg, with average of 142.18 mg/kg, and it is relatively high in K2a coal [64].

The Songzao coalfield is southeast of Chongqing, and it includes the Yuyang, Shihao, Fengchun, Songzao, and Tonghua coal mines [44]. The main coal strata is the Longtan Formation of the Permian, containing 6 to 11 coal-seams, and Nos. 6, 7, 8, 11 and 12 are recoverable coal in the coalfield [19]. The fluorine is enriched (average 429.0 mg/kg, CC > 5), and is mainly found in kaolinite [23]. The Nantong coalfield, an important coking-coal base of SW China, is in the southwest of Chongqing where Nos.4 and six coals of the Longtan Formation (late Permian) are primarily mined. The fluorine content averages 431.0 mg/kg and 425.0 mg/kg for two coal seams, respectively. The mode of F occurrence is inorganic and exists in minerals [20].

3.4.2. Yunnan & Guizhou Coal Producing Area

Yunnan province is one of the most important coal production areas in China, with numerous coal deposits in the region, such as the Xuanwei, Lincang, and Zhaotong coal enrichment areas.

The Xuanwei coalfield is situated in eastern Yunnan and the coal strata is the Xuanwei Formation [31]. There are four to 14 coal-seams in the Xinde mine of the Xuanwei coalfield and the fluorine concentration varies among them, from 84.0 to 199.0 mg/kg (average 124.0 mg/kg) in C_1 and C_{2+1} coal and 60.8 mg/kg in C_2, C_3 coal. Fluorine concentrations are relatively high in the upper parts of coal seams, and low in the lower parts, mainly occurring in kaolinite with an uneven distribution [31]. The Taoshuping mine is in the southeastern margin of the Xuanwei coalfield, and the main recoverable coal is k_{2+1} and k_{21} coal of the upper Longtan Formation (late Permian). The elements V, Cr, Co, Ni, and Cu are enriched, the F is depleted in coal with a value of 51.2 mg/kg, and it has a positive correlation with P_2O_5, suggesting that F is associated with P-minerals [52]. In addition, Yangchang coal [9], Laochang coal [7], Enhong coal, Fuyuan coal [21], and Songshan coal [42] are F-enriched.

Bangmai basin is located at Lincang, in Yunnan province, filled by the Miocene coal-bearing Bangmai Formation, which was divided into six zones from bottom to top, and the coal is located in zones N_1b_2, $N_1b_{4–5}$, and N_1b_6. The Dazhai and Zhongzhai mines are the main coal producing areas. The X1, Z2, and S3 coal, the main recoverable coal seams, are enriched with Be, Ge, and W, and the F content is 123.0 mg/kg, 167.0 mg/kg, and 364.0 mg/kg, respectively. In S3 coal, the F is similar to Li, Ga, Cu, V, Cr, Co, Ni, and Zn in modes of occurrence and exists in minerals [31]. In Luquan coal, middle Devonian Haikou Formation, the F concentration is 181.0 mg/kg on average and is enriched in the upper and lower parts and depleted in middle parts of the coal seams [21]. F has an average level of enrichment (a mean of 115.0 mg/kg) in Mahe coal from the Longtan and Changhe Formations of the Permian era in the Zhaotong coalfield [64].

Coal reserves are abundant in Guizhou province, including the Guiding, Xingren, Zhijin, Nayong, and Puan coalfields [60]. The Guiding coalfield is located in central of Guizhou and the main coal strata is the Wujiaping Formation of the upper Permian, including M1 and M3 coal. The F is unusually enriched and ranges from 1296.0 to 3575.0 mg/kg (average 2076.0 mg/kg), mainly occurring in verdelite [25]. The Zhijin coalfield in the west of Guizhou consists of Late Permian coal-bearing strata, including the Upper Permian Emeishan Formation (P1e), the Late Permian Longtan Formation (P2l), the Late Permian Changxin Formation (P2ch), and the Late Permian Dalong Formation (P2d). The F concentration is enriched with average of 500.0 mg/kg (CC > 5) [24]. The Puan coalfield is in SW Zhijin, and the Longtan Formation (P2l) is the main coal-bearing formation in the area. The fluorine concentration varies from 51.7 to 112.3 mg/kg, normal levels compared to other Chinese coal [18].

3.4.3. Other Coal Producing Areas of SW China

Apart from Chongqing, Sichuan, Yunnan, and Guizhou in SW China, Guangxi has large coal resources. The Heshan coalfield is located in the center of the Guangxi Zhuang Autonomous Region, whose output accounts for the one third of the total coal production in Guangxi. The major coal-bearing strata were developed in the late Permian Heshan Formation, which is divided into upper and the lower units that total five coal seams. The F concentration ranges from 200.0 to 3000.0 mg/kg, with an average of 535.0 mg/kg, enriched (CC > 5) as compared to other Chinese coal [30]. The Fusui Coalfield is located in southern Guangxi province where the Heshan Formation is the major coal-bearing stratum, and No.1 coal is the main mining coal bed. The fluorine value ranges from 116.0 to 538.0 mg/kg, with an average 329.0 mg/kg, and the vertical distribution is similar to Mo and Cs [29].

3.5. Fluorine Deposited in Tibetan Coal of China

There are few reports on Tibetan coal. The Muli coalfield is located along the northern Tibetan Plateau. Coal-bearing strata in the Muli Coalfield include the Muli and Jiangcang Formations, located in the lower and upper portions of the middle Jurassic system. The coal is generally dominated by inertinite-group macerals. The fluorine is slightly enriched and mainly occurs in fluorapatite, ranging from 60.0 to 441.0 mg/kg, and an average of 253.0 mg/kg [49].

4. Genetic Factors of Trace Elements Enrichment in Chinese Coal

The accumulation and distribution of trace elements in coal are controlled by multiple factors during the geological processes. During peat formation, the major factors include, the nature of source rocks, sedimentary environments, the type of coal-forming plant, microbial action, climate variability, and hydrological conditions. During the coalification process, the main factors are from diagenesis of roof and floor rock, microbial action, tectonism, magma and hydrothermal activity, and groundwater movements [10].

According to previous report [9], several genetic types of trace elements were found in Chinese coal: source rock controlled, sedimentation environment controlled, magmatic or hydrothermal controlled, fault controlled, and groundwater-controlled. Another recent study included, source-rock-controlled, marine-environment-controlled, hydrothermal-fluid-controlled (including magmatic-, low-temperature-hydrothermal fluid-, and submarine-exhalation-controlled subtypes), groundwater-controlled, and volcanic-ash-controlled [13]. The element F and most other trace elements that are enriched in coal, are influenced by one or more particular geological factors. More details are as follows.

4.1. Weathering of Source Rock

The condition of the source rock is always a key factor for the elemental enrichment, especially for the coal that is deposited in small scale fault basins. Because the source region is near the basin, detrital materials can be transported to the interior of the coal basin and elements with high concentrations in the source rock are commonly enriched in this coal [13].

The composition of coal in North China is generally influenced by the nature of the source rock and its weathering processes. Yili U-rich coal developed quartz, K-feldspar, coarse-grained kaolinite, illite, chlorite, sodium plagioclase, and calcite, suggesting that the components of coal mainly came from terrigenous detritus. The K-feldspar development verified that the elements were derived from felsic sediments [48,72]. In addition, trace elements (F and others) in the Shengli, Daqingshan, and Junger coalfields were derived from terrigenous sediments, the weathered and oxidized bauxite in the exposed crust of the older Benxi Formation (Pennsylvanian) [42–46].

In other districts, such as in Changhe coal from Sichuan, the trace elements (As, W, Pb, and Th) are possibly derived from the Xuefeng old land, the main sources of sediment for that coal basin [17]. The F in Taoshuping coal [52], Huayingshan coal [26], and Nantong coal [20] mainly came from the detrital of Kangdian old land.

4.2. Volcanic Ash Deposition

During coal formation, the abundance and distribution of trace elements can be affected by volcanic ash deposition, which is common in coal from SW China.

The rare earth elements (REEs) are highly enriched in Permian Longtan Formation coal from the Nantong coalfield of Chongqing province, and the floor rock samples of No.6 coal are characterized by a positive Ce anomaly and a negative Eu anomaly. There is high light rare earth elements and europium (LREY) fractionation, and Ga, Zr, Nb, Ta, and Hf are unusually enriched, all of which could be the result of an alkali volcanic ash source [20]. Volcanic quartz, such as β form was easily found in Yunnan coal, indicating that there were felsic volcanic ash inputs during peat mire accumulation;

meanwhile, kaolinite and pyrite are unusually enriched with a low content of quartz, which may suggest volcanic ash input during coal formation [23,29].

4.3. Marine Water Influence

Some elements in coal, such as Mo, U, and B, are generally enriched in marine sedimentary environments and their abundance and distribution are easily affected by ocean conditions, not only because seawater contains high content of these trace elements, but also because plankton in marine water are enriched in these elements that can change the pH and H_2S content, leading to a favorable environment for enrichment of trace elements [13].

The Permian Longtan Formation coal in the Nantong coalfield of Chongqing has a high sulfur content, indicating a marine environment [20]. The S, V, and Sr are enriched, indicating that the peat swamp of the coal had been subjected to a marine environment [23].

4.4. Hydrothermal Fluids

Hydrothermal fluids in coal basins include two types: descending (infiltrational) and ascending (exfiltrational) [73]. The former was derived from meteoric water that circulated deep below the ground and migrated by gravity from the periphery to the center of the basin [13], the latter were derived from groundwater and were mainly driven by high gas pressures, penetrating into the coal basin along faults in the floor rock [73]. Both of them may occur in each stage of coal formation.

The F abundance is higher in the upper coal bed than in the lower parts of Guanbanwusu coal from Inner Mongolia, sharing a similar distribution with Li in the upper coal bed and reverse in lower bed, indicating that a portion of F in the upper part of the coal seam occurs in the chlorite and thus was derived from epigenetic hydrothermal fluids [45].The U, Se, Re, and Mo were abundant in Yili coal, and were mainly influenced by the epigenetic infiltrational type solution during the coal deposit [48]. In the Ge-rich coal of Yunnan, SW China, Be, W, and Ge, are unusually enriched, and are mainly influenced by N_2–CO_2 mixed hydrothermal fluids [24]. Studies of Guiding late Permian coal found that the coal was deposited in an euxinic environment and was influenced by hydrothermal fluids [19]. Trace elements in Yunnan, Guizhou, and Guangxi coal were also controlled by hydrothermal fluids [31,40,43,49]. The REEs in Daqingshan coal have a M-type enrichment, while the modes of Ti occurrence and the presence of corroded zircons were caused by acid hydrothermal solutions [46].

4.5. Groundwater

Groundwater conditions could affect the solubility of aqueous media and trace element migration in source rock. Groundwater also contains abundant trace elements, such as Mn, Ca, As, and Zn, and has active microbial action. The trace elements in groundwater could penetrate coal beds through the coal fracture, and have physical and chemical reactions with coal, resulting in trace elements migration.

There are fewer studies in the literature related to groundwater influence on the enrichment of trace elements in Chinese coal. In Heidaigou and Haerwusu coal, the enriched REEs in coal and depleted REEs in coal-partings are attributed to leaching by groundwater during parting formation [13,47,57].

5. Environmental and Health Effects of Fluorine in Coal

5.1. Environmental Problems Related to Fluorine in Coal

Fluorine is one of the most hazardous elements in coal. During coal utilization a large quantity of toxic fluorine compounds, such as HF, SiF_4, and CF_4, are released into the environment, causing atmospheric pollution [4,6,74]. The amount of fluorine released into atmosphere reaches 1.5 Mt each year in China [11], and more attention should be paid to these environmental problems.

The mixed HF and SO_2 released by coal burning cause more damage to the environment than their action alone [8]. When plant leaves come into contact with fluorine, it can damage the leaves or even kill the plant, while fluorine found in plants can be transferred into human or animal bodies through the food chain. In general, coal gangue has a much higher content of fluorine than coal, which is released into the aquatic and atmospheric environment during combustion and leaching [2,75]. The F in open pit mines can damage to the surrounding environment: for example, the F concentration in Pingshuo open mine dust was 680.0 mg/kg, and the fluorine in surrounding plants was also enriched [8].

Meanwhile, fluorine has negative effects on the silkworm industry. According the report [76], if the F value is higher than 100.0 mg/kg in mulberry leaves, the silkworm cocoon will be totally destroyed.

5.2. Health Problems Induced by Fluorine in Coal

High fluoride levels not only cause serious environmental issues, but also have negative impacts on human health, such as dental fluorosis, skeletal fluorosis, impaired thyroid function, and lower intelligence in children [6,75]. The health problems caused by fluorine due to domestic coal use in SW China have been reported and many people in the area suffer from various fluorosis [2,77–79].

In Zhaotong, Yunnan province (one of the endemic fluorosis areas), F, As, Se, and Hg content in coal, corn, and chili dried by coal, mixing clay, and drinking water have been found and compared, suggesting that these elements were enriched in mixing clay, and corn and chili dried by coal, and depleted or normal in others, as a result, the main reasons for endemic fluorosis are the mixing clay in coal and food dried by coal [80], because the wet corn and chili very easily absorb the fluorine volatilized by the burning of the coal in the process of indoor drying and storing [81], most of the F in corn and chilies probably occurs either in smoke dusts attached to the surface or is adsorbed onto the outer peel, rather than being absorbed by the inner part [82]. Meanwhile, based on other reports [74,77–83], the main cause of the endemic fluorosis in SW China is the use of F-rich mixing clay. Fluorine pollution is controlled by the acidity of coal and SW Chinese coal has a very high acidity, which can have chemical reactions with mixing clay that produce HF gas under specific conditions, like heating or burning [84]. While a new study [85,86] is clearly against the fluorine source from volcanic ash for the endemic disease in Guizhou Province.

Although numerous steps have been taken to decrease coal-fluorine pollution, such as the promotion of stoves to reduce fluorine [81], endemic fluorosis is quite serious in China and more practical and economic measures should be taken to prevent it, in addition to developing F-sequestration technologies, changing the living habits of the residents in the endemic area [82].

6. Conclusions

The existing literature has clearly described the geochemical features of fluorine in Chinese coal, including its abundance, modes of occurrence, distribution, and genetic factors.

The average fluorine content in Chinese coal is 130.0 mg/kg, higher than the average value worldwide (88.0 mg/kg). The abundance of F in SW and north China coal is slightly higher than the Chinese average (130.0 mg/kg). The concentration coefficient (CC) is used to estimate fluorine enrichment, where CC > 2 (F concentration higher 176.0 mg/kg) means the coal is F-enriched, and while F-rich coal is typically deposited in SW China, other districts have some unusually enriched coal as well. Fluorine occurs in several forms in Chinese coal, primarily as independent minerals and mineral adsorption, isomorphism, and water-soluble forms have also been detected. The genetic factors influencing trace element accumulation are the weathering of source rock and hydrothermal fluid effects; in addition, volcanic ash, marine water influence, and groundwater influence could also affect the enrichment of elements in coal. The environmental effects of fluorine include atmospheric pollution and health problems that are currently very serious and require urgent action to resolve them.

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