



# Article Effects of Minerals Type and Content on the Synthetic Graphitization of Coal: Insights from the Mixture of Minerals and Anthracite with Varied Rank

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Abstract: The challenge of how to effectively treat minerals in coal before synthetic graphitization is a practical problem. It is unrealistic to remove minerals completely via physical or chemical methods. So, it is essential to clarify the role of minerals in the synthetic graphitization of coal. Based on the complex mineral composition, the mixture samples consisting of coal and mineral are used to obtain the effect of minerals type and content on the synthetic graphitization of coal. The role of minerals in synthetic graphitization is closely associated with the mineral content and type, as well as the rank. As to the lower-rank anthracite, quartz, kaolinite, and calcite have the role of inhibitor for the yields and defect degrees of corresponding samples after synthetic graphitization derived from the mixtures, but the role of catalyzer for their crystal structure (the degree of graphitization, stacking height, lateral size). The increasing content of quartz, kaolinite, and calcite is harmful for the yield, but useful for the crystal structure and defect degrees; the increasing content of pyrite is harmful for the yield, degree of graphitization, and stacking height, and it is useful for defect degrees. As to the higher-rank anthracite, quartz, kaolinite, and calcite have the role of inhibitor for the yield of corresponding samples after synthetic graphitization, catalyzer for their crystal sizes (stacking height, lateral size), and inertia for their degrees of graphitization. The increasing content of quartz, kaolinite, calcite, and pyrite is harmful for the yield and crystal size. A lower coal rank indicates being more prone to positive mineral effects on synthetic graphitization. The role of minerals in the synthetic graphitization of coal is complex and also represents a coupling relationship with the thermal transformation of anthracite.

Keywords: synthetic graphitization; coal; minerals type; minerals content; mixture; anthracite

## 1. Introduction

A large number of studies have shown the gap in the graphitization capacity of coal [1–6]. Even coals of similar rank also show different evolutionary paths [5]. Coal simply consists of two parts: organic matter and minerals. Organic matter, the most important component [7,8], is the main part of synthetic graphitization. Minerals are often considered catalysts for synthetic graphitization, although they cannot be converted to graphite [4,9–14]. The crystallinity of carbon materials can be enhanced by certain additives, such as metals or minerals, a process referred to as catalytic graphitization [15]. Some common inorganic elements (such as aluminum, calcium, iron, silicon, etc.) have also been used as graphitizing catalysts for carbon materials [10,16–19]. Clay minerals (such as illite and kaolinite), the main component of minerals in coal [7,20], have been observed as being effective catalysts for carbon materials [2,10,11,17–19]. The presence of iron can also improve the structural order of carbonaceous materials during high-temperature heating treatment [10,17,18].



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**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/). Graphitization is the combination of carbon deformation and decomposition [10,12,14,16,19,21–25]. The carbon spheres are formed by catalytic graphitization, and the formation and decomposition of carbides (Fe<sub>3</sub>C) with iron can be the catalyst. Iron preferentially reacts with carbon atoms at the boundary of basic structural units (BSUs), freely orienting each other on the surface of the liquid carbides to form a planar carbides of carbon layers parallel to the surface [22]. Other metallic elements may also play a similar role in the formation of carbon spheres [26]. An increase in temperature may cause the catalyst to sublimate or decompose, leaving a more stable graphite structure at higher temperatures. Therefore, the formation of a graphite structure must relate to the presence of minerals in the precursor and the catalytic action of the minerals through the catalytic graphitization mechanism, which includes both the formation and decomposition of carbides and the dissolution of metal compounds of carbon [27].

However, the presence of minerals in coal is usually detrimental to its graphitization [28], and the minerals in coal severely limit the comprehensive utilization of coal [29]. Minerals in anthracite exhibit a limited ability to catalyze graphitization [30]. During synthetic graphitization, minerals can form irregular pore defects on the surface of graphite, which will affect the material properties of anthracite-based graphite [30]. Minerals in the anthracite will also undergo the corresponding changes, such as fragmentation, agglomeration, melting, etc., which will also affect the transformation of organic matter [31]. During the recrystallization of carbon in coal, the minerals in the coal will melt at high temperature, resulting in a large number of defects in the graphite layer. Even if the mineral has little effect on the graphitization degree of anthracite, it will restrain the directional development of the graphite layer. As a result of high-temperature melting and agglomeration, minerals will be embedded in the continuous splicing, stacking between the graphite layer, hindering the accumulation of graphite carbon.

The synthetic graphitization of coal can also be influenced by mineral content. The order degree of graphite prepared from anthracite increases gradually with mineral content [4,10]. In addition, the intrinsic relationship between minerals and organic matter, the mode of occurrence of minerals, also play important roles in the synthetic graphitization of anthracite [10]. It has also been found that the presence of minerals in local areas where they come into contact with organic matter may reduce the temperature required for graphite formation [9].

Furthermore, in discussions of the effect of organic matter in coal on the structure of coal-based graphite, many studies have tries to remove the minerals in coal with acid and alkali (such as concentrated hydrochloric acid and hydrofluoric acid) to mitigate the effects of the minerals [32–35]. However, it is not possible to completely remove the minerals from coal via a chemical method, and the excessive acid, alkali, and waste liquid are not friendly to the environment. So, the effect of minerals in the process of synthetic graphitization of coal cannot be ignored. Therefore, the mechanism of synthetic graphitization of coal should not only aim at the organic matter in coal, but also the role of minerals. However, etc.), it is a challenge to clarify the role of minerals in the process of synthetic graphitization. In this study, the mixture samples of coal/mineral are used to discuss (1) the effect of mineral content (type) on the corresponding samples after synthetic graphitization and (2) the action mechanism of minerals in the synthetic graphitization of coal. This study aims to answer the problem of how to effectively treat the minerals in coal before synthetic graphitization.

## 2. Samples and Methods

# 2.1. Samples

The coal samples were collected from the Ningxia region, including Baijigou (BJG) and Jiangoushan (JGS) anthracites. The detailed information is shown in Table 1 and Figure 1. The important characteristic of the selected coal samples is low ash content (3.55% and 0.82%, respectively). A low content of minerals can reduce the interference of endogenous

minerals without chemical treatment. And, the high rank of BJG/JGS anthracite is also an excellent carbon resource for synthetic graphitization.

**Table 1.** The basic characteristics of selected coal samples.

Sample	Coalfield	Coal Mine	Coal Seam	R <sub>o,max</sub> (%)	Pı A	roxima malysi (wt%)	te is		Ultimate Analyses (wt%)				Maceral Composition (vol%)			
					M <sub>ad</sub>	A <sub>d</sub>	V <sub>daf</sub>	С	Н	Ν	0	St	V	Ι	L	Μ
BJG	Helanshan	Baijigou	4	2.82	1.08	3.55	8.32	95.71	3.19	0.79	0.28	0.03	89.6	7.6	0.0	2.8
JGS	Xiangshan	Jiangoushan	8	5.87	4.19	0.82	2.34	96.61	1.75	0.59	0.17	0.88	70.2	22.0	0.0	7.8

R<sub>o,max</sub>, The mean maximum reflectance; M, moisture; ad, air-dry basis; A, ash yield; d, dry basis; V, volatile matter; daf, dry and ash-free basis; C, carbon; H, hydrogen; N, nitrogen; S<sub>t</sub>, total sulfur; O, oxygen, by difference; V, vitrinite; I, inertinite; L: liptinite; M, mineral;.



Figure 1. The distributions of natural coal samples in the Ningxia region.

Silicates are the largest, most complex, and generally the most abundant group of minerals in coal; silicates are the hosts of many elements found in coal, particularly of major elements including Si and Al; silicates include clay minerals, the most diverse and generally most abundant mineral group in coal, and quartz, perhaps the most common mineral in coal [20]. A wide range of sulfide minerals have been found in coal, with pyrite being far and away the most common [36]. Carbonates are present in coal, and the most common carbonate minerals is calcite (CaCO<sub>3</sub>) [37]. Therefore, kaolinite, calcite, quartz, and pyrite are suitable to represent the typical minerals in coal. Taking geological conditions into account, the added content of kaolinite, calcite, and quartz is high, and the low amount of added content of pyrite is determined (Table 2). After completely uniform mixing, the mixture samples of coal/mineral are obtained.

Туре	Material Composition	Mass Ratio (Coal:Mineral)
Clay minerals	Kaolinite $(Al_4[Si_4O_{10}](OH)_8)$	100:5, 100:10, 100:20, 100:40
Carbonate	Calcite ( $CaCO_3$ )	100:5, 100:10, 100:20, 100:40
Oxide	Quartz (SiO <sub>2</sub> )	100:5, 100:10, 100:20, 100:40
Sulfide	Pyrite ( $FeS_2$ )	100:1, 100:2, 100:5, 100:10, 100:20

Table 2. The composition characteristics of the added minerals.

#### 2.2. Analytical Methods

Coal and mixture samples in the high-purity crucible are heated slowly from room temperature to 1000 °C under argon gas atmosphere at a heating rate of 5 °C/min and kept at 1000 °C for 1 h in a medium frequency induction graphitization furnace. Then, the sample continues to be heated to 3000 °C at a heating rate of 20 °C/min and kept at 3000 °C for 3 h. The corresponding residue samples are obtained. The above heating process is the common synthetic graphitization process.

Microscopic component quantification and vitrinite reflectance measurements of the coal samples are performed according to ASTM standard D2798 and D2799 (West Conshohocken, PA, USA), respectively. The vitrinite reflectance measurements under the non-polarized light are conducted on a Leica DM4500P (Leica, Wetzlar, Germany) reflected light microscope equipped with a CRAIC microscope photometer (20/30, CRAIC Technologies, Inc., San Dimas, CA, USA). The microscope is linearly calibrated with standard materials before the measurements. The maceral observations are conducted the reflected light and fluorescent light, and no less than 500 points were counted in each sample. X-ray diffraction (XRD) on corresponding residue samples after the synthetic graphitization is performed on a Rigaku Smart Lab SE X-ray diffractometer (SmartLab SE, Rigaku Corporation, Tokyo, Japan) (40 kv, 30 mA) with Cu ( $\lambda$  = 0.15406 nm) irradiation, over the interval  $5^{\circ}$ –90° 20, at a scanning rate of  $2^{\circ}$ /min. Raman spectra of corresponding residue samples after the synthetic graphitization are obtained from a HORIBA Scientific Lab RAM HR Evolution spectrometer (LabRAM HR Evolution, HORIBA, Kyoto, Japan) that utilizes an argon ion laser of 532 nm wavelength (24.3 mV) and equipped with a 1024 Pixel CCD camera. These spectra are recorded in the range of 1000 to 3000 cm<sup>-1</sup>. Three spectrum points are measured on each sample. Each spectrum is subjected to peak fitting using Origin software 2022 (OriginLab Corporation, Northampton, MA, USA).

## 3. Results

#### 3.1. Yields

The yield of synthetic graphitization ( $W_R/W_C$ ) is defined as the mass rate of raw coal sample ( $W_C$ ) to corresponding samples after synthetic graphitization ( $W_R$ ). Obviously, the yields of synthetic graphitization for the mixture samples vary across a wide range and closely relate the type and content of the added mineral, as well as that of the coal. Then, the changes in the yield of synthetic graphitization for the mixture relative to the raw coal ( $\Delta W_R/W_C$ ) are calculated (Table 3).

## 3.2. XRD

The XRD curves of corresponding samples after the synthetic graphitization derived from the coal and the mixture samples are similar (Figures 2 and 3). The (002) and (100) peaks of corresponding samples are all highly notable and sharp [38,39].

				BJG Co	al Series		JGS Coal Series						
Туре	Mass Ratio (Coal:Minerals)	Samples	W <sub>C</sub> (g)	W <sub>M</sub> (g)	W <sub>R</sub> (g)	W <sub>R</sub> /W <sub>C</sub> (%)	ΔW <sub>R</sub> /W <sub>C</sub> (%)	Samples	W <sub>C</sub> (g)	W <sub>M</sub> (g)	W <sub>R</sub> (g)	W <sub>R</sub> /W <sub>C</sub> (%)	ΔW <sub>R</sub> /W <sub>C</sub> (%)
	Raw coal	В	10.0000	/	7.7726	77.73		J	10.0000	0.5000	8.8043	88.04	
Kaolinite	100:5	BK5	10.0000	0.5000	8.1514	81.51	3.79	JK5	10.0000	0.5000	8.1195	81.20	-6.84
(K)	100:10	BK10	10.0000	1.0000	7.9855	79.86	2.13	JK10	10.0000	1.0000	7.7564	77.56	-10.48
. ,	100:20	BK20	10.0000	2.0000	6.6215	66.22	-11.51	JK20	10.0000	2.0000	7.4933	74.93	-13.11
	100:40	BK40	10.0000	4.0000	5.8253	58.25	-19.47	JK40	10.0000	4.0000	7.2265	72.27	-15.77
Calcite	100:5	BC5	10.0000	0.5000	7.4890	74.89	-2.84	JC5	10.0000	0.5000	8.8644	88.64	0.60
(C)	100:10	BC10	10.0000	1.0000	7.4792	74.79	-2.93	JC10	10.0000	1.0000	8.6185	86.19	-1.85
. ,	100:20	BC20	10.0000	2.0000	7.3617	73.62	-4.11	JC20	10.0000	2.0000	8.3998	84.00	-4.04
	100:40	BC40	10.0000	4.0000	7.7031	77.03	-7.70	JC40	10.0000	4.0000	8.3172	83.17	-4.87
Quartz	100:5	BQ5	10.0000	0.5000	7.2342	72.34	-5.38	JQ5	10.0000	0.5000	8.5921	85.92	-2.12
(Q)	100:10	BQ10	10.0000	1.0000	6.9112	69.11	-8.61	JQ10	10.0000	1.0000	8.2457	82.46	-5.58
	100:20	BQ20	10.0000	2.0000	6.6735	66.74	-10.99	JQ20	10.0000	2.0000	8.0526	80.53	-7.51
	100:40	BQ40	10.0000	4.0000	5.9774	59.77	-17.95	JQ40	10.0000	4.0000	7.7170	77.17	-10.87
Pyrite	100:1	BP1	10.0000	0.1000	8.3960	83.96	6.23	JP1	10.0000	0.1000	8.9522	89.52	1.48
(P)	100:2	BP2	10.0000	0.2000	8.4232	84.23	6.51	JP2	10.0000	0.2000	8.8824	88.82	0.78
	100:5	BP5	10.0000	0.5000	8.3962	83.96	6.24	JP5	10.0000	0.5000	8.6309	86.31	-1.73
	100:10	BP10	10.0000	1.0000	8.1515	81.52	3.79	JP10	10.0000	1.0000	8.5788	85.79	-2.25
	100:20	BP20	10.0000	2.0000	7,7881	77.88	0.16	IP20	10.0000	2.0000	8.2387	82.24	-5.80

**Table 3.** Yields of synthetic graphitization for the coal and the mixture of coal/mineral samples.  $W_C$ : the weight of raw coal before the synthetic graphitization;  $W_M$ : the weight of added minerals;  $W_R$ : the weight of the corresponding residue after synthetic graphitization.  $W_R/W_C$ : the yield of synthetic graphitization; the  $\Delta$  value is the mixture samples minus the raw coal samples, representing the change caused by the added mineral.





Then, the crystalline structural parameters of corresponding samples after the synthetic graphitization including interlayer spacing ( $d_{002}$ ), crystallite size along the *c*-axis ( $L_c$ ) and the layer sheet direction ( $L_a$ ), the average number of stacked aromatic layers ( $N_{ave}$ ), and the degree of graphitization (G) are obtained (Table 4). And, the changes in the crystalline structural parameters of corresponding samples are also calculated (Table 5). The  $d_{002}$ ,  $L_a$ , and  $L_c$  are calculated using the Braggs and Scherrer formulas [40]:

$$d_{002} = \lambda / (2\sin \theta_{002})$$
$$L_a = 1.84\lambda / (\beta_{100} \cos \theta_{100})$$
$$L_c = 0.89\lambda / (\beta_{002} \cos \theta_{002})$$



**Figure 3.** XRD spectra of corresponding residue samples after the synthetic graphitization derived from the raw JGS coal and the mixture samples determined via XRD spectra. (**A**) JQ, the mixture of JGS coal and quartz; (**B**) JC, the mixture of JGS coal and calcite; (**C**) JK, the mixture of JGS coal and kaolinite; (**D**) JP, the mixture of JGS coal and pyrite; (**E**) J, the JGS coal.

 $\beta_{002}$  and  $\beta_{100}$  are the full width at half maximum (FWHM) of (002) and (100) peaks, and  $\theta_{002}$  and  $\theta_{100}$  are their corresponding scattering angles.

 $N_{\text{ave}}$  is determined by  $N_{\text{ave}} = L_c/d_{002}$  [38]. The degree of graphitization (*G*) is calculated using the following relationship [40]:  $G = (0.3440 - d_{002})/(0.3440 - 0.3354)$ , where 0.3440 nm is the interlayer spacing of carbon with no graphitic order, and 0.3354 nm is the interlayer spacing of graphite [41].

## 3.3. Raman

The first-order (1000 to 1800 cm<sup>-1</sup>) and second-order (2300 to 3000 cm<sup>-1</sup>) Raman spectra of corresponding samples after the synthetic graphitization derived from the raw coal and the mixture samples are similar (Figures 4 and 5). Second-order Raman spectra, the combination of first-order Raman spectral vibrations [42], closely relate to the structural *c*-axis order or the graphite crystal structure [43]. The G peaks are the characteristic peaks of graphite belonging to the  $E_{2g2}$  vibration of the aromatic plane; D peak relates to the  $A_{1g}$  vibration of the amorphous hexagonal irregular lattice structure [44,45], which is attributed to the defect between the disordered structure and the aromatic structural unit. The narrow G peak relates to the enhanced condensation of aromatic rings and the shortening of alkyl chains [46].

		BJG Co	al Series					JGS Coa	al Series		
Samples	d <sub>002</sub> (nm)	L <sub>c</sub> (nm)	L <sub>a</sub> (nm)	Nave	G	Samples	d <sub>002</sub> (nm)	L <sub>c</sub> (nm)	L <sub>a</sub> (nm)	Nave	G
В	0.3359	18.25	33.69	54	0.94	J	0.3338	38.97	76.82	117	1.19
BK5	0.3366	13.26	30.74	39	0.86	JK5	0.3339	43.35	82.60	130	1.18
BK10	0.3370	13.26	33.33	39	0.81	JK10	0.3338	42.07	79.99	126	1.19
BK20	0.3349	23.50	43.40	70	1.05	JK20	0.3337	40.90	78.85	123	1.20
BK40	0.3351	28.51	58.41	85	1.04	JK40	0.3336	37.26	80.44	112	1.21
BC5	0.3355	16.98	32.23	51	0.99	JC5	0.3338	48.31	85.56	145	1.19
BC10	0.3360	18.91	34.91	56	0.94	JC10	0.3338	45.24	79.92	136	1.19
BC20	0.3359	20.00	35.52	60	0.94	JC20	0.3338	39.77	73.54	119	1.19
BC40	0.3341	30.33	63.22	91	1.15	JC40	0.3338	33.53	66.30	100	1.18
BQ5	0.3355	23.13	42.57	69	0.98	JQ5	0.3336	40.35	82.55	121	1.21
BQ10	0.3348	21.76	46.55	65	1.07	JQ10	0.3335	40.61	80.83	122	1.22
BQ20	0.3347	21.66	45.28	65	1.09	JQ20	0.3337	38.74	80.47	116	1.20
BQ40	0.3339	31.43	68.49	94	1.18	JQ40	0.3338	36.11	78.59	108	1.19
BP1	0.3349	17.21	35.54	51	1.05	JP1	0.3335	42.51	84.63	127	1.22
BP2	0.3360	16.86	30.68	50	0.93	JP2	0.3335	41.72	80.83	125	1.22
BP5	0.3365	15.98	32.04	47	0.88	JP5	0.3337	41.53	82.68	124	1.20
BP10	0.3358	16.11	32.54	48	0.95	JP10	0.3338	43.01	83.25	129	1.19
BP20	0.3361	13.22	29.54	39	0.92	JP20	0.3338	44.77	85.30	134	1.19

**Table 4.** Structural parameters of corresponding samples after the synthetic graphitization derived from the coal and the mixture samples determined via XRD spectra.

**Table 5.** Changes in the structural parameters determined via XRD/Raman spectra of corresponding samples after the synthetic graphitization derived from the mixture samples. The  $\Delta$  value is the mixture samples minus the raw coal samples, representing the change caused by the added mineral.

	JGS Coal Series								
Samples	$\Delta L_{\rm c}$ (nm)	ΔL <sub>a</sub> (nm)	$\Delta G$	$\Delta I_{\rm D}/I_{\rm G}$	$\Delta A_{\rm D}/A_{\rm G}$	Samples	$\Delta L_{\rm c}$ (nm)	ΔL <sub>a</sub> (nm)	$\Delta G$
BK5	-4.99	-2.95	-0.09	0.0186	0.0220	JK5	4.38	5.78	4.38
BK10	-4.99	-0.36	-0.13	-0.0051	-0.0095	JK10	3.10	3.17	3.10
BK20	5.25	9.71	0.11	-0.0039	-0.0090	JK20	1.93	2.03	1.93
BK40	10.26	24.72	0.09	-	-	JK40	-1.71	3.62	-1.71
BC5	-1.27	-1.45	0.04	0.0286	0.0636	JC5	9.34	8.74	9.34
BC10	0.66	1.22	-0.01	0.0192	0.0411	JC10	6.27	3.10	6.27
BC20	1.75	1.84	0.00	0.0134	0.0318	JC20	0.80	-3.28	0.80
BC40	12.08	29.53	0.20	-0.0023	-0.0055	JC40	-5.43	-10.52	-5.43
BQ5	4.88	8.88	0.04	0.0066	0.0131	JQ5	1.38	5.73	1.38
BQ10	3.51	12.87	0.12	0.0005	0.0030	JQ10	1.64	4.01	1.64
BQ20	3.41	11.59	0.14	-0.0016	0.0080	JQ20	-0.23	3.65	-0.23
BQ40	13.18	34.80	0.23	-	-	JQ40	-2.86	1.77	-2.86
BP1	-1.04	1.85	0.11	0.0531	0.0895	JP1	3.54	7.81	3.54
BP2	-1.39	-3.01	-0.02	0.0480	0.0816	JP2	2.75	4.01	2.75
BP5	-2.27	-1.65	-0.07	0.0340	0.0506	JP5	2.56	5.86	2.56
BP10	-2.14	-1.15	0.01	-0.0028	-0.0052	JP10	4.04	6.43	4.04
BP20	-5.03	-4.15	-0.02	-	-	JP20	5.80	8.48	5.80



**Figure 4.** Raman spectra of corresponding samples after the synthetic graphitization derived from the raw BJG coal and the mixture determined via Raman spectra. (**A**) BQ, the mixture of BJG coal and quartz; (**B**) BC, the mixture of BJG coal and calcite; (**C**) BK, the mixture of BJG coal and kaolinite; (**D**) BP, the mixture of BJG coal and pyrite; (**E**) B, the BJG coal.

Then, the Raman parameters are used to evaluate the degree of crystallinity or defect in carbonaceous materials, including the positions of G and D peaks, full width at half maximum (FWHM), intensity (height) ratio ( $I_D/I_G$ ), and integrated intensity (area) ratio ( $A_D/A_G$ ) (Table 6).  $I_D/I_G$  and  $A_D/A_G$  represent the defect degree of aromatic rings [47]. And, the changes in the defect degree of aromatic rings of corresponding residue samples are also calculated (Table 5). It is worth noting that the D peak of the corresponding residue samples after synthetic graphitization derived from the raw coal and the mixture of JGS coal/mineral samples disappears (Figure 5). Thus, the effect of minerals on the defect degree of aromatic rings is obtained with difficultly.



**Figure 5.** Raman spectra of corresponding samples after the synthetic graphitization derived from the raw JGS coal and the mixture samples determined via Raman spectra. (**A**) JQ, the mixture of JGS coal and quartz; (**B**) JC, the mixture of JGS coal and calcite; (**C**) JK, the mixture of JGS coal and kaolinite; (**D**) JP, the mixture of JGS coal and pyrite; (**E**) J, the JGS coal.

**Table 6.** Structural parameters of corresponding samples after synthetic graphitization derived from the raw BJG coal and the mixture samples determined via Raman spectra.

Commission 100	D Peak	(cm <sup>-1</sup> )	G Peak	(cm <sup>-1</sup> )	т /т	$A_{\rm D}/A_{\rm G}$	
Samples	Position	FWHM	Position	FWHM	$I_{\rm D}/I_{\rm G}$		
В	1346	44	1570	25	0.0312	0.0563	
BK5	1344	41	1572	26	0.0378	0.0694	
BK10	1344	39	1570	22	0.0317	0.0593	
BK20	1351	36	1579	21	0.0296	0.0643	
BK40	-	-	1577	20	-	-	

Commlas	D Peak	$(cm^{-1})$	G Peak	$(cm^{-1})$	– In/Ic	$A_{\rm D}/A_{\rm G}$	
Samples	Position	FWHM	Position	FWHM	- 1 <sub>D</sub> /1 <sub>G</sub>		
BC5	1350	43	1580	21	0.0598	0.1199	
BC10	1352	46	1578	24	0.0504	0.0974	
BC20	1347	45	1574	23	0.0446	0.0881	
BC40	1349	38	1577	22	0.0289	0.0508	
BQ5	1342	43	1569	23	0.0498	0.0783	
BQ10	1339	46	1565	25	0.0261	0.0468	
BQ20	1344	47	1569	22	0.0273	0.0473	
BQ40	-	-	1578	20	-	-	
BP1	1349	43	1579	25	0.0843	0.1458	
BP2	1349	46	1576	27	0.0792	0.1379	
BP5	1346	43	1575	26	0.0652	0.1069	
BP10	1354	38	1580	21	0.0284	0.0511	
BP20	-	-	1578	18	-	-	

Table 6. Cont.

# 4. Discussion

4.1. The Effect of Mineral Content and Type on the Corresponding Residue Samples after Synthetic Graphitization from the Mixture of Coal/Mineral Samples

The effect of mineral content and type on the synthetic graphitization of coal generally focuses on the yield of synthetic graphitization, degree of graphitization (*G*), stacking height ( $L_c$ ), lateral size ( $L_a$ ), and defect degree of aromatic rings ( $I_D/I_G$  and  $A_D/A_G$ ) for the corresponding sample after the synthetic graphitization derived from the mixture sample.

## 4.1.1. Yield

In terms of increasing content, the addition of quartz, calcite, kaolinite, and pyrite are all unfavorable to the yield of synthetic graphitization of coal in the mixture samples, regardless of BJG and JGS coal. The yields of synthetic graphitization of mixture samples showed negative correlations with added mineral content (Figure 6A,B).



**Figure 6.** The relationships between the content of minerals added to the coal and the yield of synthetic graphitization for the mixture samples. (**A**) the BJG coal series; (**B**) the JGS coal series.

In terms of type, the existence of quartz and calcite in the mixture samples is certainly unfavorable to the yield of synthetic graphitization of BJG coal, as well as the existence of kaolinite with high added content (more than about 10%). The existence of pyrite is beneficial to the yield of synthetic graphitization, but when pyrite is added to reach a certain content (about 20%), the positive effect will disappear (Figure 6A). As to the JGS coal, the existence of quartz, calcite, kaolinite, and pyrite are basically unfavorable to the yield of synthetic graphitization (Figure 6B).

The influence degree of pyrite on the yield of synthetic graphitization of BJG coal is best, followed by the kaolinite, calcite, and quartz, in turn. It is worth nothing that the influence degrees of kaolinite and quartz are close at high added content (more than about 20%) (Figure 6A). The influence degree of calcite on the yield of synthetic graphitization of JGS coal is best, followed by the pyrite, quartz, and kaolinite, in turn (Figure 6B).

## 4.1.2. The Degree of Graphitization (G)

The effects of mineral content and type on the changes in the degree of graphitization ( $\Delta G$ ) of the corresponding samples, after the synthetic graphitization derived from the mixture samples, are closely associated with the coal. As to that of BJG coal, the effects are obvious (Figure 7A). The effects of mineral content and type on that of JGS coal are very weak (Figure 7B). The increasing content of quartz, calcite, and kaolinite is beneficial to obtain the corresponding samples after the synthetic graphitization derived from the mixture samples with a higher degree of graphitization. In terms of types, the existence of quartz, calcite, and kaolinite is mostly beneficial to the degree of graphitization except for the kaolinite and calcite with low contents (less than about 10%). However, the effect of pyrite content varies limitedly with some deviations. The comparison between the influence degree of quartz, calcite, kaolinite, and pyrite is complex and relates to the content.



**Figure 7.** The relationships between the content of minerals added to the coal and the changes in the degree of graphitization ( $\Delta G$ ) of the corresponding samples after the synthetic graphitization derived from the mixture of coal/mineral samples. (**A**) The BJG coal series; (**B**) the JGS coal series.

## 4.1.3. The Stacking Height $(L_c)$

The effects of mineral content and type on the changes in the stacking height ( $\Delta L_c$ ) of corresponding samples after the synthetic graphitization derived from the mixture samples are also closely associated with the coal. As to that of BJG coal, with the increasing mineral content, there are positive correlations between the changes in the stacking height ( $\Delta L_c$ ) and added content of quartz, calcite, and kaolinite, while there is a negative relationship



for the pyrite/coal mixture (Figure 8A). It is opposite to the that of JGS coal with regard to the effect of mineral content (Figure 8B).

**Figure 8.** The relationships between the content of minerals added to the coal and the changes in the stacking height ( $\Delta L_c$ ) of the corresponding samples after the synthetic graphitization derived from the mixture samples. (**A**) the BJG coal series; (**B**) the JGS coal series.

As to that of BJG coal, in terms of mineral type, the existence of pyrite in the mixture is certainly unfavorable to the stacking height, but the existence of quartz, calcite, and kaolinite is mostly useful except for the kaolinite with low added contents (less than about 10%) (Figure 8A). This is opposite to that of JGS coal in terms of the effect of mineral type (Figure 8B). The existence of quartz, calcite, kaolinite and pyrite is useful in all cases except for quartz, calcite, and kaolinite with high added content (more than about 20%). The influence degree of quartz on the BJG coal is best, followed by that of calcite and kaolinite, in turn (Figure 8A). And, the influence degree of minerals on the JGS coal relates to the mineral content (Figure 8B).

## 4.1.4. The Lateral Size $(L_a)$

The effects of mineral content and type on the changes in the lateral size ( $\Delta L_a$ ) of corresponding samples after the synthetic graphitization derived from the mixture samples are still closely associated with the coal. As to that of the BJG coal series mixture samples, with the increasing content, there are positive correlations between the changes in the lateral size ( $\Delta L_a$ ) and the added content of quartz, calcite, and kaolinite, while there is a negative relationship for the pyrite/coal mixture samples (Figure 9A). This is opposite to the that of the JGS coal series mixture samples in terms of the effect of mineral content (Figure 9B). This situation is similar to the situation of the stacking height.

As to that of the BJG coal series mixture samples, in terms of mineral type, the existence of pyrite in the mixture samples is certainly unfavorable to the lateral size, but the existence of quartz, calcite, and kaolinite is mostly useful (Figure 5A). The existence of quartz, calcite, kaolinite, and pyrite is useful in all cases to the JGS coal series mixture samples, in terms of the effect of mineral type, except for the calcite with high added content (more than about 20%) (Figure 5B). It is worth nothing that the negative influence degree of the calcite with high added content (more than about 20%) is very strong on the JGS series mixture samples (Figure 9B).



**Figure 9.** The relationships between the content of minerals added to the coal and the changes in the lateral size ( $\Delta L_a$ ) of the corresponding samples after the synthetic graphitization derived from the mixture samples. (**A**) the BJG coal series; (**B**) the JGS coal series.

# 4.1.5. Defect Degrees $(I_D/I_G \text{ and } A_D/A_G)$

The changes in the defect degrees of aromatic rings ( $\Delta I_D/I_G$  and  $\Delta A_D/A_G$ ) of the corresponding samples after the synthetic graphitization derived from the BJG coal series mixture samples are mostly negatively associated with the added content of quartz, calcite, kaolinite, and pyrite (Figure 10). In fact, the effects of quartz and kaolinite content are both limited. However, the existence of pyrite and calcite in the mixture is certainly harmful to the defect degrees of aromatic rings. The impact of pyrite at the added content of 10% and calcite at the added content of 40% is very weak. The negative influence degree of calcite is higher. Due to the very low defect degrees of aromatic rings of the corresponding samples after the synthetic graphitization derived from the BJG anthracite (Table 6), the negative influence of minerals on the BJG coal series mixture samples is actually limited.



**Figure 10.** The relationships between the content of minerals added to the coal and the changes in the defect degrees of aromatic rings ( $\Delta I_D/I_G$  and  $\Delta A_D/A_G$ ) of the corresponding residue samples after the synthetic graphitization derived from the mixture of BJG series mixture samples. (**A**)  $\Delta I_D/I_G$ ; (**B**)  $\Delta A_D/A_G$ .

The importance evaluation relating to the effect of mineral content and type among kaolinite, calcite, quartz, and pyrite on the yield, degree of graphitization, stacking height, lateral size, and defect degrees of aromatic rings on the corresponding samples, after the synthetic graphitization derived from the mixture samples, is roughly measured based on the relationships between these changes and the mineral content/type (Table 7).

**Table 7.** The importance comparisons of the effect of mineral content and type among the transformation of kaolinite, calcite, quartz, and pyrite on the yields, degrees of graphitization, stacking heights, lateral sizes, and defect degrees of aromatic rings on the corresponding samples after the synthetic graphitization derived from the mixture samples. +, the positive effect; + +, the strong positive effect; /, the weak effect; -, the negative effect; - -, the strong negative effect.

Evaluation Parameters	Variable	Samples	Quartz	Kaolinite	Calcite	Pyrite
Yield	Content	BJG		_	_	_
		JGS	_	_	_	_
	Type	BJG	_	_	_	+
		JGS	_	_	_	_
Degree of graphitization	Content	BJG	+	+	+	_
0 1		JGS	/	/	/	/
	Туре	BJG	+	+	+	+
		JGS	/	/	/	/
Stacking height	Content	BJG	+ +	+ +	+	_
		JGS	_		_	+
	Туре	BJG	+	+ +	+ +	/
		JGS	+	+	+	+
Later size	Content	BJG	+ +	+ +	+ +	/
		JGS	_		_	+
	Туре	BJG	+ +	+ +	+ +	/
		JGS	+	+	+	+
Defect degree	Content	BJG	+	+	+	+
	Туре	BJG	—	—	—	-

As to the lower-rank BJG anthracite ( $R_{o,max}$ , 2.82%), quartz, kaolinite, and calcite have the role of inhibitor for the yield and defect degree, but the role of catalyzer for the crystal structure (the degree of graphitization, stacking height, lateral size); the role of pyrite is catalyzer for the yield and degree of graphitization, catalyzer for the crystal size (stacking height, lateral size), and inertia for the defect degree. The increasing added content of quartz, kaolinite and calcite is harmful for the yield but useful for the crystal structure and defect degree; the increasing added content of pyrite is harmful for the yield, degree of graphitization, and stacking height, and it is good for the defect degree. As to the higher-rank BJG anthracite ( $R_{o,max}$ , 5.87%), quartz, kaolinite and calcite have the role of inhibitor for the yield, catalyzer for the crystal size (stacking height, lateral size), and inertia for the degree of graphitization. A lower coal rank indicates being more prone to positive mineral effects on synthetic graphitization.

#### 4.2. The Action Mechanism of Minerals in the Synthetic Graphitization of Coal

Synthetic graphitization is usually defined as the conversion of the initial non-graphite carbon to graphite carbon via high-temperature heating treatment [48]. With the increasing temperature, synthetic graphitization consists of carbonization and graphitization, in turn. Carbonization is regarded as a chemical process of eliminating heteroatoms and forming aromatic carbon skeletons [49–52]. Heteroatom atoms are eliminated mainly in the form of volatiles, and carbon content is enriched [5]. It is thought that a temperature of 1500 °C is required for the carbonization of high-rank coal [5,53]. Most S has been driven off at 1000 °C, and the remnant S element remains inert until 1950 °C [54]. The pure carbon will not be obtained until 2000 °C [5]. Moreover, below 2000 °C, the interplanar spacing is still

above 0.3440 nm [54]. However, the total content of heteroatom atoms is low to less than 5% due to the high rank of the used BJG and JGS anthracite. Thus, the carbonization possibly less affects the structure of BJG and JGS anthracite. Above 2500 °C, the layer spacing of the graphite-like crystal structure shrinks rapidly and approaches the ideal graphite [55]. The main reason why anthracite can be graphitized at high temperature (above 2500 °C) is that the ultra-micro-pores between the carbon atomic layers of anthracite are flat, the pore structure is destroyed, and the ultra-micro-pores disappear; when the anthracite is treated at high temperature, the carbon layer spacing is reduced to complete the synthetic graphitization process [11].

When the presence of minerals is introduced into the synthetic graphitization process of organic matter in coal, the mechanism of artificial graphitization becomes more complex. During the high-temperature heating treatment, the composition of minerals will undergo corresponding changes. There is also a coupling relationship between the effect of minerals on synthetic graphitization and the thermal transformation of minerals during synthetic graphitization.

The cryogenic quartz ( $\alpha$ -quartz) transforms into high-temperature quartz ( $\beta$ -quartz) or square quartz [56]. SiO<sub>2</sub> is thermally stable and does not decompose with the increasing temperature. SiO<sub>2</sub> will melt at 1715 °C. However, SiC will formed from SiO<sub>2</sub> and C (from the coal) at about 2200 °C and decompose to Si and C again at about 2500 °C [14]. The minerals form carbides, specifically SiC, at ~2200 °C, which then decompose before 2500 °C. The reaction between quartz and disordered carbons in the coal to form silicon carbide and graphitic carbon have been authenticated via High-Resolution Transmission Electron Microscopy [14]. This carbide formation decomposition process is responsible for the superior graphitization properties of anthracite.

Kaolinite is decomposed to kaolinite at about 450 °C and converted to mullite-like glass at 1400 °C ( $xAl_2O_3 \cdot ySiO_2$ ) [56]. This glass structure may be similar to that of quartz albite [57] and g-Al<sub>2</sub>O<sub>3</sub> [58]. However, based on their melting/boiling point, the effect of kaolinite may be equal to the combination effect of SiC and Al<sub>2</sub>O<sub>3</sub>, in turn. The boiling point of Al<sub>2</sub>O<sub>3</sub> is up to 2980 °C. The difference in effect between kaolinite and quartz is possibly attributed to Al<sub>2</sub>O<sub>3</sub>. The interaction of metallic elements and carbon to form a carbide that decomposes at a higher temperature is known to enhance graphitization [10,16–19]. The metallic elements will preferentially react with disordered carbon rather than aromatic carbon because aromatic  $sp^2$  carbon is more thermodynamically stable than disordered  $sp^3$  carbon [22,59].

Pyrite (FeS<sub>2</sub>) begins to decompose to the pyrrhotite (Fe<sub>1-x</sub>S) after 500 °C by desulphurization under the argon gas atmosphere. And, pyrite will completely transform into pyrrhotite at 700 °C with the increasing temperature, and pyrrhotite will decompose to Fe and S. The boiling point of Fe is up to 2862 °C. The importance of the formation and decomposition of carbides (Fe<sub>3</sub>C) with iron on graphitization has been widely discussed [10,12,14,16,19,21–25].

Calcite will decompose into metastable polycrystals such as aragonite (CaCO<sub>3</sub>) or spherical calcium carbonate (CaCO<sub>3</sub>), which can also be partially decomposed into lime (CaO) between 675 °C and 950 °C. When the calcite is further heated, the calcite is decarboxylated completely to lime and carbon dioxide [56]. CaO is also thermally stable and does not decompose with the increasing temperature. The effect of calcite is equal to the CaO. However, CaO will melt at 2572 °C and evaporate at 2850 °C. In other words, the effect of calcite will disappear after 2850 °C. Calcium oxide (CaO) catalyzed the graphitization of coal to form graphitic carbon through the carbide formation and decomposition reaction (such as CaC<sub>2</sub>) [19]. Similarly to the behavior of moderator nuclear graphite, the carbide decomposes to metals and reactive carbons and then reforms into crystalline graphite. The neutron strikes the graphite lattice, causing the displacement of carbon atoms into the interlayer spaces between the graphene layers. These carbon atoms migrate through the graphite lattice, either recombining with a graphene layer or causing other carbon atoms to be displaced as well. As the number of displaced carbon atoms increases, the larger carbon molecules and graphene layer is produced [60].

However, previous studies on the mechanism of minerals on the synthetic graphitization of coal have only qualitatively explained their beneficial effects. It is impossible to explain the harmful effects of minerals in coal, especially the opposite effects of minerals on the synthetic graphitization of coal with rank. In addition, more works are needed to explain these phenomena, such as comparisons among different minerals, the differences in evaluation parameters, and the effect of mineral content.

Actually, minerals in the mixture are external, not endogenic. The main difference is the occurrence of or the close association with organic matter. But, by the time the minerals are ready to function, they are already decomposed and have melted, and by this time, there is less difference between the forms of the occurrence of exotic and endogenous minerals. In geological conditions, coal may contain kaolinite, calcite, quartz, pyrite, or more, and their compositions (content) are multivariate. This situation, namely, the succession and/or combination effects of minerals in synthetic graphitization, is possible based on the transformation temperature of minerals. It is speculated in our study that the effect of  $SiO_2$  (quartz and the thermal decomposition product of kaolinite) is first, followed by pyrite, calcite, and  $Al_2O_3$  (thermal decomposition product of kaolinite), in turn or simultaneously. Another possibility is that the combination effects of minerals are the result of the chemical interaction of minerals or auxo-action/inhibitory action simply among the minerals. This situation is complex but essential to clarify the role of minerals in the synthetic graphitization of coal.

## 5. Conclusions

In this work, the roles of kaolinite, calcite, quartz, and pyrite in the synthetic graphitization of anthracite, with different ranks in terms of mineral type and content, are clear based on the change in the yield, degree of graphitization, stacking height, lateral size, and defect degrees of aromatic rings on the corresponding samples, after the synthetic graphitization derived from the coal/mineral mixture samples. As to the lower-rank anthracite ( $R_{o,max}$ , 2.82%), quartz, kaolinite, and calcite have the role of inhibitor for the yield and defect degree, but the role of catalyzer for the crystal structure (the degree of graphitization, stacking height, lateral size). The increasing content of quartz, kaolinite and calcite is harmful for the yield but useful for the crystal structure and defect degree; the increasing content of pyrite is harmful for the yield, degree of graphitization, and stacking height, and it is useful for defect degrees. But, the focus of the effect among these minerals is different to the low degree of quartz to stacking height. As to the higher-rank anthracite ( $R_{o,max}$ , 5.87%), quartz, kaolinite, and calcite have the role of inhibitor for the yield, catalyzer for the crystal size (stacking height, lateral size), and inertia for the degree of graphitization. A lower coal rank indicates being more prone to positive mineral effects on synthetic graphitization.

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