

Special Issue Reprint

Graphite Minerals and Graphene

Edited by Qinfu Liu, Kuo Li and Shuai Zhang

mdpi.com/journal/minerals



Graphite Minerals and Graphene

Graphite Minerals and Graphene

Guest Editors

Qinfu Liu Kuo Li Shuai Zhang



Basel • Beijing • Wuhan • Barcelona • Belgrade • Novi Sad • Cluj • Manchester

Guest Editors Qinfu Liu School of Geosciences and Surveying Engineering China University of Mining and Technology (Beijing) Beijing China

Kuo Li School of Geosciences and Surveying Engineering China University of Mining and Technology (Beijing) Beijing China Shuai Zhang School of Geosciences and Surveying Engineering China University of Mining and Technology (Beijing) Beijing China

Editorial Office MDPI AG Grosspeteranlage 5 4052 Basel, Switzerland

This is a reprint of the Special Issue, published open access by the journal *Minerals* (ISSN 2075-163X), freely accessible at: www.mdpi.com/journal/minerals/special_issues/Graphite_Minerals.

For citation purposes, cite each article independently as indicated on the article page online and using the guide below:

Lastname, A.A.; Lastname, B.B. Article Title. Journal Name Year, Volume Number, Page Range.

ISBN 978-3-7258-3090-9 (Hbk) ISBN 978-3-7258-3089-3 (PDF) https://doi.org/10.3390/books978-3-7258-3089-3

© 2025 by the authors. Articles in this book are Open Access and distributed under the Creative Commons Attribution (CC BY) license. The book as a whole is distributed by MDPI under the terms and conditions of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) license (https://creativecommons.org/licenses/by-nc-nd/4.0/).

Contents

Kuo Li, Yinghao Zhu, Haiyue Cao, Hao Zhang, Yingke Wu and Xiaoguang Li et al. Graphite Made from Coal by High-Temperature Treatment: An Insight into the Nanometric Carbon Structural Evolution Reprinted from: Minerals 2024, 14, 1092, https://doi.org/10.3390/min14111092
 Jifei Zheng, Lei Chen, Cun Zhang, Yue Liu, Ruicong Tian and Jinlin Wu et al. Constraints on Crystallinity of Graphite Inclusions in Nephrite Jade from Xinjiang, Northwest China: Implications for Nephrite Jade Formation Temperatures Reprinted from: <i>Minerals</i> 2023, <i>13</i>, 1403, https://doi.org/10.3390/min13111403 17
Peng Luo, Yuegang Tang, Ruiqing Li and Minmin JuEffects of Minerals Type and Content on the Synthetic Graphitization of Coal: Insights from theMixture of Minerals and Anthracite with Varied RankReprinted from: Minerals 2023, 13, 1024, https://doi.org/10.3390/min1308102430
Zhifei Liu, Daiyong Cao, Gaojian Chen, Zhongwei Bi and Qingtong ChenExperimental Verification for the Graphitization of InertiniteReprinted from: Minerals 2023, 13, 888, https://doi.org/10.3390/min13070888Statement Statement S
Ju-Hwan Kim, Young-Jun Kim, Seok-Chang Kang, Hye-Min Lee and Byung-Joo Kim Preparation and Characterization of Asphalt Pitch-Derived Activated Carbons with Enhanced Electrochemical Performance as EDLC Electrode Materials Reprinted from: <i>Minerals</i> 2023 , <i>13</i> , 802, https://doi.org/10.3390/min13060802 66
 Haiyue Cao, Kuo Li, Hao Zhang and Qinfu Liu Investigation on the Mineral Catalytic Graphitization of Anthracite during Series High Temperature Treatment Reprinted from: <i>Minerals</i> 2023, 13, 749, https://doi.org/10.3390/min13060749 85
Leonard T. Krebbers, Bernd G. Lottermoser and Xinmeng Liu Computed Tomography of Flake Graphite Ore: Data Acquisition and Image Processing Reprinted from: <i>Minerals</i> 2023, 13, 247, https://doi.org/10.3390/min13020247 103
Yan Shao, Shaoqing Wang and Xueqi Li The Effect of Silicon-Containing Minerals on Coal Evolution at High-Temperature Pre-Graphitization Stage Reprinted from: <i>Minerals</i> 2022, 13, 20, https://doi.org/10.3390/min13010020
Gaojian Chen, Daiyong Cao, Anmin Wang, Yingchun Wei, Zhifei Liu and Meng Zhao A High-Temperature Thermal Simulation Experiment for Coal Graphitization with the Addition of SiO ₂ Reprinted from: <i>Minerals</i> 2022 , <i>12</i> , 1239, https://doi.org/10.3390/min12101239
Fiuqing Li, Yong Qin, Yilin Chen and Jian Shen Microstructural Characteristics of Graphite Microcrystals in Graphitized Coal: Insights from Petrology, Mineralogy and Spectroscopy Reprinted from: <i>Minerals</i> 2022 , <i>12</i> , 1189, https://doi.org/10.3390/min12101189





Article Graphite Made from Coal by High-Temperature Treatment: An Insight into the Nanometric Carbon Structural Evolution

Kuo Li ^{1,*}, Yinghao Zhu ¹, Haiyue Cao ¹, Hao Zhang ², Yingke Wu ^{3,4}, Xiaoguang Li ⁵, Zhanjie Xu ⁶ and Qinfu Liu ¹

- ¹ College of Geoscience and Surveying Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China
- ² School of Chemical and Environmental Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China
- ³ BTR New Material Group Co., Ltd., Shenzhen 518083, China
- ⁴ Yongtsing Graphene Research Institute Co., Ltd., Yong'an 366000, China
- ⁵ Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China
- ⁶ Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, China
 - * Correspondence: kuo.li@cumtb.edu.cn or likuo0818@gmail.com

Abstract: Graphite made from coal will not only widen the graphite mineral resource, but also significantly improve the value of coal utilization. In this study, anthracite coal was heated in the temperature range of 500 to 2900 °C to study the size increase of nanometric graphite crystallites from anthracite to real graphite. The carbon content rapidly increases to 99.2% when heated from room temperature to 1600 °C, and then gradually increases to 100% when the treated temperature increases to 2900 °C. The FTIR results show that methyl, methylene, and aromatic hydrocarbon, preexisting in the raw anthracite, were preserved in the JZS-500 sample, but that when the treated temperature ≥ 1000 °C, these C-H bonds almost disappear. The basic structural units (nano graphitic carbon) grow into distorted columns, and the basic structural units and micro-columns re-oriented and coalesced to form local molecular oriented domains with the temperature increase from anthracite to JZS-1500. When the temperature \geq 1600 °C, amorphous carbon, onion-like carbon, turbostratic layers, and graphitic carbon co-occur within the graphitized coals. At the sub-micron scale, carbonization is a homogenous process, whereas graphitization is a heterogenous process. The average graphite crystalline size (La, lateral extension; Lc, stacking height) rapidly increases as the treatment temperature increases from 1600 to 2300 °C. Three coal structural transformation stages were classified according to the nanometric carbon structural evolution with temperature. This study will contribute to the efficient and value-added utilization of coal to make graphite materials.

Keywords: coal-based graphite; anthracite; high-temperature treatment; carbon structural evolution; graphitic carbon; graphitization

1. Introduction

As a traditional low-cost fossil fuel, coal is mainly used for power stations, steel production, house heating, etc. [1]. But, with environmental protection targets mandated by global organizations and the rapid development of green energies like solar, wind, geothermal power, etc., many countries plan to decrease using high carbon emission energy sources [2]. This will challenge the traditional coal industry and force the transformation of coal utilization from simply burning to other low-carbon emission applications. The materialization of coal is one of the directions toward its clean utilization [3,4]. As a porous carbon-rich material, coal has been used for preparing active carbon, carbon black, carbon quantum dots, etc., and recently many researchers have paid attention to the production of synthetic graphite from coal with different ranks [5,6].



Citation: Li, K.; Zhu, Y.; Cao, H.; Zhang, H.; Wu, Y.; Li, X.; Xu, Z.; Liu, Q. Graphite Made from Coal by High-Temperature Treatment: An Insight into the Nanometric Carbon Structural Evolution. *Minerals* **2024**, 14, 1092. https://doi.org/10.3390/ min14111092

Academic Editor: Huifang Xu

Received: 10 September 2024 Revised: 23 October 2024 Accepted: 25 October 2024 Published: 28 October 2024



Copyright: © 2024 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/).

1

Graphite is a layered mineral that shows great physical and chemical properties, including lubricity, conductivity, anti-corrosion, and high melting point under non-oxidizing conditions, etc. [7]. Currently, graphite products have been widely applied to many cuttingedge technological fields such as aerospace, nuclear, and military industries. [8]. Graphite is an excellent electrode material for use in rechargeable batteries, which are commonly used in electric vehicles, e-bikes, drones, etc. [9,10]. As such, it is expected that graphite consumption will increase dramatically in the near future. Coal is an abundant natural resource, is rich in aromatics, and contains some aliphatic chains, heteroatoms, and functional groups crosslinking those aromatics [11]. When the coal rank reaches the anthracite stage, it contains ~92%–98% carbon, almost all of which is present as condensed aromatic rings (it is actually nanoscale graphite crystallite) that are bridged by minor aliphatic and/or ether groups in the macromolecular structure of coal [12,13]. Being rich in nano-sized graphitic carbons of anthracite make it an ideal natural material for preparing graphite, and the low cost of coal will significantly lower the synthetic graphite price. The excellent electrochemical performance of synthetic graphite and graphene made from bituminous coal and anthracite when used as anode in lithium-ion batteries has been reported by researchers [14–16]. This means that graphite made from coal can compare to natural graphite or synthetic graphite made from petroleum coke, both of which have already been commercialized for use in lithium-ion batteries. More recently, our group found that the graphitic carbon made from coal using high-temperature treatment can be used as fillers of styrene butadiene rubber, improving its mechanical properties significantly [6].

Franklin found that anthracite can achieve a better degree of graphitization than natural graphite when the treated temperature >2500 °C; that's because the thermal decomposition of the crosslinks enables the parallel oriented aromatic layers in coal to grow more quickly and to produce a graphitic carbon structure [17]. Several groups examined the properties of starting anthracites, mineral matter catalysis, peak graphitization temperature, and duration time at peak temperature on the influence of the graphitized degree of coal after high-temperature treatment [18–24]. In our previous study, based on the analyses of petrographic, X-ray diffraction (XRD), and micro-Raman spectroscopy, we found that the carbonization of anthracite occurs in the temperature range between room temperature and ~1700 °C, whereas the graphitization of anthracite occurs between ~1700 and 2900 °C. A significant increase in graphite crystallite size occurs in the temperature region of 1700 to 2300 °C [25]. A similar carbon structural evolution was also found in treated Taixi anthracite (anthracite from another mining area of China) by Zeng et al. [26]. Though significant work has been carried out on the graphitization of coal under high-temperature treatments, few papers pay attention to the nanometric graphite crystallites increase from anthracite to graphite. Spectroscopy approaches like Raman and FTIR measured on powder samples only give an average carbon structural evolution, while the growth into the graphite lamellae from dense anthracite particle does not proceed homogenously and provide an ordered graphite structure. Rather, multiple nano carbon phases occur during high-temperature treatment [27].

Following our previous study, a narrower interval of high-temperature treated anthracites, ranging from room temperature to 2900 °C, were chosen to study the subtle carbon structural change using high resolution transmission electron microscopy (HRTEM) coupled with XRD, FTIR, chemical analysis, and scanning electron microscopy (SEM). This work will enhance our knowledge of the carbon structural evolution from amorphous macromolecules of coal to the long-range ordered carbon structure of graphite. This will help us move towards the efficient and clean utilization of coal resources when seeking to produce value-added coal-based graphite materials.

2. Samples and Experiments

2.1. High-Temperature Treatment

Anthracite collected from the Jinzhushan colliery (JZS-raw) of central Hunan province, China, was heated at a series of temperatures ranging from 500 to 2900 °C, including 500,

1000, 1300, 1400, 1500, 1600, 1700, 1750, 1800, 1900, 2000, 2100, 2300, 2500, 2600, and 2900 °C. Samples within the range of 500–1500 °C were processed in a tube furnace with N₂ as the shielding gas; the airflow rate was 130 mL/min. To avoid the N₂ reacting with anthracite at the higher temperature ranges (1600 to 2900 °C), the protection gas was switched to an Ar atmosphere, which was heated in a graphitization furnace. The heating rate was maintained at 10 °C/min, and each sample was held at the setting peak temperature for 3 h before naturally cooling down to ambient conditions. The series treated samples were denoted as JZS plus temperature; for example, anthracite treated at 500 °C was named as JZS-500.

2.2. Elements Composition Analysis

The elements composition analysis was conducted at the Institute of Processes, Chinese Academy of Sciences, employing a German Elementar Vario MACRO cube analyzer with TCD detection. High grade graphite and ammonia sulfonate were used as interior calibration standards for the analysis of elements C, H, N, and S following the standard GB/T 31391-2015 [28], and oxygen was calculated by difference.

2.3. X-Ray Diffraction Analysis

X-ray diffraction (XRD) data were measured on the powder samples using a Rigaku D/MAX-2500PC X-ray diffractometer (Rigaku, Tokyo, Japan) at China University of Mining and Technology, Beijing. Copper was chosen as the target of the X ray source $(\lambda = 0.154056 \text{ nm})$, the X-ray tube voltage was set at 40 kV, the current is 100 mA, the scanning range is $2.5-80^\circ$, and the scanning speed is 2° /min. The two peaks in the XRD pattern (the 2 θ range is 20–30° and 40–50°, respectively) are the corresponding positions of (002) and (100) of standard graphite XRD diffraction. The peak position and full width at half maximum of the diffraction pattern were measured by Jade 5.0. Carbon layer spacing d_{002} is calculated according to Bragg equation. The average structural parameters, L_a (lateral crystal size along *a*-axis of graphite) and L_c (stacking height along *c*-axis of graphite), were calculated according to Scherrer formula: $L_a = 1.84\lambda/\beta_{100} \cos(\varphi_{100})$ and $L_c = 0.9\lambda/\beta_{002}\cos(\varphi_{002})$, where β and φ are the full width at half maximum (FWHM) and diffraction angles, respectively, of the corresponding crystallographic plane. For those (10) band separated into (100) and (101) peaks in the XRD patterns, La was calculated based on the (100) peak; for those only showing two-dimensional (10) bands, L_a was calculated directedly based on the (10) band following the previous work [29,30]. DOG was calculated according to DOG = $(3.440 - d_{002})/(3.440 - 3.354)$ [31].

2.4. Fourier Transform Infrared Spectroscopy Analysis

FTIR spectra were acquired using a Nicolet 6700 IR spectrometer (Thermo Fisher Scientific Inc. Waltham, Massachusetts, USA) at China University of Mining and Technology, Beijing. To mitigate the effects of water, a drying agent was used to maintain a low humidity level during the experiments. The powder samples were held by spectral grade KBr to perform FTIR analysis. Before the experiment, KBr was dewatered in a drying oven at 100 °C for 3 h. Then, 200 mg of KBr was mixed with 1–2 mg of dried samples by hand grinding with an agate mortar, followed by pressing the mixture into a circular die to make KBr pellets under 10 MPa pressure for 2 min. The KBr pellets were then dried again in a vacuum oven at 100 °C for 30 min to reduce the effect of water. Infrared spectra were obtained by conducting 128 scans at a resolution of 4 cm⁻¹, covering the middle infrared range from 400 to 4000 cm⁻¹. OMNIC 9.0 software was used to make baseline calibrations and produce qualitative analyses for the spectra of series samples.

2.5. SEM Analysis

SEM analysis was conducted at Zhongkebaice, a commercial testing company in Beijing, China using a Japan Hitachi SU8020 (Hitachi, Tokyo, Japan). Before SEM analysis, the powdered samples were affixed onto conductive tape to ensure proper adhesion. Subsequently, the surface of the particles was sprayed with gold to enhance its electrical conductivity and increase the imaging resolution. The Hitachi SU8020 was employed to investigate micron and sub-micron scale surface features of the samples. For each sample, at least ten fields of view were randomly selected, and the surface morphology within these fields was examined to ensure comprehensive characterization.

2.6. TEM Analysis

TEM analysis was performed at the Beijing Physical and Chemical Testing Center using a Tecnai G2 F30 instrument manufactured by FEI, USA. Samples < 200 mesh were manually ground gently to an extremely fine powder, and then 1 mg of each sample was mixed with 5 mL ethanol. The suspension was then sonicated for 10–30 min until the samples were totally dispersed. The mixture was then dropped onto the carbon microgrids. Electron acceleration voltage was set at 300 kV, and high-resolution TEM images were captured at magnifications of $300,000 \times$ and $500,000 \times$ to observe the lattice fringes of the samples. During the observation, the full picture of the sample was first observed at low magnification and the most suitable observation site was selected. Then the magnification was increased to capture high-resolution images and selected area electron diffractions.

3. Results and Discussion

3.1. Bulk Characteristics of Series Samples from Anthracite to Graphite

3.1.1. Elemental Compositions

The element compositions (C, H, N, and S) show significant change when treated with temperature increases (Figure 1 and Table 1). The carbon content shows a relatively rapid increase over temperatures ranging from 90.22% to 99.02% under conditions ranging from room temperature to 1600 °C. Once the carbon content reaches ~99%, it only shows a slow increasing trend from 1700 to 2900 °C (Figure 1a), for the sample heated to 2900 °C, almost pure carbon achieved. The hydrogen content shows a significant decrease from 2.19% to 0.44% for the samples treated at 500 and 1000 °C, respectively, and then shows a general decreasing trend with temperatures > 1000 °C (Figure 1b). The nitrogen and sulfur content are low in the raw anthracite (both < 1%, Table 1), and show an overall decrease trend with increasing temperature, and both N and S almost disappeared in the samples treated above 2300 °C (Figure 1c,d).



Figure 1. Elemental content changes with increasing treated temperature. (**a**) Carbon; (**b**) Hydrogen; (**c**) Nitrogen; (**d**) Sulphur, trending is indicated by the green dot line.

Sample	С	Н	Ν	S	0
JZS-raw	90.2	2.63	0.84	0.37	5.96
JZS-500	92.44	2.19	0.88	0.34	4.15
JZS-1000	94.08	0.44	0.81	0.29	4.38
JZS-1300	95.46	0.31	0.6	0.34	3.28
JZS-1400	98.23	0.26	0.42	0.32	0.77
JZS-1500	97.19	0.27	0.61	0.31	1.62
JZS-1600	99.02	0.25	0.04	0.51	0.18
JZS-1700	98.8	0.24	0.55	0.32	0.09
JZS-1750	99.01	0.32	0	0.38	0.29
JZS-1800	98.9	0.29	0.02	0.4	0.39
JZS-1900	99.04	0.27	0.07	0.34	0.28
JZS-2000	98.85	0.22	0.31	0.28	0.35
JZS-2100	98.97	0.21	0.03	0.19	0.6
JZS-2300	98.82	0.19	0.04	0.07	0.88
JZS-2500	99.7	0.06	0.02	0.01	0.23
JZS-2600	99.21	0.16	0.03	0.08	0.52
JZS-2900	100	0	0	0	0

Table 1. Elemental composition (Wt. %) of the series treated samples.

3.1.2. Powder XRD Characterization

Powder XRD analysis shows two obvious peaks (bands) at ~22–28°2 θ and ~42–45°2 θ in the pattens of series samples, corresponding to the (002) and (10) diffraction peaks of graphitic structure, respectively. For the samples treated ≤ 1500 °C, a broad (002) peak appears at $\sim 25^{\circ}2\theta$ (Figure 2a), suggesting all these samples possess an amorphous carbon structure. With the treated temperature increase from 1600 to 2900 °C, the (002) peaks exhibit a gradual right-shift and their relative intensities gradually strengthen with the increasing treated temperature (Table 2). This is because the amorphous carbon of untreated anthracite becomes more and more orderly with the treated temperature increase. The (002) diffraction peaks of samples JZS-1800 and JZS-2100, as shown in Figure 2b, were asymmetric, suggesting a typical partly graphitized structure in these samples [25]. The (10) band in the samples treated above 2500 °C separates into two defined (100) and (101) peaks (Figure 2c), suggesting that a graphitic ordering occurs in these highly graphitized samples. The average crystalline size indicators L_a and L_c (L_a : lateral extension; L_c : vertical stacking) derived from XRD patterns did not change much from raw anthracite up to JZS-1500, but then a prominent increase occurred in the temperature range from 1600 to 2600 °C (Figure 3a). During the treatments between 2600 and 2900 °C, both the L_a and L_c show an indistinct increase again (Figure 3a). The value of L_a/L_c can be used to reveal the preferential increase direction of graphite crystal with treated temperature increase [32]. For the series samples in this study, the L_a/L_c shows an increase trend from room condition to 1500 °C, and then a decrease from 1500 to 2300 °C, and then a final increase again from 2300 to 2900 °C (Figure 3b). This indicate that the nano-graphitic layers in anthracite gradually show the lateral extension priority initially during carbonization, and then the vertical stacking become the preferential increase compare to lateral growth at the early graphitization stage, and at the late graphitization stage, the lateral growth back to priority again from 2300 to 2900 °C.



Figure 2. XRD pattern of the series treated samples, the overall change (**a**), enlargement of (002) peaks (**b**) and (10) bands (**c**) of part samples.



Figure 3. Graphite crystalline sizes change with temperature. Vertical stacking (L_c) and lateral extension (L_a) versus temperature (**a**), and L_a/L_c versus temperature showing the preferential increase direction (**b**).

Sample	°2θ	d ₀₀₂ (nm)	DOG	FWHM (002)/°	L _c (nm)	L _a (nm)	L _a /L _c
JZS-raw	25.37	0.3505		4.512	1.73	4.59	2.65
JZS-500	25.83	0.3511		4.457	1.8	4.8	2.67
JZS-1000	24.47	0.3646		5.699	1.41	5.69	4.04
JZS-1300	25.89	0.3646		5.272	1.53	7.38	4.82
JZS-1400	24.92	0.3593		4.87	1.66	8.01	4.83
JZS-1500	25.25	0.354		4.269	1.89	8.22	4.35
JZS-1600	25.89	0.3453		2.537	3.18	10.5	3.3
JZS-1700	25.96	0.3453		2.757	2.93	10.66	3.64
JZS-1750	26.02	0.3435	0.058	2.121	3.8	11.7	3.08
JZS-1800	25.96	0.3438	0.023	1.552	5.19	12.18	2.35
JZS-1900	26.02	0.3436	0.047	1.422	5.67	12.69	2.24
JZS-2000	25.96	0.3435	0.058	1.302	6.21	14.09	2.27
JZS-2100	26.15	0.3409	0.360	0.785	10.27	17.7	1.72
JZS-2300	26.28	0.3395	0.523	0.496	16.31	30.11	1.85
JZS-2500	26.48	0.3373	0.779	0.449	17.95	43.5	2.42
JZS-2600	26.41	0.3378	0.721	0.402	20.06	60.83	3.03
JZS-2900	26.48	0.3373	0.779	0.375	21.57	67.98	3.15

Table 2. Average graphite crystalline parameters derived from XRD patterns. Note: for samples treated ≥ 2500 °C, their (10) band separated into (100) and (101), L_a was calculated based on the (100) peak; for the other samples only show (10) band, L_a was calculated based on the (10) band.

3.1.3. FTIR Characterization

The FTIR spectra of the series samples were shown in Figure 4. The absorption band at 3100–3000 cm⁻¹ is attributed to the aromatic C-H stretching vibration, the 3000–2800 cm⁻¹ region represents aliphatic stretching band, and the band at 900–700 cm^{-1} is attributed to aromatic out-of-plane deformation modes [33,34]. The aromatic C-H stretching bands of the series samples are fairly weak; this is probably because the stretching vibration mode of condensed aromatics (nanoscale graphite) with a more or less crystalline structure is not sensitive to the IR signal, which is similar to high rank coals with weak aromatic C-H stretching band, which were reported previously [35]. The out-of-plane deformation of aromatic C-H can be clearly observed at the JZS-raw and JZS-500 sample but disappear at the samples treated above 1000 °C, suggesting the aromatic C-H bond is already lower than the FTIR detection limit in these samples. The aliphatic CHx stretching band at $3000-2800 \text{ cm}^{-1}$ is also observable in the JZS-raw and JZS-500 samples; however, the weak CH_2 asymmetric vibration at 2920 cm⁻¹ and CH_3 symmetric vibration at 2860 cm⁻¹ can still be detected even at JZS-2000. This is abnormal since the hydrogen content already decreased to an extremely low level in these samples (Table 1). This abnormal phenomenon is probably related to instrument system error since we always observed these two peaks at the background spectra with different FITR instruments. The FTIR results show that the functional groups like methyl, methylene, and aromatic rings in the raw anthracite were still preserved at JZS-500. When the heated temperature ≥ 1000 °C, all these C-H bonds almost disappear, consistent with the low-level non-carbon components (Table 1). A previous study by Guo et al. [36] found that when the pyrolysis temperature increased to 950 °C, the heat treatment destroyed the coal chemical structure and erased the structural differences among coals of different ranks.



Figure 4. FTIR of untreated anthracite and representative heated samples.

3.2. Micon Scale Morphological Change

The morphological characteristics of the series samples observed under SEM are shown in Figure 5. The JZS-raw and JZS-500 samples are always broken into dense particles, and, on the surface, show a jagged texture and irregular shape (Figure 5a). The dense coal particles with jagged surface and irregular shape were the dominant particle type up to JZS-1500 (Figure 5b,c); meanwhile, the de-volatile pores can be seen occasionally in the JZS-1000, -1300, -1400, and -1500 samples (Figure 5b,c). A similar result was also observed under microscopy by Li et al. [25]. The lamellar-like texture was observed from samples treated at 1600 $^{\circ}$ C (Figure 5d), and as the treated temperature increased, the lamellar-like texture becomes increasingly clear (Figure 5e,f). Based on the analysis of a natural series of graphitized coal, Li et al. [37] found these lamellar-like textures are the initial state during the graphite flake crystal formation, and the dense particles are those of amorphous carbon. The dense coal particles are also common in these samples from JZS-1600 to JZS-2100; the co-occurrence of lamellar-like textural and dense coal particles in these samples suggests a non-homogenous graphitization process. Once the temperature increases to 2300 °C, the layer texture of the graphite mineral can be observed clearly (Figure 5g); these graphite flakes, with size $< 1 \mu m$, show an irregular shape (Figure 5h), and each flake is an individual graphite microcrystal. The small graphite microcrystals always occur as tightly connected aggregates (Figure 5g,i), suggesting they were transformed from dense coal particles under extremely high-temperature treatments.



Figure 5. Representative SEM images of series samples. (a) JZS-raw; (b) JZS-1000; (c) JZS-1400; (d) JZS-1600; (e) JZS-1900; (f) JZS-2100; (g) JZS-2300; (h) and (i) JZS-2600.

3.3. Nano Scaled Graphite Crystallites Growth

HRTEM images reveal the nanometric carbon structure in the series heated samples from anthracite to graphite [38,39]. In the JZS-raw treated samples, the lattice-fringes are short and mainly consist of a few stacked layers with nano graphite crystallite size <2 nm (Figure 6a). These nanometric layers are diffraction images of the side plane of condensed aromatic rings, and they were also documented as basic structure units (BSUs) for carbonaceous materials [40]. The carbon structure of JZS-500 is similar to the raw anthracite, showing that treatment at 500 °C does not change much of the anthracite structure (Figure 6b). For the JZS-1000 sample, the lattice fringes show an obvious increase in the lateral extension along the aromatic plane and stacked layers, the rigid connected areas with nano-graphitic layers known as the micro-column of graphite (Figure 6c). As the treatment temperature increases from 1000 to 1500 °C, these micro-columns grow into local molecular-oriented domains [41], LMOD; micro-columns and BSUs also exist in these same samples. In the LMOD, the nano-graphitic layers are not completely isolated from each other; these layers are more or less bonded by the weakly connected fringes laterally or stacked vertically, and the lattice defects in the LMODs always occur along the adjacent micro-columns [42]. In the JZS-1500 sample, the size of some LMODs can be up to 10 nm (Figure 6f), which is consistent with the calculated La from XRD pattern, but they do not belong to the real graphite, because the selected area electron diffraction (SAED) patterns are still ring shaped (the SAED pattern is inserted in Figure 6f), suggesting that no periodic order of three dimension has been formed in the JZS-1500 sample.



Figure 6. Representative HRTEM images and SAED of samples treated from room condition to 1500 °C. (a) JZS-raw, BSUs-basic structure units; (b) JZS-500, BSUs-basic structure units; (c) JZS-1000; (d) JZS-1300, LMOD-local molecular oriented domain; (e) JZS-1500, LMOD-local molecular oriented domain, (f) JZS-1500, LMOD-local molecular oriented domain, the corresponding SAED pattern. The SAED collected on these wrinkled carbon areas is always inserted.

The amorphous carbons consisting of the LMODs were also common in the samples treated between 1600 and 2300 °C (Figure 7a), but the preferentially oriented areas of LMODs increase with the treated temperature (Figure 7e). In the temperature range of 1600 to 2300 °C, concentric carbon nanostructures similar to previously reported onion-like carbon were observed (Figure 7b), and the bent aromatic fringes were distributed only on the outside, presenting a hollow shape inside. Harris suggests that certain pentagonal and heptagonal carbon rings present in the bent condensed aromatic layers help to make the structure curve and to be thermodynamically stable, just like the fullerene structure [43]. Long-range wrinkled layers were observed in the samples treated above 1600 °C (Figure 7c); this type of carbon structure consists of preferential oriented LMODs or/and micro columns, but the edge defects and angular inconsistency among adjacent lattice fringes means that the overall carbon structure is organized in a wavy-like pattern [38]. The SAED collected on these wrinkled carbon areas always show an arc type diffraction pattern (the SAED pattern is inserted in Figure 7c). Meanwhile, the graphitic layers, with a highly ordered and continuously layered stacking structure of graphite at a tens of nanometer scale, can be seen in the HRTEM images (Figure 7d,f). The SAED collected on the graphitic layers shows diffraction points (the SAED pattern is inserted in Figure 7d), suggesting that real graphite was formed. The discrete SAED points stacked together into a cycle pattern, showing that the single crystal size is still at sub-micron scale, with polycrystals occurring together.



Figure 7. HRTEM images and SAED of series samples treated from 1600 to 2300 °C. (**a**) JZS-1600, amorphous carbon, corresponding SAED pattern inserted; (**b**) JZS-1700, onion-like structure; (**c**) JZS-1700, turbostratic layers, corresponding SAED pattern inserted; (**d**) JZS-1700, graphitic layers, corresponding SAED pattern inserted; (**d**)

The sub-micron scale polycrystal graphite was even observable in the JZS-1700 sample (Figure 8a). The single graphite microcrystal size increases with the treated temperature increase (JZS-2500 in Figure 8b), and the stacked layers of lattice fringes with fewer defects become more rigid (Figure 8c). Despite this, and even in the JZS-2900 sample, the turbostratic layers and amorphous carbon can occasionally be observed (Figure 8d,e). Interestingly, nanometric polygon pores with graphite carbon layers as pore walls are present in the extremely high-temperature treated samples (above 2500 °C), these graphitic pore walls were in the size between several nanometers to hundreds of nanometers (Figure 8f). The polygonal carbon structure was also observed by Zhang et al. [44] in coals treated at 3000 °C. The most common carbon structure is polycrystal graphite in those samples treated at extreme temperatures (Figure 8g). Certain graphite single crystal can reach the micron scale, and they present as stiff stacked graphene layers with perfectly dispersed SAED points (the SAED pattern is inserted in Figure 8h). This polycrystal graphite always occur as aggregates, and the banded graphite features were observable even at micron scale based on their morphological characters (Figure 8f,g).



Figure 8. TEM images and SAED of series samples treated from 1700 to 2900 °C. (**a**) JZS-1700; (**b**) JZS-2500 single graphite crystal, (**c**) JZS-2500, graphitic layers, collected area from (**b**); (**d**–**g**) JZS-2900, (**h**) JZS-2900 graphitic layers, corresponding SAED pattern inserted.

3.4. Carbon Structural Evolution from Coal to Graphite: Homogenous and Heterogenous

The results obtained from elemental analysis, FTIR, and HRTEM show the raw anthracite was composed of large quantity of short nano scale graphite crystallites (BSUs), and these BSUs were crosslinked by minor amount aliphatic carbon, heteroatoms, ligand, etc. [16,45]. Relatively low pyrolysis temperature (≤500 °C) does not change the structure of anthracite. Based on FTIR and Raman spectroscopy, Guo et al. found aliphatic chains were almost entirely consumed at 700 °C, and aromatic hydrocarbons disappear at 950 °C [36]. He et al. found that CO_2 and CO were released from coal under 300–600 °C treatment, while H₂ was released from coal at relatively higher temperatures during treatment at \sim 700–800 °C. [46]; this is consistent with the significant hydrogen loss from anthracite during pyrolysis at 500 to 1000 °C in the current study. When the treatment temperature increases to 1000 °C and above, condensation of the macromolecular skeleton was clearly observed, accompanied by decomposition of functional groups and released in the form of light gas [46]. The gaseous release process was traced by the pores observed under SEM. The nano graphite crystallites are laterally extended and vertically stacked to form micro-columns and locally molecular oriented domains (LMODs) for the samples treated between 1000 and 1500 °C, and the average crystalline size increases as the treatment temperature increases (Table 2). However, the ring pattern of the selected-area electron diffraction patterns measured on these samples shows that the samples treated \leq 1500 °C still preserved an amorphous carbon structure (the real graphite has not formed); this is also evidenced by the broad (002) band of their XRD patterns. As such, the overall carbon structural evolution at micron scale from raw anthracite to JZS-1500 can be regarded as a homogenous increase process.

From the JZS-1600 sample, a significant narrowing of the XRD (002) diffraction peak appears. This was accompanied with a lamellar-like texture, visible under SEM, and ordered graphitic carbon, visible under TEM (Figures 5, 7 and 8). The co-existence of amorphous carbon, turbostratic layers, and graphitic layers shows the heterogeneity of the initially graphitized anthracite. With the treatment temperature continuing to increase, different nanometric carbon phases were still observable, and even in the JZS-2900 sample,

four carbon phases could be seen (Figure 8), showing that the graphitization of anthracite is a heterogenous process. Though multiple carbon phases were present during graphitization of anthracite, the graphitized particles became more and more common and the amorphous decrease as the treatment temperature increased. In particular, for samples treated in the range of 1700 to 2300 °C, the graphite crystal size rapidly increased. The prominent carbon structural improvement to an orderly state can been seen in the micron scale layer texture observed under SEM (Figure 5); this implies that the amorphous coal particles rapidly transformed into graphitized carbon particles in this temperature range.

Based on the above analysis, the increasement of crystallites from anthracite to coalbased graphite is illustrated in Figure 9. The nanometric graphitic layers (BSUs with size < 2 nm) grow progressively into local molecular oriented domains (<10 nm) as the treatment temperature increases to 1600 °C. There are no real graphite forms during this carbonization process; thus, this process can be regarded as homogenous at the micron scale. Graphite crystallites with stiff stacked layers > 10 nm start to appear in samples treated at temperatures above 1600 °C; meanwhile, amorphous carbon phases and turbostratic layers are preserve up to treatment temperatures of 2900 °C, implying a heterogenous process during graphitization. Despite this, more graphite forms as the other carbon phases are spent, and the graphite size can grow to sub-micron scales.



Figure 9. The illustration of homogenous and heterogenous graphite crystallites increasement of coal during high-temperature treatment (illustration was modified based on references [17,38]). BSU-basic structural unit; LMOD- local molecular oriented domain; Turbo-turbostratic layers.

Two carbon structural evolution stages were used to describe the process of thermal treatment of carbonaceous materials (CMs), of which the carbonization of CMs corresponds to the elimination of heteroatoms and the formation of nanosized polyaromatic carbon structures, but their structure still remains amorphous, whereas for the graphitization, long-range oriented condensed aromatic layers occur and structural defects are eliminated gradually [25,40]. Based on the narrow treatment temperature interval and the corresponding structural and morphological change in the current study, the structural evolution from anthracite to graphite was classified into three stages (Figure 10). Stage 1 corresponds to the carbonized coal stage; the temperature ranges from room temperature to \sim 1600 $^{\circ}$ C at this stage. The removal of non-carbon elements, the enrichment of carbon content and polycondensation all contribute to forming local molecular orientated domains. The growth in width but without much growth in height of aromatic planes at this stage was also reported by Kercher and Nagle [47]. Stage 2 is the initial graphitization stage of coal (~1600–2300 °C), in which large amount of amorphous carbon rapidly transform into micron scale graphite. Multiple phases of carbon co-occur at this stage, so this stage can be called the main carbon phase transition process. The last stage (Stage 3, with temperatures ≥ -2300 °C) is the late graphitization stage of coal, marked by single crystal size increase, and some graphite flakes grown to micron scales (observed under SEM, Figure 5h,i). However, even at temperatures



of 2900 $^{\circ}$ C, the amorphous carbon and turbostratic layers can be occasionally observed, showing the heterogeneity of carbon structural evolution for coal graphitization.

Figure 10. Three coal structural transformation stages are classified based on the nanometric graphite crystallites increasement characteristics.

4. Conclusions

Graphite was successfully prepared from coal under extremely high treatment temperatures. With the treated temperature increase from room condition to 2900 $^{\circ}$ C, the XRD results show the nano scaled graphite crystallites were enlarged along both the a-axis and c-axis. The aromatic layers in anthracite exhibit lateral preferential extension from room temperature to 1600 °C, and then vertical stacking becomes the preferential increase direction during early graphitization stage from 1600 to 2300 °C. At the late graphitization stage, the lateral growth once again becomes the priority from 2300 to 2900 °C. According to the chemical composition change and carbon structural transformation, the structural evolution from coal to graphite was classified into three stages. Stage 1 corresponds to the carbonized coal stage (from room temperature to ~1600 $^{\circ}$ C); the growth in width but without much growth in height of aromatic planes occurs at this stage. Stage 2 is the initial coal graphitization stage (~1600–2300 °C), during which a large amount of amorphous carbon is rapidly transformed into sub-micron scale graphite, and multiple phases of carbon co-occur. Stage 3 is the late coal graphitization stage, with temperatures \geq 2300 °C. The graphite growth is marked by single crystal size increase, that some graphite flakes grow to micron scales.

During carbonization, the nano graphite crystallites grow into distorted columns, the BSUs and micro-columns reorient and coalesce with each other to form local molecular orientation domains, and no stiff micron scale graphitic carbon formed. The carbon structural evolution at the micron scale during carbonization can be regarded as a homogenous process. During graphitization, the submicron scale preferentially oriented carbon and graphitic carbon become common as temperatures increase. The amorphous carbon, onion-like carbon, turbostratic layers, and graphitic carbon co-occurrence in anthracites treated above 1600 °C demonstrates the heterogeneity of graphitized anthracite. Even under pyrolysis at 2900 °C, a few amorphous carbons and turbostratic layers carbons were still preserved, showing the graphitization of coal is a heterogenous process.

Author Contributions: Conceptualization, K.L.; methodology, K.L., Y.Z., H.C., H.Z., Y.W., X.L. and Z.X.; formal analysis, K.L., Y.Z., H.C. and H.Z.; resources, Y.W., X.L., Z.X. and Q.L.; data curation, K.L. and Q.L.; writing—K.L. and Y.Z.; writing and reviewing editing—K.L.; project administration, Q.L.; funding acquisition, K.L. and Q.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Natural Science Foundation of China (Nos. 42472229 and 42002187) and the Fundamental Research Funds for the Central Universities (Nos. 2022XJDC01 and 2023ZKPYDC08).

Data Availability Statement: All the data supporting the results are presented in the paper, the raw data are available on request from the corresponding author.

Acknowledgments: We thank Wenhao Fan of Beijing Physicochemical Test Center for help with the HRTEM data collection. Comments and suggestions from the Editors and three anonymous reviewers highly improve the manuscript.

Conflicts of Interest: Yingke Wu is employee of BTR New Material Group Co., Ltd., Shenzhen and Yongtsing Graphene Research Institute Co., Ltd., Yong'an. The paper reflects the views of the scientists and not the company.

References

- 1. Pudasainee, D.; Kurian, V.; Gupta, R. Coal: Past, present, and future sustainable use. In *Future Energy*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 21–48.
- Nejat, P.; Jomehzadeh, F.; Taheri, M.M.; Gohari, M.; Majid, M.Z.A. A global review of energy consumption, CO₂ emissions and policy in the residential sector (with an overview of the top ten CO₂ emitting countries). *Renew. Sustain. Energy Rev.* 2015, 43, 843–862. [CrossRef]
- Andrésen, J.M.; Burgess, C.E.; Pappano, P.J.; Schobert, H.H. New directions for non-fuel uses of anthracites. *Fuel Process. Technol.* 2004, *85*, 1373–1392. [CrossRef]
- 4. Zang, X.; Dong, Y.; Jian, C.; Ferralis, N.; Grossman, J.C. Upgrading carbonaceous materials: Coal, tar, pitch, and beyond. *Matter* **2022**, *5*, 430–447. [CrossRef]
- 5. Shao, Y.; Wang, S.; Li, X. The Effect of Silicon-Containing Minerals on Coal Evolution at High-Temperature Pre-Graphitization Stage. *Minerals* **2023**, *13*, 20. [CrossRef]
- Zhang, H.; Ding, X.; Yang, Y.; Liu, Q.; Ji, L.; Li, K.; Sun, J.; Sun, Z.; Ma, Q.; Wu, Y.; et al. Temperature-dependent evolution of synthetic coal-derived graphite fillers and their reinforcement in styrene butadiene rubber composites. *Compos. Sci. Technol.* 2024, 258, 110883. [CrossRef]
- 7. Jara, A.D.; Betemariam, A.; Woldetinsae, G.; Kim, J.Y. Purification, application and current market trend of natural graphite: A review. *Int. J. Min. Sci. Technol.* 2019, 29, 671–689. [CrossRef]
- 8. Zondlo, J.W. Graphite: Structure, properties, and applications. In *Graphite, Graphene, and Their Polymer Nanocomposites*; CRC Press: Boca Raton, FL, USA, 2012; pp. 1–56. [CrossRef]
- Zhang, M.; Song, X.; Ou, X.; Tang, Y. Rechargeable batteries based on anion intercalation graphite cathodes. *Energy Storage Mater.* 2019, 16, 65–84. [CrossRef]
- 10. Wang, R.; Rish, S.K.; Wang, J.; Lee, S.; Tahmasebi, A.; Yu, J. Synthesis of 3D graphitic carbon foams via pressurized pyrolysis of Victorian brown coal as anode material for Li-ion battery. *J. Anal. Appl. Pyrolysis* **2022**, *164*, 105489. [CrossRef]
- 11. Haenel, M.W. Recent progress in coal structure research. *Fuel* **1992**, *71*, 1211–1223. [CrossRef]
- 12. Mathews, J.P.; Chaffee, A.L. The molecular representations of coal—A review. *Fuel* **2012**, *96*, 1–14. [CrossRef]
- 13. Li, K.; Liu, Q.; Hou, D.; Wang, Z.; Zhang, S. Quantitative investigation on the structural characteristics and evolution of high-rank coals from Xinhua, Hunan Province, China. *Fuel* **2021**, *289*, 119945. [CrossRef]
- 14. Wang, T.; Wang, Y.; Cheng, G.; Ma, C.; Liu, X.; Wang, J.; Qiao, W.; Ling, L. Catalytic Graphitization of Anthracite as an Anode for Lithium-Ion Batteries. *Energy Fuels* **2020**, *34*, 8911–8918. [CrossRef]
- 15. Xing, B.; Zhang, C.; Cao, Y.; Huang, G.; Liu, Q.; Zhang, C.; Chen, Z.; Yi, G.; Chen, L.; Yu, J. Preparation of synthetic graphite from bituminous coal as anode materials for high performance lithium-ion batteries. *Fuel Process. Technol.* **2018**, 172, 162–171. [CrossRef]
- 16. Hao, J.; Zhao, R.; Xu, L.; Chi, C.; Li, H. Conversion of Coal into Graphitized Microcrystalline Carbon with a Hierarchical Porous Structure for Electrochemical Hydrogen Storage. *J. Electron. Mater.* **2023**, *52*, 2034–2043. [CrossRef]
- 17. Franklin, R.E. Crystallite growth in graphitizing and non-graphitizing carbons. *Proc. R. Soc. Lond Ser. A Math. Phys. Sci.* **1951**, 209, 196–218. [CrossRef]
- Atria, J.V.; Rusinko, F.; Schobert, H.H. Structural Ordering of Pennsylvania Anthracites on Heat Treatment to 2000–2900 °C. Energy Fuels 2002, 16, 1343–1347. [CrossRef]
- 19. González, D.; Montes-Morán, M.; Young, R.; Garcia, A. Effect of temperature on the graphitization process of a semianthracite. *Fuel Process. Technol.* **2002**, *79*, 245–250. [CrossRef]
- 20. Luo, P.; Tang, Y.; Li, R.; Ju, M. Effects of Minerals Type and Content on the Synthetic Graphitization of Coal: Insights from the Mixture of Minerals and Anthracite with Varied Rank. *Minerals* **2023**, *13*, 1024. [CrossRef]
- 21. Pappano, P.J.; Schobert, H.H. Effect of natural mineral inclusions on the graphitizability of a Pennsylvania anthracite. *Energy Fuels* **2009**, *23*, 422–428. [CrossRef]
- 22. Chen, G.; Cao, D.; Wang, A.; Wei, Y.; Liu, Z.; Zhao, M. A High-Temperature Thermal Simulation Experiment for Coal Graphitization with the Addition of SiO₂. *Minerals* **2022**, *12*, 1239. [CrossRef]
- 23. Rodrigues, S.; Suarez-Ruiz, I.; Marques, M.; Camean, I.; Flores, D. Microstructural evolution of high temperature treated anthracites of different rank. *Int. J. Coal Geol.* **2011**, *87*, 204–211. [CrossRef]

- 24. Liu, Z.; Cao, D.; Chen, G.; Bi, Z.; Chen, Q. Experimental Verification for the Graphitization of Inertinite. *Minerals* **2023**, *13*, 888. [CrossRef]
- 25. Li, K.; Cao, H.; Rimmer, S.M.; Zhang, H.; Li, X.; Zhang, Y.; Liu, Q. Petrographic features and carbon structural evolution of a series of high-temperature treated anthracites. *Int. J. Coal Geol.* **2023**, *277*, 104356. [CrossRef]
- Zeng, H.; Xing, B.; Cao, Y.; Xu, B.; Hou, L.; Guo, H.; Cheng, S.; Huang, G.; Zhang, C.; Sun, Q. Insight into the microstructural evolution of anthracite during carbonization-graphitization process from the perspective of materialization. *Int. J. Min. Sci. Technol.* 2022, 32, 1397–1406. [CrossRef]
- 27. Edwards, I.A.; Marsh, H.; Menendez, R. Introduction to Carbon Science; Butterworth-Heinemann: Oxford, UK, 2013.
- 28. GB T31391-2015; Ultimate Analysis of Coal. Standards Press of China: Beijing, China. (In Chinese)
- 29. Warren, B.E. X-ray Diffraction in Random Layer Lattices. Phys. Rev. 1941, 59, 693–698. [CrossRef]
- Lu, L.; Sahajwalla, V.; Kong, C.; Harris, D. Quantitative X-ray diffraction analysis and its application to various coals. *Carbon* 2001, 39, 1821–1833. [CrossRef]
- 31. Seehra, M.S.; Pavlovic, A.S. X-ray diffraction, thermal expansion, electrical conductivity, and optical microscopy studies of coal-based graphites. *Carbon* **1993**, *31*, 557–564. [CrossRef]
- 32. Cao, H.; Li, K.; Zhang, H.; Liu, Q. Investigation on the mineral catalytic graphitization of anthracite during series high temperature treatment. *Minerals* **2023**, *13*, 749. [CrossRef]
- 33. Presswood, S.M.; Rimmer, S.M.; Anderson, K.B.; Filiberto, J. Geochemical and petrographic alteration of rapidly heated coals from the Herrin (No. 6) Coal Seam, Illinois Basin. *Int. J. Coal Geol.* **2016**, *165*, 243–256. [CrossRef]
- 34. Li, R.; Tang, Y.; Song, X.; Wang, S.; Che, Q.; Chen, C. Chemical Structure Evolution of Thermally Altered Coal during the Preparation of Coal-Based Graphene and Division of Thermally Altered Zone: Based on FTIR and Raman. *ACS Omega* **2024**, *9*, 34397–34412. [CrossRef]
- Chen, Y.; Mastalerz, M.; Schimmelmann, A. Characterization of chemical functional groups in macerals across different coal ranks via micro-FTIR spectroscopy. *Int. J. Coal Geol.* 2012, 104, 22–33. [CrossRef]
- Guo, X.; Tang, Y.; Schobert, H.H.; Eble, C.F.; Chen, C. Inspired by the Optical Properties of Char and Coke: A Study on Differences between Them from Perspectives of Organic Elemental Contents and the Carbon Nanostructure. *Energy Fuels* 2024, *38*, 3713–3727. [CrossRef]
- 37. Li, K.; Zhang, H.; Wu, Y.; Hu, M.; Liu, Q. Graphite microcrystals growth in naturally graphitized coal from Hunan, China. J. Cryst. Growth 2022, 582, 126530. [CrossRef]
- Li, K.; Liu, Q.; Cheng, H.; Hu, M.; Zhang, S. Classification and carbon structural transformation from anthracite to natural coaly graphite by XRD, Raman spectroscopy, and HRTEM. Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 2021, 249, 119286. [CrossRef] [PubMed]
- 39. Fernandez-Alos, V.; Watson, J.K.; Wal, R.v.; Mathews, J.P. Soot and char molecular representations generated directly from HRTEM lattice fringe images using Fringe3D. *Combust. Flame* **2011**, *158*, 1807–1813. [CrossRef]
- 40. Oberlin, A. Carbonization and graphitization. Carbon 1984, 22, 521–541. [CrossRef]
- 41. Li, R.; Tang, Y.; Che, Q.; Ma, P.; Luo, P.; Lu, X.; Dong, M. Effects of Coal Rank and Macerals on the Structure Characteristics of Coal-Based Graphene Materials from Anthracite in Qinshui Coalfield. *Minerals* **2022**, *12*, 588. [CrossRef]
- 42. Li, J.; Qin, Y.; Shen, J.; Chen, Y. Evolution of carbon nanostructures during coal graphitization: Insights from X-ray diffraction and high-resolution transmission electron microscopy. *Energy* **2024**, *290*, 130316. [CrossRef]
- 43. Harris, P.J.F. New Perspectives on the Structure of Graphitic Carbons. Crit. Rev. Solid State Mater. Sci. 2005, 30, 235–253. [CrossRef]
- Zhang, X.; Wang, S.; Chen, H.; Wang, X.; Deng, J.; Li, X.; Zhang, Y. Observation of carbon nanostructure and evolution of chemical structure from coal to graphite by high temperature treatment, using componential determination, X-ray diffraction and high-resolution transmission electron microscope. *Fuel* 2023, 332, 126145. [CrossRef]
- 45. Xing, B.; Zeng, H.; Huang, G.; Zhang, C.; Yuan, R.; Cao, Y.; Chen, Z.; Yu, J. Porous graphene prepared from anthracite as high performance anode materials for lithium-ion battery applications. *J. Alloys Compd.* **2019**, *779*, 202–211. [CrossRef]
- 46. He, Q.; Cheng, C.; Zhang, X.; Guo, Q.; Ding, L.; Raheem, A.; Yu, G. Insight into structural evolution and detailed non-isothermal kinetic analysis for coal pyrolysis. *Energy* **2022**, 244, 123101. [CrossRef]
- 47. Kercher, A.K.; Nagle, D.C. Microstructural evolution during charcoal carbonization by X-ray diffraction analysis. *Carbon* **2003**, *41*, 15–27. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.





Article Constraints on Crystallinity of Graphite Inclusions in Nephrite Jade from Xinjiang, Northwest China: Implications for Nephrite Jade Formation Temperatures

Jifei Zheng^{1,2}, Lei Chen³, Cun Zhang⁴, Yue Liu⁴, Ruicong Tian⁵, Jinlin Wu⁶, Yu Wu⁷ and Shouting Zhang^{1,2,*}

- School of Earth Sciences and Resources, China University of Geosciences Beijing, 29 Xueyuan Road, Beijing 100083, China; 3001180144@cugb.edu.cn
- ² Frontiers Science Center for Deep-Time Digital Earth, China University of Geosciences (Beijing), Beijing 100083, China
- ³ Shandong Geological Survey Institute, 17 Jingshan Road, Jinan 250020, China; chenlei2009@163.com
- ⁴ School of Materials Science and Engineering, Qilu University of Technology (Shandong Academy of Sciences), 3501 Daxue Road, Jinan 250353, China; gemzhangc@qlu.edu.cn (C.Z.); liuyue001102@163.com (Y.L.)
- ⁵ School of Geography and Tourism, Qilu Normal University, Jinan 250020, China; tommyclerk88@gmail.com
- ⁶ National Gemstone Testing Center Shenzhen Laboratory Company Ltd., Shenzhen 518020, China; wujl@ngtc.com.cn
- ⁷ Gemological Inspection Institute of Xinjiang Zhongjian, Xinjiang 830002, China; qinmenyuan@163.com
- * Correspondence: zst@cugb.edu.cn

Abstract: Graphite usually occurs in mineral/rock associations in the form of solid inclusions and plays an important role in tracing regional metamorphic degree, ore-forming temperature, fluid evolution, as well as the deep carbon cycle of the Earth. In this study, we investigate the placer black nephrite jade where the co-occurrence of abundant graphite inclusions and jade remains extraordinary. By employing petrographic, mineral-chemical, and Raman spectroscopic methods, we characterize the textures and crystallinity of graphite inclusions that exist in nephrite jade. EPMA and petrological data indicate that the main constituents of black jade are tremolite and graphite, with minor phases of diopside, calcite, dolomite, epidote, and apatite. Micro-Raman spectroscopic thermometry of carbonaceous material shows that most of the formation temperatures of graphite inclusions are between 378 and 556 °C, and only a few temperatures may be above 650 °C, indicating that graphite inclusions were formed at medium- to high-temperature metamorphic facies. The petrologic and spectral investigations of graphite inclusions in these nephrite jade samples show major metamorphic signatures with mixed features associated with fluid precipitation. Our results allow us to propose that primary nephrite jade was formed under multi-stage tectonic evolution conditions, and regional temperatures were predominately driven by the late continent-continent collision, while the ore-controlling temperatures of nephrite jade formation were found in a mediumto high-temperature environment.

Keywords: graphite inclusions; Raman spectroscopy; formation temperatures; placer nephrite jade; Northwest China

1. Introduction

Nephrite jade with high economic values consists mainly of fibrous amphibole, which includes mostly tremolite and actinolite to ferro-actinolite together with minor accessory or secondary minerals [1–3]. Previous investigations have been carried out on worldclass nephrite jade deposits to determine their genesis through gemological properties, geochronology, mineral chemistry, major and trace elements, as well as H-O and Sr isotopic compositions [4–8]. Recently, Zhang et al. [2] summarized the spatial and temporal distribution, metallogenic mechanisms, and genetic types of nephrite deposits in China, and provided insights for genetic discrimination, future exploration of the reserves, occurrence



Citation: Zheng, J.; Chen, L.; Zhang, C.; Liu, Y.; Tian, R.; Wu, J.; Wu, Y.; Zhang, S. Constraints on Crystallinity of Graphite Inclusions in Nephrite Jade from Xinjiang, Northwest China: Implications for Nephrite Jade Formation Temperatures. *Minerals* 2023, *13*, 1403. https://doi.org/ 10.3390/min13111403

Academic Editors: Jan Marten Huizenga, Qinfu Liu, Kuo Li and Shuai Zhang

Received: 21 September 2023 Revised: 16 October 2023 Accepted: 24 October 2023 Published: 1 November 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/). states of nephrite jade deposits, as well as tectonic models for nephrite jade formation. However, only a few studies have focused on mineral inclusions in nephrite jade, especially graphite inclusions, which exert important implications for evaluating geological evolution processes and non-metallic metallogenic tectonic settings [4,8]. Zhang et al. [9] indicated that the graphite inclusions in green nephrite jade from Liaoning Province, China, were formed either in high- or low-temperature metamorphic facies, suggesting the difference in the formation stages of nephrite jade. Moreover, Yui et al. [4] obtained temperature information of 410-430 °C for the Hualien green nephrite jade in Taiwan Province, China, indicating that the jade should have formed in a low P/T environment. These studies were limited to the crystallization characteristics and formation temperatures of graphite inclusions in green nephrite jade generated from the eastern nephrite jade belt along the Pacific Ocean based on Raman micro-thermometry [4,9]. In contrast, the graphite inclusions are especially enriched in white jade-type (WJ-type) nephrite jade, especially in placer black nephrite jade with high economic value from Xinjiang Province [4]. According to previous research, the two types of black nephrite jade can be defined as (1) jade with tremolite and actinolite as the main components; and (2) jade with tremolite and graphite as the main minerals [2,5,6]. Although the types and origin of black nephrite jade have been studied in detail, the formation temperatures, regional metamorphic degree, and the relationship between graphite inclusions and jade formation have not yet been fully investigated, and further research is needed.

The transformation of carbonaceous materials (CM) to graphite during metamorphism, a process termed as graphitization, is a function of the degree of metamorphism and can be quantitatively constrained by Raman spectroscopy [10–12]. This process provides robust information for studying graphitic carbon, which offers the significant advantages of rapid, minimal, non-destructive sample preparation and in situ analysis, thus preserving the original textural information. The approximate disorder mode (D1), disorder of edge carbon (D2), and ordered mode (G) structures, as well as quantitative parameters D1/G intensity ratio (R1), D1/(D1 + G) area ratio (R2), and the G band full width at half maximum (FWHM) of the Raman spectra of graphite can be used as indicators of the metamorphic grade and processes, as well as for determining the thermal alteration (maturity) of organic matter (OM) and aiding in the identification of fluid-precipitated graphite [9,13–16]. However, no detailed studies have been conducted so far to characterize the occurrence and genesis of these graphite inclusions by Raman spectroscopy in placer or secondary black nephrite jade.

The objective of this study is to characterize abundant graphite inclusions generated in placer black nephrite jade from Xinjiang, Northwest China, based on petrology, EPMA, and Raman spectroscopy, with a view to trace the nature of the graphite and the formation temperatures of graphite and nephrite jade. This paper presents interesting research samples and new thoughts on carbon sequestration and deep carbon cycling. Our approach also provides an indicative window in relation to graphite crystallization associated with the formation of nephrite jade at different stages of metamorphism.

2. Materials and Methods

2.1. Geological Background of Xinjiang Nephrite Jade Belt

The WJ-type nephrite jade deposits are mainly generated in the Nephrite Jade Belt of the West Kunlun and Altun Mountains in the southern Xinjiang province, China (Figure 1). The spatial distribution of these deposits in this area present NW–EW–NE linear structures, extending from Tashinkurgan to Ruoqiang County. A large number of primary deposits hosted in the 1300 km range of mountains were excavated, which can be subdivided into Shache-Yecheng, Hetian-Yutian, and Qiemo-Ruoqiang, respectively [2,5,6,17,18] (Figure 1b). Moreover, the Yurungkash River (White Jade River) and the Kharakash River (Black Jade River) are rich in high-quality placer or secondary nephrite jade (Figure 1b). Particularly, the black nephrite jade with abundant graphite inclusions is produced from the latter. Previous investigations suggest that their primary ore bodies generally occur in the contact zones of dolomitic marbles and intermediate-felsic rocks or mafic rocks, while the placer nephrite jade is transported by glacial meltwater and then deposited into a river (or bed) from the primary deposits in the Kunlun Mountains [2,5,6] (Figure 1b). Notably, the black nephrite jade with graphite inclusions could play an important role in revealing the complex cycle of graphite formation and tectonic evolutionary history of primary ore deposits.



Figure 1. (a) Generalized geological and tectonic framework of China, showing different subdivision units. The sampling locality for this study is also shown (modified after Zhang et al. [18]). (b) Geological sketch of Nephrite Jade Belts in Xinjiang, northwest China (after Liu et al. [5,6]; Tang et al. [19]). The placer nephrite jade deposits are located at Yurungkash River (White Jade River) and the Kharakash River (Black Jade River). While, the sampling area for our present study is shown in the red box.

2.2. Materials

Graphite-bearing nephrite jade samples (labeled as QHL) for this study were collected from Kharakash River (Black Jade River). The nephrite jade samples with a waxy-grease luster show fine textures and block structures, and the color is mostly gray-black to black, with some samples containing opaque white flocculi inside (Figure 2). In appearance, the color of nephrite jade is attributed to graphite inclusions instead of chemical elements, thus being defined as black nephrite jade. The graphite inclusions are mostly distributed in the white cryptocrystalline tremolite particles in the form of bands, and well-crystallized graphite crystals show flaky characteristics with semi-metallic luster. The whole placer materials present spheroidal or nearly elliptic features, with a small number of pores and cracks being observed on the surface (Figure 2). This is because nephrite jade has experienced fluvial abrasion and collision during the process of transportation from the primary ore to the river (or bed).



Figure 2. Representative hand specimen photographs of the different types of graphite in this study: (a) The cut placer nephrite jade sample is composed of banded graphite inclusions, showing "flow" characteristics. (b) The cut black nephrite jade sample is composed of disseminated graphite inclusions. (c) Abundant of well-crystallized flaky graphite existed in placer nephrite jade. (d) Nephrite jade with weathered skins or crust shows good roundness, showing typical placer characteristics. The yellow dotted lines in Figure (a,c) represent the distribution of graphite inclusions.

2.3. Methods

The electron microprobe analyses (EPMA) and backscattered electron (BSE) and surface scanning of the samples were performed at the Shandong Institute of Geological Sciences (SIGS) using a JEOL JXA-8230 microprobe with an accelerating voltage of 15 kV, a beam current of 2×10^{-8} A, and a beam spot diameter of 0.5 µm. The data collection time was 20–60 s. The ZAF method was used to correct the data, and the analysis accuracy was less than 1%. The chemical compositions of different samples were analyzed using Wavelength Dispersive Spectroscopy (WDS). The standard samples used were Canadian Astimex company series standard samples, and the detection standards were as follows: potassium feldspar (K), jadeite (Na), corundum (Al), quartz (Si), forsterite (Mg) and rutile (Ti), hematite (Fe), calcite (Ca), fluorite (F) and rock salt (Cl), apatite (P), huebnerite (Mn), chromic oxide (Cr), and nickelic (Ni) oxide.

Raman spectroscopy of graphite was performed at the National Gemstone Testing Center Shenzhen Lab., using a Renishaw instrument on glass plates. The wavelength used was 532 nm, and the instrument setup allowed a spectral resolution of 1 cm^{-1} . We used a scanning time of 10 s of spectrum in an extending mode spanning $100 \sim 4000 \text{ cm}^{-1}$ with a grating of 1800 I/mm and a $50 \times$ lens. Filters allowed us to set the laser power on the sample at around 1 mW to avoid degradation of the carbonaceous material (CM). Before

each session, the spectrometer was calibrated with a silicon standard. Because the Raman analysis of graphite can be affected by several analytical mismatches, we closely followed the analytical protocol established by Beyssac et al. [10,11].

3. Results and Discussion

3.1. Petrology

Petrographic studies using a polarizing microscope show that the QHL samples occur predominantly in distinct textural associations. The main textures of nephrite jade are felt-like aphanoblastic and microfibrous, indicating its high-quality properties. The main mineral compositions of nephrite jade are tremolite, and the accessory or secondary minerals are diopside, calcite, apatite, epidote, and graphite (Figure 3a–f). Most of the graphite disseminations occur in association with the main minerals. Under reflected light, the graphite inclusions show a light yellow-brownish color (Figure 3d), and occur as platy or spotted crystals. They most commonly occur as flakes and lamellae, and some of the graphite crystals show "flow" textures, possibly from being filled along cracks or veins (Figure 3d). Generally, the graphite grains are distributed randomly among tremolite grains, suggesting the absence of obvious contacting reaction boundaries.



Figure 3. Representative photomicrographs under cross-polarized light (a-c) and plane-polarized light (d-f), respectively, showing enrichments of graphite inclusions in placer nephrite jade. (a) Graphite occurs in association with tremolite and calcite. (b) Graphite occurs in association with apatite. (c) Tremolite showing porphyrioblastic texture. (d-f) Graphite inclusions occurs in random distribution in terms of flakes and spots. Tr: tremolite Cal: calcite Gr: graphite Ap: apatite Ep: epidote.

3.2. Mineral Chemistry

The mineral EPMA analysis results are presented in Figure 4 and Tables 1–3. The EPMA data suggest the mineral assemblages are tremolite, diopside, calcite, dolomite, and apatite, which is consistent with the assemblages observed in the petrographic study (Tables 1 and 2). The predominant chemical components of the tremolite are SiO2, MgO, and CaO, in the ranges of 56.47–59.03 wt.%, 23.85–24.62 wt.% and 12.25–13.43 wt.%, with the average values of 58.34 wt.%, 24.28 wt.%, and 12.74 wt.%, respectively. The contents of FeO are low, ranging from 0.16–0.63 wt.% with average value of 0.36 wt.%, suggesting that it could not cause the samples to appear black colors. Calcic amphiboles are characteristically Mg-rich, with $Mg^{2+}/(Mg^{2+} + Fe^{2+})$ ranging between 0.99 and 1.00, which further indicates that the main mineral of black nephrite jade is tremolite (Figure 1; Table 1). The chemical compositions of apatite show that the contents of P_2O_5 range from 41.93 to 43.86 wt.%, with an average value of 42.75 wt.%. The contents of CaO range from 54.95 to 55.87 wt.%, with an average value of 55.42 wt.%. The contents of F range from 2.32 to 3.10 wt.%, with an average value of 2.67 wt.%, while the contents of Cl range from 0.06 to 0.23 wt.%, with an average value of 0.14 wt.% (Table 3). Generally, the contents of F are much higher than that of Cl, which indicates typical fluorapatite characteristics, suggesting indicating that the formation and evolution of primary nephrite jade was accompanied by complex F volatilization cycle.

Table 1. Representative Electron probe microanalysis of tremolite in different black nephrite jade samples.

Sample Num.	QHL- 1/6-5	QHL- 2/2-2	QLH- 2/2-3	QLH- 2/2-4	QHL- 3/1-1	QHL- 3/1-2	QHL- 3/1-5	QHL- 3/1-7	QHL- 3/1-11	QHL- 3/1-12	QHL- 6/1-2
SiO ₂	58.210	58.997	58.786	58.711	57.778	56.472	58.698	57.980	59.033	58.970	58.075
Al_2O_3	0.419	0.434	0.460	0.387	0.663	2.218	0.600	0.954	0.280	0.247	0.498
TiO ₂	0.039	0.021	0.004	0.000	0.068	0.315	0.000	0.000	0.071	0.000	0.000
Cr_2O_3	0.000	0.000	0.000	0.020	0.018	0.009	0.000	0.004	0.000	0.000	0.025
FeO	0.392	0.234	0.223	0.302	0.628	0.164	0.487	0.515	0.306	0.255	0.487
MnO	0.026	0.198	0.152	0.073	0.033	0.000	0.059	0.013	0.192	0.152	0.073
NiO	0.015	0.000	0.000	0.000	0.000	0.020	0.000	0.023	0.018	0.013	0.000
MgO	23.852	24.401	24.348	24.485	24.617	24.022	24.111	24.158	24.260	24.548	24.325
CaO	12.867	12.663	12.951	12.639	12.249	13.430	12.254	13.349	12.679	12.788	12.309
Na ₂ O	0.051	0.068	0.121	0.077	0.103	0.240	0.104	0.109	0.052	0.113	0.186
K ₂ O	0.050	0.046	0.056	0.055	0.076	0.164	0.154	0.023	0.060	0.033	0.076
Total	95.921	97.062	97.101	96.749	96.233	97.054	96.467	97.128	96.951	97.119	96.054
Si	8.018	8.022	8.001	8.011	7.941	7.731	8.029	7.914	8.039	8.020	7.990
Al	0.068	0.070	0.074	0.062	0.107	0.358	0.097	0.153	0.045	0.040	0.081
Ti	0.004	0.002	0.000	0.000	0.007	0.032	0.000	0.000	0.007	0.000	0.000
Cr	0.000	0.000	0.000	0.002	0.002	0.001	0.000	0.000	0.000	0.000	0.003
Fe ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe ²⁺	0.045	0.027	0.025	0.034	0.072	0.019	0.056	0.059	0.035	0.029	0.056
Mn	0.003	0.023	0.018	0.008	0.004	0.000	0.007	0.002	0.022	0.018	0.009
Ni	0.002	0.000	0.000	0.000	0.000	0.002	0.000	0.003	0.002	0.001	0.000
Mg	4.894	4.942	4.936	4.977	5.040	4.899	4.913	4.912	4.921	4.973	4.985
Ca	1.898	1.844	1.888	1.847	1.803	1.969	1.795	1.951	1.849	1.863	1.814
Na	0.014	0.018	0.032	0.020	0.027	0.064	0.028	0.029	0.014	0.030	0.050
K	0.009	0.008	0.010	0.010	0.013	0.029	0.027	0.004	0.010	0.006	0.013
Total	14.955	14.954	14.983	14.972	15.017	15.103	14.950	15.026	14.944	14.978	15.000
Mg/(Fe + Mg)	0.991	0.995	0.995	0.993	0.986	0.996	0.989	0.988	0.993	0.994	0.989
Ca/(Ca + Na + K)	0.988	0.986	0.978	0.984	0.978	0.955	0.971	0.983	0.987	0.981	0.966
Mineral	Tremolite	Tremolite	Tremolite								



Figure 4. The ratios $Mg^{2+}/(Mg^{2+} + Fe^{2+})$ vs. Si⁴⁺ are shown in red square demonstrate that the placer nephrite jade is composed only of tremolite. Tr, tremolite.

		, 1					
Sample Num.	QHL-1/2-1	QHL-1/6-4	QHL-6/1-1	QHL-1/6-7	QHL-1/1-1	QHL-1-1-6	QHL-6/1-1
SiO ₂	0.042	55.490	54.602	56.106	0.029	0.000	54.602
TiO ₂	0.000	0.018	0.000	0.000	0.022	0.019	0.000
Al_2O_3	0.008	0.259	0.085	0.176	0.000	0.000	0.085
Cr_2O_3	0.014	0.025	0.000	0.032	0.000	0.023	0.000
FeO	0.000	0.052	0.101	0.196	0.022	0.000	0.101
MnO	0.000	0.040	0.020	0.000	0.007	0.040	0.020
MgO	0.024	18.620	18.922	18.213	12.682	0.855	18.922
CaO	52.499	25.216	25.423	25.291	41.915	58.270	25.423
NiO	0.000	0.000	0.000	0.020	0.000	0.000	0.000
Na ₂ O	0.027	0.033	0.046	0.100	0.014	0.000	0.046
K ₂ O	0.000	0.000	0.004	0.003	0.000	0.004	0.004
Total	52.614	99.753	99.203	100.137	54.691	59.211	99.203
Mineral	Calcite	Diopside	Diopside	Diopside	Dolomite	Calcite	Diopside

Table 2. Representative Electron probe microanalysis of accessory minerals in different black nephrite jade samples.

Table 3. Representative Electron probe microanalysis of Apatite in different black nephrite jade samples.

Sample Num.	QHL-6/1-3	QHL-1-6-6	QHL-2-2-1	QHL-1/1-3
P ₂ O ₅	42.914	41.928	42.291	43.858
SiO ₂	0.059	0.084	0.136	0.048
TiO ₂	0.063	0.037	0.000	0.000
Al_2O_3	0.001	0.000	0.005	0.000
FeO	0.000	0.000	0.000	0.000
MnO	0.018	0.018	0.036	0.018
MgO	0.027	0.038	0.000	0.051
CaO	54.948	55.108	55.745	55.866
Na ₂ O	0.000	0.031	0.033	0.038
K ₂ O	0.009	0.008	0.001	0.013
SO_3	0.011	0.000	0.000	0.004
F	2.582	2.322	2.696	3.095
Cl	0.227	0.173	0.080	0.061
Total	99.721	98.730	99.870	101.735
Mineral	Apatite	Apatite	Apatite	Apatite

3.3. Raman Spectroscopy: Structural Features of Graphite Inclusions

The results of the Raman spectroscopic analyses of graphite inclusions are displayed in Figures 5–9, and the data are given in Table 4. Raman spectroscopy shows that peaks of 225 cm⁻¹ are attributed to the lattice vibration of tremolite, but the 395 cm⁻¹ is between cation to oxygen vib. (M-O) (e.g., Ca, Mg-O). The peak at 550 cm⁻¹ represents the bending vibration of Si-O. The peaks at 673-679 cm⁻¹ are due to the Si-O-Si stretching vibration and can be attributed to substituting Mg²⁺ with the heavier Fe²⁺ [20]. The peaks at 928–932 cm⁻¹ are due to the stretching O-Si-O vibration, and peaks at 1025 to 1060 cm⁻¹ are the antisymmetric Si-O-Si of tremolite. The peaks at 3669–3670 cm⁻¹ belong to the OH stretching vibration [20]. The small difference in wave numbers indicates it may be related to the interionic substitution and occupation. The above spectral peaks indicate that the main mineral of black nephrite jade is tremolite, which is consistent with the results of petrographic studies.







Figure 6. Representative Raman spectra of QHL-2 nephrite jade samples, showing graphite and tremolite peaks. Tr: tremolite.



Figure 7. Representative Raman spectra of QHL-3 nephrite jade samples, showing graphite and minor tremolite peaks. Tr: tremolite.



Figure 8. Representative Raman spectra of QHL-4 nephrite jade samples, showing graphite and tremolite peaks. Tr: tremolite.

Raman spectroscopy of graphite inclusions in black nephrite jade is mainly divided into two order regions: the first-order region $(1100-1800 \text{ cm}^{-1})$ and the second-order region $(2300-3400 \text{ cm}^{-1})$, respectively (Figures 5–9). The first-order region mainly includes three main peaks: D1, G, and D2 peaks [21]. No disordered "graphitic carbon" peaks were detected at D3 and D4 in any of the nephrite jade samples [22]. The second-order region predominately consists of five peaks, namely S1, S2, S3, and S4. The G and S2 peak positions were determined at maximum intensity, and the results show that the sharp G peak is in the range of 1576–1580 cm⁻¹, while the stable peak S2 varies from 2710 to 2716 cm⁻¹. The band full width at half maximum of the G band of graphite varies from 16.31 to 59.56 (Table 4). These values indicate similar the structural features and good crystallinity of graphite, suggesting that it formed under medium- to high-temperature conditions [14]. Previous investigation suggested that metamorphic graphite in the forms of disordered to ordered flakes shows variable crystallinity, while the fluid-deposited graphite exhibits high crystallinity and homogeneity at high-temperature settings [23]. In this study, the petrographic features of most graphite types show affinity to regional metamorphic graphite [24]. The variation and differentiation in the spectroscopic characteristics of graphite inclusions in black nephrite jade reveal that the jade experienced gradual and progressive regional metamorphism during its formation processes. However, the obvious asymmetrical peak at 2710–2714 cm⁻¹ of the S band in the sample QHL-4 indicates typically well-crystallized graphite, which has reached perfect three-dimensional ordering, revealing hydrothermal graphitic C [25–27]. These features are similar to graphite precipitated from carbonic fluid infiltration during higher-temperature metamorphism.



Figure 9. Representative Raman spectra of QHL-5 nephrite jade samples, showing graphite and tremolite peaks. Tr: tremolite.

3.4. Formation Temperatures of Graphite Inclusions

The first order region of Raman spectrum of graphite was decomposed by Lorentz function peak fitting method using software Origin 9.0, and the results are presented in Table 4. However, the graphite Raman geothermometers used do not work for the carbon spectrum without the D band, indicating that the formation temperature was above the upper limit. In this study, the metamorphic temperatures of graphite inclusions of black nephrite jade are estimated using the quantitative parameter of area ratio (R2), which is defined as D1/(G + D1 + D2) (R2), while the D2 peak area is generally negligible [10,11,23,28,29]. The decomposition peak in the first order region of graphite Raman spectrum show that the R2 varies by 0.28–0.59 with an average value of about 0.41, except for partial QHL-4 samples that exceeded its working limit. The graphite inclusions formation temperatures were calculated by Equations (1) and (2), based on Beyssac et al. [10,11] and Aoya et al. [29], respectively.

$$T(^{\circ}C) = -445 \times R2 + 641 \ (330 < T < 650), R2 = 0.96 \pm 50 \ ^{\circ}C \tag{1}$$

$$T(^{\circ}C) = 91.4 \times (R2) 2 - 556.3 \times R2 + 676.3 \pm 30 \ ^{\circ}C$$
(2)

Most metamorphic temperatures ranged from 378 to 556 °C as calculated by the above equations, indicating that the graphite inclusions that existed in nephrite jade were formed in a moderate- to high-temperature environment. (Table 4). Previous investigations speculated that the P/T conditions for the formation of the primary nephrite jade deposit in Xinjiang were medium to low pressure (100–200 MPa) and at temperatures of 330–550 °C based on nephrite zonal structure and minor minerals [5,6,23]. The results of our present

study are consistent with the previous conjecture, which further confirms the reliability of the temperature constraint. The sample QHL-4 shows a high degree of crystallization with similar properties to fluid-precipitated graphite, which may represent peak metamorphism.

Sample	Peak D1 _{I1}	Peak G ₁₂	D1/G In- tensity R1 Ratio	Peak D1 _{A1}	Peak G _{A2}	D1/(G + D1 + D2) R2 Area Ratio	Position of the G	Position of the S2	G FWHM	Equation (1)/T (°C)	Equation (2)/T (°C)
QHL- 1/1-1	10,451	17,881	0.58	530,407	416,809	0.56	1580	2711	23.39	391.82	393.45
QHL- 1/1-2	10,408	17,809	0.58	530,813	417,109	0.56	1579	2711	23.43	391.81	393.45
QHL- 1/1-3	23,643	59,248	0.40	1,241,670	1,265,554	0.50	1577	2711	18.57	420.62	423.22
QHL- 1/1-4	15,269	39,202	0.39	236,027	813,779	0.22	1578	2714	16.84	540.95	555.85
QHL- 2/1-1	13,930	48,465	0.29	910,337	2,213,573	0.29	1580	2717	13.90	511.32	521.95
QHL- 2/1-2	12,153	22,997	0.53	681,820	785,513	0.46	1580	2711	29.03	434.22	437.54
QHL- 2/2-1	18,099	53,542	0.34	1,061,735	2,768,686	0.28	1579	2711	18.76	517.65	529.12
QHL- 2/2-2	18,388.2	42,488	0.43	658,790	1,026,631	0.39	1579	2712	17.12	467.06	472.82
QHL- 2/3-1	21,422	75,648	0.28	727,249	1,826,157	0.28	1579	2716	16.31	514.26	525.27
QHL- 3/1-1	30,507	50,849	0.60	1,665,856	1,138,157	0.59	1579	2715	20.83	376.63	378.06
QHL- 3/1-2	26,394	44,506	0.59	1,057,764	2,848,420	0.28	1579	2711	19.90	520.50	532.36
QHL- 3/1-3	21,925	30,496	0.72	1,135,422	928,298	0.55	1579	2713	26.97	396.17	397.90
QHL- 4/1-1	14,453	63,097	0.23	1,274,335	3,005,349	0.30	1579	2711	14.94	508.50	518.76
QHL- 4/1-2	0	41,639	0.00	n. d.	n. d.	n. d.	1577	2714	n. d.	641.00	676.30
QHL- 4/1-3	0	39,422	0.00	n. d.	295,479	n. d.	1577	2711	16.33	641.00	676.30
QHL- 4/1-4	0	38,924	0.00	n. d.	254,790	n. d.	1579	2712	18.13	641.00	676.30
QHL- 4/1-5	0	44,316	0.00	n. d.	n. d.	n. d.	1577	2714	n. d.	641.00	676.30
QHL- 5/1-1	47,844	83 <i>,</i> 589	0.64	4,161,000	4,449,380	0.49	1576	2711	59.56	425.95	428.81

Table 4. Quantitative parameters of Raman spectroscopy and formation temperatures of different graphite inclusions in placer black nephrite jade samples.

T (°C) = $-445 \times R2 + 641$, R2 = 0.96 (1); T (°C) = $91.4 \times (R2) 2 - 556.3 \times R2 + 676.3$ (2) [10,11,29]. Note: D1_{I1}: intensity of D1, G_{I2}: intensity of G, D1_{A1}: peak area of D1, G_{A1}: peak area of G, Full width at half maximum (FWHM), R2 area ratio of graphite spectrums were obtained using the Peakfit software Origin 9.0. n. d. = not discernible S. E. = Standard Error. In sample QHL-4/1-2 to QHL-4/1-5, the graphite Raman geothermometers used do not work for the carbon spectrum without the D band.

3.5. Implication for Graphite Growth and Nephrite Jade Formation

Graphite usually generated in meta-sediments, meta-carbonates, and skarn rocks can be attributed to distinct processes, and its carbon sources and the structural characteristics of Raman spectroscopy show different properties [27,30,31]. Generally, the WJ-type nephrite jade from Xinjiang was formed through the skarn-type metasomatism of intermediate-felsic granitic rocks and Precambrian dolomite marble [2,5,6,8]. Our recent work proposes that the formation mechanism model of WJ-type nephrite jade was formed through metamorphism/metasomatism during continent–continent collision [29]. The original carbon-bearing material may have been deposited in the carbonate rocks and subsequently subducted. The low crystallinity of graphite may also be due to the rapid deposition kinetics, possibly playing an underestimated role in the structural transformation of carbon. The micro and cryptocrystalline texture of the jade reflects conditions of high

supersaturation of amphibole crystallization, probably caused by the rapid infiltration of SiO_2 -rich fluid with a non-equilibrium composition. Defective carbon can also precipitate from the fluid at high supersaturation [32]. In our present investigation, it can be assumed the crystalline graphite inclusions were finally formed at medium- to high-temperature metamorphic facies driven by late continental collisions, revealing the temperature changes experienced by the main minerals during the formation processes. Moreover, previous studies have confirmed that the graphite structures tend to record the peak metamorphic temperatures and do not recrystallize under retrograde conditions except in some extreme cases where they will be destroyed [12,23]. The metamorphic temperatures of 378~556 °C obtained from graphite Raman micro-thermometry provide a new perspective depicting the formation temperatures of nephrite jade.

4. Conclusions

Abundant graphite inclusions are enriched in the placer black nephrite jade in Xinjiang Province, Northwest China, which mostly show the characteristics of bands and flakes. This type of nephrite jade is colored by graphite inclusions instead of chemical elements. The Raman spectroscopic analyses show that the graphite inclusions generally present a good degree of crystallization, and the mineralization temperature of most of the graphite inclusions is under ~380–560 °C, indicating the regional metamorphic temperature in different stages or facies. Only a few crystalline graphite inclusions show fluid-related characteristics, and their carbon sources may be derived from magmatic intrusion during orogeny. The association of graphite inclusions and nephrite jade indicates that the metamorphic grade of primary nephrite deposits is situated in the facies of medium- and high-temperature transformation.

Author Contributions: Conceptualization, J.Z., C.Z. and S.Z.; methodology, C.Z., Y.L. and J.W.; writing—original draft preparation, J.Z., L.C., C.Z., Y.L., R.T., J.W., Y.W. and S.Z.; writing—review and editing, J.Z. and C.Z.; supervision, S.Z. and C.Z.; funding acquisition, S.Z and C.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was jointly supported by "Deep-time Digital Earth" Science and Technology Leading Talents Team Funds for the Central Universities for the Frontiers Science Center for Deep-time Digital Earth, China University of Geosciences (Beijing) (Fundamental Research Funds for the Central Universities; grant number: 2652023001) to Shouting Zhang and basic research project of science, education and production integration pilot project of Qilu University of Technology (Shandong Academy of Sciences) (grant number: 11240455) to Cun Zhang.

Data Availability Statement: All data are contained within the work.

Acknowledgments: We are grateful to the Editor-in-Chief and the Academic Editors, as well as two anonymous reviewers for their constructive comments and suggestions that greatly improve this manuscript.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- 1. Yu, X.Y. Colored Gemmology, 2nd ed.; Geology Press: Beijing, China, 2016; pp. 236–244. (In Chinese)
- 2. Zhang, C.; Yang, F.; Yu, X.; Liu, J.; Carranza, E.J.M.; Chi, J.; Zhang, P. Spatial-temporal distribution, metallogenic mechanisms and genetic types of nephrite jade deposits in China. *Front. Earth Sci.* **2023**, *11*, 1047707.
- Liu, F.; Yu, X.Y. Types of Deposits and Mineralogical Characteristics of Nephrite in China. *Miner. Resour. Geol.* 2009, 23, 375–380, (In Chinese with English Abstract)
- 4. Yui, T.F.; Usuki, T.; Chen, C.Y.; Ishida, A.; Sano, Y.; Suga, K.; Iizuka, Y.; Chen, C.T. Dating thin zircon rims by NanoSIMS: The Fengtien nephrite (Taiwan) is the youngest jade on Earth. *Int. Geol. Rev.* **2014**, *56*, 1932–1944.
- Liu, Y.; Deng, J.; Shi, G.H.; Sun, X.; Yang, L. Geochemistry and petrogenenesis placer nephrite from Hetian, Xinjiang Northwest China. Ore Geol. Rev. 2011, 41, 122–132. [CrossRef]
- Liu, Y.; Zhang, R.Q.; Abuduwayiti, M.; Wang, C.; Zhang, S.P.; Shen, C.H.; Zhang, Z.Y.; He, M.Y.; Zhang, Y.; Yang, X.D. SHRIMP U–Pb zircon ages, mineral compositions and geochemistry of placer nephrite in the Yurungkash and Karakash River deposits, West Kunlun, Xinjiang, northwest China: Implication for a Magnesium Skarn. Ore Geol. Rev. 2016, 72, 699–727.

- 7. Adams, C.J.; Beck, R.J.; Campbell, H.J. Characterisation and origin of New Zealand nephrite jade using its strontium isotopic signature. *Lithos* **2007**, *97*, 307–322.
- 8. Jiang, Y.; Shi, G.H.; Xu, L.G.; Li, X.L. Mineralogy and Geochemistry of Nephrite Jade from Yinggelike Deposit, Altyn Tagh (Xinjiang, NW China). *Minerals* **2020**, *10*, 418.
- 9. Zhang, C.; Yu, X.Y.; Jiang, T.L. Mineral association and graphite inclusions in nephrite jade from Liaoning, northeast of China: Implications for metamorphic conditions and ore genesis. *Geosci. Front.* **2019**, *10*, 425–437.
- Beyssac, O.; Goffé, B.; Chopin, C.; Rouzaud, J.N. Raman spectra of carbonaceous material in metasediments: A new geothermometer. J. Metamorph. Geol. 2002, 20, 859–871.
- 11. Beyssac, O.; Rouzaud, J.N.; Goffé, B.; Brunet, F.; Chopin, C. Graphitization in a high-pressure, low-temperature metamorphic gradient: A Raman microspectroscopy and HRTEM study. *Contrib. Mineral. Petrol.* **2002**, *143*, 19–31.
- 12. Buseck, P.R.; Beyssac, O. From Organic Matter to Graphite: Graphitization. *Elements* 2014, 10, 421–426.
- Henry, D.G.; Jarvis, I.; Gillmore, G.; Stephenson, M. Raman spectroscopy as a tool to determine the thermal maturity of organic matter: Application to sedimentary, metamorphic and structural geology. *Earth-Sci. Rev.* 2019, 198, 102936.
- 14. Wopenka, B.; Pasteris, J.D. Structural characterization of kerogens to granulite-facies graphite: Applicability of Raman microprobe spectroscopy. *Am. Miner.* **1993**, *78*, 533–557.
- 15. Huizenga, J.M. Thermodynamic modelling of a cooling C–O–H fluid–graphite system: Implications for hydrothermal graphite precipitation. *Miner. Depos.* **2011**, *46*, 23–33. [CrossRef]
- 16. Huizenga, J.M.; Jacques Touret, J.L.R. Granulites, CO₂ and graphite. Gondwana Res. 2012, 22, 799-809.
- 17. Gao, K.; Shi, G.H.; Wang, M.L.; Xie, G.; Wang, J.; Zhang, X.C.; Fang, T.; Lei, W.Y.; Liu, Y. The Tashisayi nephrite deposit from South Altyn Tagh, Xinjiang, northwest China. *Geosci. Front.* **2019**, *10*, 1597–1612.
- 18. Zhang, C.; Yu, X.Y.; Yang, F.; Santosh, M.; Huo, D. Petrology and geochronology of the Yushigou nephrite jade from the North Qilian Orogen, NW China: Implications for subduction related processes. *Lithos* **2021**, *380–381*, 105894.
- 19. Tang, Y.L.; Chen, B.Z.; Jiang, R.H. *Chinese Hetian Nephrite*, *Xinjiang*; Xinjiang People's Publishing House: Urumqi, China, 1994; pp. 103–206. (In Chinese)
- Bersani, D.; Andò, S.; Scrocco, L.; Gentile, P.; Salvioli-Mariani, E.; Lottici, P.P. Study of the composition of amphiboles in the tremolite–ferro–actinolite series by micro-Raman and SEM-EDXS. In Proceedings of the 11th GeoRaman International Conference, St. Louis, MO, USA, 15–19 June 2014.
- 21. Al-Ani, T.; Ahtola, T.; Cutts, K.; Torppa, A. Metamorphic evolution of graphite in the Paleoproterozoic Savo Schist Belt (SSB), Central Finland: Constraints from geothermetric modeling. *Ore Geol. Rev.* **2022**, *141*, 104672.
- 22. Ferrari, A.C.; Robertson, J. Raman Signature of Bonding and Disorder in Carbons. MRS Online Proc. Libr. 1999, 593, 1946–4274.
- Beyssac, O.; Pattison, D.R.M.; Bourdelle, F. Contrasting degrees of recrystallization of carbonaceous material in the Nelson aureole, British Columbia and Ballachulish aureole, Scotland, with implications for thermometry based on Raman spectroscopy of carbonaceous material. J. Metamorph. Geol. 2019, 37, 71–95.
- 24. Pasteris, J.D. Secondary graphitization in mantle-derived rocks. *Geology* **1988**, *16*, 804–807. [CrossRef]
- 25. Pasteris, J.D. Causes of the uniformly high crystallinity of graphite in large epigenetic deposits. *J. Metamorph. Geol.* **1999**, *17*, 779–787.
- Galvez, M.E.; Beyssac, O.; Martinez, I.; Benzerara, K.; Chaduteau, C.; Malvoisin, B.; Malavieille, J. Graphite formation by carbonate reduction during subduction. *Nat. Geosci.* 2013, 6, 473–477. [CrossRef]
- Rahl, J.M.; Anderson, K.M.; Brandon, M.T.; Fassoulas, C. Raman spectroscopic carbonaceous material thermometry of low-grade metamorphic rocks: Calibration and application to tectonic exhumation in Crete, Greece. *Earth Planet. Sci. Lett.* 2005, 240, 339–354. [CrossRef]
- Aoya, M.; Kouketsu, Y.; Endo, S.; Shimizu, H.; Mizukami, T.; Nakamura, D.; Wallis, S. Extending the applicability of the Raman carbonaceous-material geothermometer using data from contact metamorphic rocks. *J. Metamorph. Geol.* 2010, 28, 895–914. [CrossRef]
- Zhang, C.; He, X.F.; Sun, L.X.; Santosh, M.; Chi, J.; Yu, X.Y.; Li, Z.S.; Meng, Y.X. Graphitization in Paleoproterozoic granulites from the Taihua Complex, North China Craton: Constraints from laser Raman spectroscopy, carbon isotopes and geochronology. *Lithos* 2023, 454–455, 107266. [CrossRef]
- 30. Cao, S.Y.; Neubauer, F. Graphitic material in fault zones: Implications for fault strength and carbon cycle. *Earth-Sci. Rev.* **2019**, *194*, 109–124. [CrossRef]
- Tumiati, S.; Recchia, S.; Remusat, L.; Tiraboschi, C.; Sverjensky, D.A.; Manning, C.E.; Vitale Brovarone, A.; Boutier, A.; Spanu, D.; Poli, S. Subducted organic matter buffered by marine carbonate rules the carbon isotopic signature of arc emissions. *Nat. Commun.* 2022, *13*, 2909. [CrossRef]
- 32. Muirhead, D.K.; Parnell, J.; Taylor, C.; Bowden, S.A. A kinetic model for the thermal evolution of sedimentary and meteoritic organic carbon using Raman spectroscopy. *J. Anal. Appl. Pyrolysis* **2012**, *96*, 153–161. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.




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

Peng Luo, Yuegang Tang *D, Ruiqing Li and Minmin Ju

College of Geoscience and Surveying Engineering, China University of Mining and Technology (Beijing), D11, Xueyuan Road, Beijing 100083, China; pengluo375@163.com (P.L.); lrq_qrl@yeah.net (R.L.); juminmin@163.com (M.J.)

* Correspondence: tyg@vip.163.com

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].



Citation: Luo, P.; Tang, Y.; Li, R.; Ju, M. Effects of Minerals Type and Content on the Synthetic Graphitization of Coal: Insights from the Mixture of Minerals and Anthracite with Varied Rank. *Minerals* **2023**, *13*, 1024. https:// doi.org/10.3390/min13081024

Academic Editor: Bekir Genc

Received: 15 June 2023 Revised: 14 July 2023 Accepted: 24 July 2023 Published: 31 July 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/). 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 (Fe₃C) 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, due to the complex composition 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 Coal Mine Seam	Coal Seam	oal R _{o,max} eam (%)	Pı A	roxima malysi (wt%)	te s		Ultim	ate Ana (wt%)	alyses		C	Mace Compo (vol	eral sition %)	
					M _{ad}	A _d	V _{daf}	С	Н	Ν	0	St	V	Ι	L	Μ
BJG JGS	Helanshan Xiangshan	Baijigou Jiangoushan	4 8	2.82 5.87	1.08 4.19	3.55 0.82	8.32 2.34	95.71 96.61	3.19 1.75	0.79 0.59	0.28 0.17	0.03 0.88	89.6 70.2	7.6 22.0	0.0 0.0	2.8 7.8

R_{0,max}, 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_t, 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 (CaCO₃) [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 ₂)	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 (λ = 0.15406 nm) irradiation, over the interval 5° –90° 2 θ , at a scanning rate of 2° /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⁻¹. 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].

Minerals 2023, 13, 1024

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 Δ value is the mixture samples minus the raw coal samples, representing the change caused by the added mineral.

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $				BIG Co	al Series					IGS Coa	ul Series		
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Mass Ratio (Coal:Minerals)	Samples	W _C (g)	(g)	W _R (g)	W _R /W _C (%)	ΔW _R /W _C (%)	Samples	W _C (g)	(g)	W _R (g)	W _R /W _C (%)	$\frac{\Delta W_R/W_C}{(\%)}$
BK51000000.50008.151481.513.79JK510.00001.90007.756481.20 -6.844 BK1010.00001.00002.00007.985579.86 2.133 JK1010.00007.756477.56 -10.48 BK2010.00002.00007.00005.825358.25 -19.47 JK4010.00007.793374.93 74.93 -15.77 BK5110.00000.50007.48907.489 -2.844 JC510.00002.00008.644488.64 0.60 BC1010.00001.00002.00007.479274.79 -2.933 JC1010.00002.00008.644488.64 0.60 BC1010.00002.00007.479274.79 -7.703 -7.70 JC4010.00002.00008.644488.64 0.60 BC24010.00002.00007.361773.62 -11.51 JC2010.00002.00008.364488.64 0.60 BC310.00002.00002.00007.703177.03 -7.70 JC4010.00002.00008.364488.64 0.60 BC4010.00002.00002.00007.361773.6272.32 -1.185 38.17 -4.87 BC4010.000010.00002.00002.00000.50008.394884.00 -7.361 -7.51 38.74 85.92 -2.12 BQ1010.00002.00002.00000.50008.3956 65.74	w coal	В	10.0000	/	7.7726	77.73		ſ	10.0000	0.5000	8.8043	88.04	
BK1010.0001.0007.95579.852.13JK1010.0007.756477.56-10.48BK2010.00002.00006.621566.22-11.51JK2010.00002.00007.493374.93-13.11BK2010.00002.00005.825358.25-19.47JK4010.00002.00007.493374.93-13.17BC510.00000.50007.49007.8907.89-2.84JC5JC1010.00007.2657.227-15.77BC1010.00001.00007.49227.479-2.933JC1010.00001.00008.6188.64488.640.60BC1010.00001.00007.703177.03-7.70JC4010.00001.00008.31728.117-4.87BC2010.00000.50007.731277.03-7.70JC4010.00001.00008.317283.17-4.87BC3010.00000.50006.971269.11-8.61JC1010.00000.50008.592185.92-2.12BQ1010.00000.100006.971266.74-10.99JC2010.00000.50008.592185.92-2.12BQ2010.00000.100008.39566.574-17.95JQ4010.00000.50008.945785.92-2.12BQ200.00000.100008.39566.574-17.95JQ4010.00000.10008.952289.52-17.83BP1	100:5	BK5	10.0000	0.5000	8.1514	81.51	3.79	JK5	10.0000	0.5000	8.1195	81.20	-6.84
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	100:10	BK10	10.0000	1.0000	7.9855	79.86	2.13	JK10	10.0000	1.0000	7.7564	77.56	-10.48
BK4010.0004.0005.825358.25 -19.47 JK4010.0004.0007.226572.27 -15.77 BC510.0000.50007.48907.489 -2.84 JC510.0000.50008.64488.640.60BC1010.00001.00001.00000.50008.618586.19 -1.85 BC2010.00002.00007.361773.62 -4.11 JC2010.00008.618584.00 -4.04 BC4010.00002.00007.361777.03 -7.70 JC4010.00008.317283.17 -4.04 BC4010.00000.50007.361777.03 -7.70 JC4010.00008.37283.17 -4.04 BC4010.00000.50007.34277.33 -7.70 JC4010.00008.317283.17 -4.04 BC4010.00001.00000.50007.734277.35JC70JC7008.592 -2.12 BQ1010.00001.00000.50005.9774 -10.99 JQ2010.0000 1.0000 8.592 -7.51 BQ2010.00002.00006.673566.74 -10.99 JQ2010.0000 2.0000 8.592 -7.51 BQ1010.00000.00000.50008.39684.23 6.74 -10.99 JQ20 10.0000 2.0000 8.592 -7.51 BQ2010.00000.00000.00000.00000.0000 0.0000 0.5000 8.592 <	100:20	BK20	10.0000	2.0000	6.6215	66.22	-11.51	JK20	10.0000	2.0000	7.4933	74.93	-13.11
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	100:40	BK40	10.0000	4.0000	5.8253	58.25	-19.47	JK40	10.0000	4.0000	7.2265	72.27	-15.77
BC1010.0001.00007.479274.79-2.93JC1010.0008.618586.19-1.85BC2010.00002.00007.361773.62-4.11JC2010.00008.399884.00-4.04BC4010.00004.00007.703177.03-7.70JC4010.00008.317283.17-4.43BQ510.00000.50007.34272.342-5.38JQ510.00008.592185.92-2.12BQ1010.00000.50007.234272.34-5.38JQ510.00001.00008.245782.46-5.58BQ1010.00000.50005.9745971-17.95JQ4010.00001.00008.245782.46-5.58BP110.00000.100006.67356.674-17.95JQ4010.00002.00008.532689.53-7.717BP110.00000.100008.396083.966.23JP110.00000.10008.952689.53-1.63BP110.00000.100000.100008.423284.236.51JP210.00000.10008.952689.53-1.63BP110.00000.20008.423284.236.51JP210.00000.10007.717077.17-10.87BP210.00000.100000.50008.3966.51JP210.00000.50008.952689.520.78BP210.00000.00000.50008.45284	100:5	BC5	10.0000	0.5000	7.4890	74.89	-2.84	JC5	10.0000	0.5000	8.8644	88.64	0.60
BC20 10.000 2.000 7.3617 73.62 -4.11 JC20 10.000 2.000 8.398 84.00 -4.04 BC40 10.0000 4.000 7.7031 77.03 -7.70 JC40 10.000 8.3172 83.17 -4.48 BC40 10.0000 4.0000 7.7031 77.03 -7.70 JC40 10.0000 8.3172 83.17 -4.48 BQ1 10.0000 0.5000 7.2342 72.34 -5.38 JQ5 10.0000 8.372 83.17 -4.48 BQ20 10.0000 0.5000 6.9112 -5.38 JQ5 10.0000 1.0000 8.2921 85.92 -7.51 BQ10 10.0000 2.0000 6.9112 -17.95 JQ40 10.0000 8.000 7.717 7.17 -10.87 BQ20 10.0000 0.1000 8.396 6.51 -17.95 JQ40 10.0000 7.7170 77.17 -10.87 BP1 10.0000 0.2000	100:10	BC10	10.0000	1.0000	7.4792	74.79	-2.93	JC10	10.0000	1.0000	8.6185	86.19	-1.85
BC40 10.000 4.000 7.703 77.03 -7.70 JC40 10.000 8.317 -4.87 BQ5 10.000 0.5000 7.2342 72.34 -5.38 JQ5 10.000 8.5921 85.92 -2.12 BQ10 10.0000 0.5000 6.6735 66.74 -10.99 JQ20 10.0000 8.2457 82.46 -5.58 BQ10 10.0000 2.0000 6.6735 66.74 -10.99 JQ20 10.0000 8.053 8.736 -5.58 BQ10 10.0000 2.0000 6.6735 66.74 -10.99 JQ20 10.0000 8.053 8.746 -5.58 BQ10 10.0000 2.0000 6.5735 66.74 -10.99 JQ20 10.0000 7.7170 77.17 71.07 BP1 10.0000 0.1000 8.396 6.23 JP1 10.0000 2.000 8.952 89.52 14.8 BP2 10.0000 0.2000 8.4232 84.23 6.5	100:20	BC20	10.0000	2.0000	7.3617	73.62	-4.11	JC20	10.0000	2.0000	8.3998	84.00	-4.04
BQ5 10.0000 0.5000 7.2342 72.34 -5.38 JQ5 10.0000 8.5921 85.92 -2.12 BQ10 10.0000 1.0000 6.9112 69.11 -8.61 JQ10 10.0000 8.5921 85.92 -5.58 BQ10 10.0000 1.0000 6.9112 69.11 -8.61 JQ10 10.0000 8.2457 82.46 -5.58 BQ20 10.0000 2.0000 6.6735 66.74 -10.99 JQ20 10.0000 2.0000 8.0526 80.53 -7.51 BQ40 10.0000 2.0000 5.9774 59.77 -17.95 JQ40 10.0000 7.7170 77.17 -10.87 BP1 10.0000 0.1000 8.396 6.23 JP1 10.0000 7.7170 77.17 -10.87 BP2 10.0000 0.2000 8.423 6.51 JP2 10.0000 0.1000 7.160 7.148 BP2 10.0000 0.5000 8.922 8.922	100:40	BC40	10.0000	4.0000	7.7031	77.03	-7.70	JC40	10.0000	4.0000	8.3172	83.17	-4.87
BQ10 10.000 1.000 6.9112 69.11 -8.61 JQ10 10.000 8.2457 82.46 -5.58 BQ20 10.0000 2.0000 6.6735 66.74 -10.99 JQ20 10.0000 8.0526 80.53 -7.51 BQ40 10.0000 2.0000 6.6735 66.74 -10.99 JQ20 10.0000 8.0526 80.53 -7.51 BQ40 10.0000 4.0000 5.9774 59.77 -17.95 JQ40 10.0000 7.7170 77.17 -10.87 BP1 10.0000 0.1000 8.3960 83.96 6.23 JP1 10.0000 7.7170 77.17 -10.87 BP2 10.0000 0.1000 8.3960 6.23 JP1 10.0000 0.1000 8.952 89.52 14.48 BP3 10.0000 0.5000 8.152 83.26 6.24 JP3 10.0000 0.1000 8.630 86.31 -1.73 BP10 10.0000 0.10000 <	100:5	BQ5	10.0000	0.5000	7.2342	72.34	-5.38	JQ5	10.0000	0.5000	8.5921	85.92	-2.12
BQ20 10.000 2.000 6.673 6.74 -10.99 IQ20 10.000 8.0526 80.53 -7.51 BQ40 10.0000 4.0000 5.9774 59.77 -17.95 JQ40 10.0000 2.000 8.0526 80.53 -7.51 BP1 10.0000 0.1000 8.3960 83.96 6.23 JP1 10.0000 7.7170 77.17 -10.87 BP1 10.0000 0.1000 8.3960 83.96 6.23 JP1 10.0000 0.1000 8.952 14.48 BP2 10.0000 0.2000 8.423 6.51 JP2 10.0000 0.2000 8.952 14.48 BP5 10.0000 0.5000 8.152 3.79 JP10 10.0000 0.5000 8.631 -1.73 BP10 10.0000 2.0000 8.152 3.79 JP10 10.0000 0.5000 8.579 -2.25 BP20 10.0000 2.0000 0.10000 0.10000 0.5000 8.	100:10	BQ10	10.0000	1.0000	6.9112	69.11	-8.61	JQ10	10.0000	1.0000	8.2457	82.46	-5.58
BQ40 10.000 4.000 5.9774 59.77 -17.95 JQ40 10.000 4.000 7.717 7.17 -10.87 BP1 10.000 0.1000 8.3960 83.96 6.23 JP1 10.0000 7.7170 77.17 -10.87 BP2 10.0000 0.1000 8.423 83.96 6.51 JP2 10.0000 0.2000 8.952 89.52 1.48 BP2 10.0000 0.5000 8.423 6.51 JP2 10.0000 0.2000 8.630 86.31 -1.73 BP10 10.0000 1.0000 0.5000 8.1515 81.52 3.79 JP10 10.0000 1.0000 8.578 85.79 -2.25 BP20 10.0000 2.0000 7.7881 77.88 0.16 JP20 10.0000 2.0000 8.579 -2.25	100:20	BQ20	10.0000	2.0000	6.6735	66.74	-10.99	JQ20	10.0000	2.0000	8.0526	80.53	-7.51
BP1 10.0000 0.1000 8.3960 83.96 6.23 JP1 10.0000 0.1000 8.952 89.52 1.48 BP2 10.0000 0.2000 8.4232 84.23 6.51 JP2 10.0000 0.2000 8.952 88.82 0.78 BP5 10.0000 0.5000 8.4232 84.23 6.51 JP2 10.0000 0.2000 8.8824 88.82 0.78 BP5 10.0000 0.5000 8.3962 6.24 JP5 10.0000 0.5000 8.631 -1.73 BP10 10.0000 1.0000 8.1515 81.52 3.79 JP10 10.0000 8.578 85.79 -2.25 BP20 10.0000 2.0000 2.0000 8.2387 82.24 -5.80	100:40	BQ40	10.0000	4.0000	5.9774	59.77	-17.95	JQ40	10.0000	4.0000	7.7170	77.17	-10.87
BP2 10.0000 0.2000 8.4232 84.23 6.51 JP2 10.0000 0.2000 8.882 0.78 BP5 10.0000 0.5000 8.3962 6.24 JP5 10.0000 0.5000 8.6309 86.31 -1.73 BP10 10.0000 1.0000 8.1515 81.52 3.79 JP10 10.0000 8.5788 85.79 -2.25 BP10 10.0000 2.0000 7.7881 77.88 0.16 JP20 10.0000 8.2387 82.24 -5.50	100:1	BP1	10.0000	0.1000	8.3960	83.96	6.23	JP1	10.0000	0.1000	8.9522	89.52	1.48
BP5 10.0000 0.5000 8.3962 6.24 JP5 10.0000 0.5000 8.6309 86.31 -1.73 BP10 10.0000 1.0000 8.1515 81.52 3.79 JP10 10.0000 8.5788 85.79 -2.25 BP20 10.0000 2.0000 7.7881 77.88 0.16 JP20 10.0000 8.2387 82.24 -5.80	100:2	BP2	10.0000	0.2000	8.4232	84.23	6.51	JP2	10.0000	0.2000	8.8824	88.82	0.78
BP10 10.0000 1.0000 8.1515 81.52 3.79 JP10 10.0000 8.5788 85.79 -2.25 BP20 10.0000 2.0000 7.7881 77.88 0.16 JP20 10.0000 8.2387 82.24 -5.80	100:5	BP5	10.0000	0.5000	8.3962	83.96	6.24	JP5	10.0000	0.5000	8.6309	86.31	-1.73
BP20 10.0000 2.0000 7.7881 77.88 0.16 JP20 10.0000 2.0000 8.2387 82.24 -5.80	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	JP20	10.0000	2.0000	8.2387	82.24	-5.80





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.

 β_{002} and β_{100} are the full width at half maximum (FWHM) of (002) and (100) peaks, and θ_{002} and θ_{100} are their corresponding scattering angles.

 N_{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⁻¹) and second-order (2300 to 3000 cm⁻¹) 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 ₀₀₂ (nm)	L _c (nm)	L _a (nm)	Nave	G	Samples	d ₀₀₂ (nm)	L _c (nm)	L _a (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 Δ value is the mixture samples minus the raw coal samples, representing the change caused by the added mineral.

		BJG Coa	al Series				JGS Co	al Series	
Samples	ΔL_{c} (nm)	ΔL _a (nm)	ΔG	$\Delta I_{\rm D}/I_{\rm G}$	$\Delta A_{\rm D}/A_{\rm G}$	Samples	$\Delta L_{\rm c}$ (nm)	ΔL _a (nm)	ΔG
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.

Commiss	D Peak	(cm ⁻¹)	G Peak	(cm ⁻¹)	т /т	A 1A
Samples	Position	FWHM	Position	FWHM	$I_{\rm D}/I_{\rm G}$	$A_{\rm D}/A_{\rm G}$
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	-	-

Samulas	D Peak	(cm ⁻¹)	G Peak	(cm ⁻¹)	T /T	A 1A
Samples	Position	FWHM	Position	FWHM	- 1 _D /1 _G	$A_{\rm D}/A_{\rm G}$
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 (ΔG) 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 (ΔG) 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 (ΔL_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 (ΔL_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 (ΔL_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 (ΔL_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 (ΔL_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 (ΔL_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 (α -quartz) transforms into high-temperature quartz (β -quartz) or square quartz [56]. SiO₂ is thermally stable and does not decompose with the increasing temperature. SiO₂ will melt at 1715 °C. However, SiC will formed from SiO₂ 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-Al₂O₃ [58]. However, based on their melting/boiling point, the effect of kaolinite may be equal to the combination effect of SiC and Al₂O₃, in turn. The boiling point of Al₂O₃ is up to 2980 °C. The difference in effect between kaolinite and quartz is possibly attributed to Al₂O₃. 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 (FeS₂) begins to decompose to the pyrrhotite (Fe_{1-x}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 (Fe₃C) with iron on graphitization has been widely discussed [10,12,14,16,19,21–25].

Calcite will decompose into metastable polycrystals such as aragonite (CaCO₃) or spherical calcium carbonate (CaCO₃), 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 CaC₂) [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 SiO₂ (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.

Author Contributions: Conceptualization, methodology, software, validation, formal analysis, investigation, resources, data curation, writing—original draft preparation, visualization, P.L.; project administration, funding acquisition, supervision, writing—review and editing, Y.T.; writing—review and editing, R.L.; writing—review and editing, M.J. All authors have read and agreed to the published version of the manuscript.

Funding: This research is supported by the Key Research of Ningxia Hui Autonomous Region, China (No. 2021BEG02015) and the National Natural Science Foundation of China (No. 41872175).

Data Availability Statement: The data that support the findings of this study are available from the corresponding author, Yuegang Tang, upon reasonable request.

Acknowledgments: We are very grateful for the valuable comments from three anonymous reviewers and from the journal editors, which have greatly improved the quality of this paper.

Conflicts of Interest: The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

References

- 1. Atria, J.V.; Rusinko, F.; Schobert, H.H. Structural Ordering of Pennsylvania Anthracites on Heat Treatment to 2000–2900 °C. *Energy Fuels* **2002**, *16*, 1343–1347. [CrossRef]
- Bonijoly, M.; Oberlin, M.; Oberlin, A. A possible mechanism for natural graphite formation. *Int. J. Coal Geol.* 1982, 1, 283–312. [CrossRef]
- 3. Deurbergue, A.; Oberlin, A.; Oh, J.; Rouzaud, J. Graphitization of Korean anthracites as studied by transmission electron microscopy and X-ray diffraction. *Int. J. Coal Geol.* **1987**, *8*, 375–393. [CrossRef]
- 4. González, D.; Montes-Morán, M.A.; Suárez-Ruiz, I.; Garcia, A.B. Structural Characterization of Graphite Materials Prepared from Anthracites of Different Characteristics: A Comparative Analysis. *Energy Fuels* **2004**, *18*, 365–370. [CrossRef]
- 5. Rodrigues, S.; Suárez-Ruiz, I.; Marques, M.; Camean, I.; Flores, D. Microstructural evolution of high temperature treated anthracites of different rank. *Int. J. Coal Geol.* **2011**, *87*, 204–211. [CrossRef]
- 6. Suárez-Ruiz, I.; García, A.B. Optical Parameters as a Tool To Study the Microstructural Evolution of Carbonized Anthracites during High-Temperature Treatment. *Energy Fuels* **2007**, *21*, 2935–2941. [CrossRef]
- 7. Ward, C.R. Analysis and significance of mineral matter in coal seams. *Int. J. Coal Geol.* 2002, 50, 135–168. [CrossRef]
- 8. Taylor, G.H.; Teichmüller, M.; Davis, A.; Diessel, C.; Robert, P. Organic Petrology; Borntraeger: Stuttgart, Germany, 1998.
- 9. Evans, E.L.; Jenkins, J.L.; Thomas, J.M. Direct Electron Microscopic Studies of Graphitic Regions in Heat-Treated Coals and Coal Extracts. *Carbon* **1972**, *10*, 637–642. [CrossRef]
- 10. González, D.; Montes-Morán, M.A.; Garcia, A.B. Influence of Inherent Coal Mineral Matter on the Structural Characteristics of Graphite Materials Prepared from Anthracites. *Energy Fuels* **2005**, *19*, 263–269. [CrossRef]
- 11. Oberlin, A.; Terriere, G. Graphitization studies of anthracites by high resolution electron microscopy. *Carbon* **1975**, *13*, 367–376. [CrossRef]
- 12. Ōya, A.; Ōtani, S. Catalytic graphitization of carbons by various metals. Carbon 1979, 17, 131–137. [CrossRef]
- 13. Ōya, A.; Fukatsu, T.; Ōtani, S.; Marsh, H. Catalytic graphitization of cokes by indigeneous mineral matter. *Fuel* **1983**, *62*, 502–507. [CrossRef]
- 14. Pappano, P.J.; Schobert, H.H. Effect of Natural Mineral Inclusions on the Graphitizability of a Pennsylvania Anthracite. *Energy Fuels* **2009**, *23*, 422–428. [CrossRef]
- 15. Fitzer, E.; Kochling, K.H.; Boehm, H.P.; Marsh, H. Recommended terminology for the description of carbon as a solid (IUPAC Recommendations 1995). *Pure Appl. Chem.* **1995**, *67*, 473–506. [CrossRef]
- 16. Dhakate, S.R.; Mathur, R.B.; Bahl, O.P. Catalytic effect of iron oxide on carbon/carbon composites during graphitization. *Carbon* **1997**, *35*, 1753–1756. [CrossRef]
- 17. Marsh, H.; Warburton, A.P. Catalysis of graphitisation. J. Appl. Chem. 1970, 20, 133–142. [CrossRef]
- 18. Ōya, A.; Marsh, H. Phenomena of catalytic graphitization. J. Mater. Sci. 1982, 17, 309–322. [CrossRef]
- 19. Wang, J.; Morishita, K.; Takarada, T. High-Temperature Interactions between Coal Char and Mixtures of Calcium Oxide, Quartz, and Kaolinite. *Energy Fuels* **2001**, *15*, 1145–1152. [CrossRef]
- 20. Finkelman, R.B.; Dai, S.; French, D. The importance of minerals in coal as the hosts of chemical elements: A review. *Int. J. Coal Geol.* 2019, 212, 103251. [CrossRef]
- Cabielles, M.; Rouzaud, J.-N.; Garcia, A.B. High-Resolution Transmission Electron Microscopy Studies of Graphite Materials Prepared by High-Temperature Treatment of Unburned Carbon Concentrates from Combustion Fly Ashes. *Energy Fuels* 2009, 23, 942–950. [CrossRef]
- 22. Oberlin, A.; Rouchy, J.P. Transformation des carbones non graphitables par traitement thermique en presence de fer. *Carbon* **1971**, *9*, 39–46. [CrossRef]
- 23. Wang, Y.-G.; Korai, Y.; Mochida, I.; Nagayama, K.; Hatano, H.; Fukuda, N. Modification of synthetic mesophase pitch with iron oxide, Fe₂O₃. *Carbon* **2001**, *39*, 1627–1634. [CrossRef]
- 24. Weisweiler, W.; Subramanian, N.; Terwiesch, B. Catalytic influence of metal melts on the graphitization of monolithic glasslike carbon. *Carbon* **1971**, *9*, 755–761. [CrossRef]
- 25. Yu, J.K.; Ueno, S.; Li, H.X.; Hiragushi, K. Improvement of graphitization of isotropic carbon by Al₂O₃ formed from aluminium chelate compound. *J. Eur. Ceram. Soc.* **1999**, *19*, 2843–2848. [CrossRef]
- 26. Deshmukh, A.A.; Mhlanga, S.D.; Coville, N.J. Carbon spheres. Mater. Sci. Eng. R Rep. 2010, 70, 1–28. [CrossRef]
- 27. Rodrigues, S.; Suárez-Ruiz, I.; Marques, M.; Flores, D. Catalytic role of mineral matter in structural transformation of anthracites during high temperature treatment. *Int. J. Coal Geol.* **2012**, *93*, 49–55. [CrossRef]
- 28. Nyathi, M.S.; Clifford, C.B.; Schobert, H.H. Characterization of graphitic materials prepared from different rank Pennsylvania anthracites. *Fuel* **2013**, *114*, 244–250. [CrossRef]
- 29. Bolat, E.; Sağlam, S.; Pişkin, S. Chemical demineralization of a Turkish high ash bituminous coal. *Fuel Process. Technol.* **1998**, 57, 93–99. [CrossRef]
- 30. Lan, C.; Tang, Y.; Huan, X.; Che, Q. Effects of Minerals in Anthracite on the Formation of Coal-Based Graphene. *Chem. Sel.* **2019**, *4*, 5937–5944. [CrossRef]

- 31. Liu, L.; Qing, M.; Wang, Y.; Chen, S. Defects in Graphene: Generation, Healing, and Their Effects on the Properties of Graphene: A Review. J. Mater. Sci. Technol. 2015, 31, 599–606. [CrossRef]
- 32. Li, R.; Tang, Y.; Che, Q.; Huan, X.; Ma, P.; Luo, P.; Mao, X. Study on the microstructure of the symbiosis of coal-based graphene and coal-based graphene quantum dots: Preparation and characterization. *Nanotechnology* **2022**, *33*, 455702. [CrossRef] [PubMed]
- 33. Li, R.; Tang, Y.; Che, Q.; Ma, P.; Luo, P.; Lu, X.; Dong, M. Effects of Coal Rank and Macerals on the Structure Characteristics of Coal-Based Graphene Materials from Anthracite in Qinshui Coalfield. *Minerals* **2022**, *12*, 588. [CrossRef]
- 34. Huan, X.; Tang, Y.-G.; Xu, J.-J.; Lan, C.-Y.; Wang, S.-Q. Structural characterization of graphenic material prepared from anthracites of different characteristics: A comparative analysis. *Fuel Process. Technol.* **2019**, *183*, 8–18. [CrossRef]
- 35. Chen, H.; Wang, S.; Zhang, X.; Zhao, Y.; Zhang, H. A study of chemical structural evolution of thermally altered coal and its effect on graphitization. *Fuel* **2021**, *283*, 119295. [CrossRef]
- 36. Finkelman, R.B.; Palmer, C.A.; Wang, P. Quantification of the modes of occurrence of 42 elements in coal. *Int. J. Coal Geol.* 2018, 185, 138–160. [CrossRef]
- 37. Ward, C.R. Analysis, origin and significance of mineral matter in coal: An updated review. *Int. J. Coal Geol.* **2016**, *165*, 1–27. [CrossRef]
- Lu, L.; Sahajwalla, V.; Kong, C.; Harris, D. Quantitative X-ray diffraction analysis and its application to various coals. *Carbon* 2001, 39, 1821–1833. [CrossRef]
- 39. Sonibare, O.O.; Haeger, T.; Foley, S.F. Structural characterization of Nigerian coals by X-ray diffraction, Raman and FTIR spectroscopy. *Energy* **2010**, *35*, 5347–5353. [CrossRef]
- 40. Seehra, M.S.; Pavlovic, A.S. X-ray diffraction, thermal expansion, electrical conductivity, and optical microscopy studies of coal-based graphites. *Carbon* **1993**, *31*, 557–564. [CrossRef]
- 41. Kwiecińska, B.; Petersen, H.I. Graphite, semi-graphite, natural coke, and natural char classification—ICCP system. *Int. J. Coal Geol.* 2004, *57*, 99–116. [CrossRef]
- 42. Nemanich, R.J.; Solin, S. First-and second-order Raman scattering from finite-size crystals of graphite. *Phys. Rev. B* 1979, 20, 392. [CrossRef]
- 43. Cancado, L.; Takai, K.; Enoki, T.; Endo, M.; Kim, Y.; Mizusaki, H.; Speziali, N.L.; Jorio, A.; Pimenta, M.A. Measuring the degree of stacking order in graphite by Raman spectroscopy. *Carbon* **2008**, *46*, 272–275. [CrossRef]
- 44. Sadezky, A.; Muckenhuber, H.; Grothe, H.; Niessner, R.; Pöschl, U. Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information. *Carbon* **2005**, *43*, 1731–1742. [CrossRef]
- 45. Beyssac, O.; Goffé, B.; Petitet, J.-P.; Froigneux, E.; Moreau, M.; Rouzaud, J.-N. On the characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2003**, *59*, 2267–2276. [CrossRef]
- 46. Ferrari, A.C.; Robertson, J. Interpretation of Raman spectra of disordered and amorphous carbon. *Phys. Rev. B* 2000, *61*, 14095. [CrossRef]
- 47. Guedes, A.; Valentim, B.; Prieto, A.C.; Rodrigues, S.; Noronha, F. Micro-Raman spectroscopy of collotelinite, fusinite and macrinite. *Int. J. Coal Geol.* **2010**, *83*, 415–422. [CrossRef]
- 48. Harris, P.J.F. New Perspectives on the Structure of Graphitic Carbons. Crit. Rev. Solid State Mater. Sci. 2005, 30, 235–253. [CrossRef]
- 49. Oberlin, A. Carbonization and graphitization. Carbon 1984, 22, 521–541. [CrossRef]
- 50. Rouzaud, J.-N.; Deldicque, D.; Charon, É.; Pageot, J. Carbons at the heart of questions on energy and environment: A nanostructural approach. *Comptes Rendus Geosci.* 2015, 347, 124–133. [CrossRef]
- 51. Kokaji, K.; Oya, A.; Maruyama, K.; Yamada, Y.; Shiraishi, M. Carbonization and graphitization behavior of decacyclene. *Carbon* **1997**, *35*, 253–258. [CrossRef]
- 52. Yuan, L.; Liu, Q.; Mathews, J.P.; Zhang, H.; Wu, Y. Quantifying the Structural Transitions of Chinese Coal to Coal-Derived Natural Graphite by XRD, Raman Spectroscopy, and HRTEM Image Analyses. *Energy Fuels* **2021**, *35*, 2335–2346. [CrossRef]
- 53. Johnson, C.A.; Patrick, J.W.; Mark Thomas, K. Characterization of coal chars by Raman spectroscopy, X-ray diffraction and reflectance measurements. *Fuel* **1986**, *65*, 1284–1290. [CrossRef]
- 54. Zhang, X.; Wang, S.; Chen, H.; Wang, X.; Deng, J.; Li, X.; Zhang, Y. Observation of carbon nanostructure and evolution of chemical structure from coal to graphite by high temperature treatment, using componential determination, X-ray diffraction and high-resolution transmission electron microscope. *Fuel* **2023**, *332*, 126145. [CrossRef]
- 55. Franklin, R.E. Crystallite growth in graphitizing and non-graphitizing carbons. *Proc. R. Soc. Lond. Ser. A Math. Phys. Sci.* **1951**, 209, 196–218.
- Reifenstein, A.P.; Kahraman, H.; Coin, C.D.A.; Calos, N.J.; Miller, G.; Uwins, P. Behaviour of selected minerals in an improved ash fusion test: Quartz, potassium feldspar, sodium feldspar, kaolinite, illite, calcite, dolomite, siderite, pyrite and apatite. *Fuel* 1999, 78, 1449–1461. [CrossRef]
- 57. Hatcher, P.G.; Faulon, J.L.; Wenzel, K.A.; Cody, G.D. A structural model for lignin-derived vitrinite from high-volatile bituminous coal (coalified wood). *Energy Fuels* **1992**, *6*, 813–820. [CrossRef]
- 58. O'Gorman, J.V.; Walker, P.L. Thermal behaviour of mineral fractions separated from selected American coals. *Fuel* **1973**, 52, 71–79. [CrossRef]

- 59. Fitzer, E.; Kegel, B. Reaktionen von Kohlenstoffgesättigter Vanadiumcarbidschmelze mit ungeordnetem Kohlenstoff (Beitrag zur katalytischen Graphitierung). *Carbon* **1968**, *6*, 433–446. [CrossRef]
- 60. Burchell, T.D. Radiation Effects in Graphite and Carbon-Based Materials. MRS Bull. 1997, 22, 29–35. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.





Zhifei Liu^{1,2,*}, Daiyong Cao^{2,*}, Gaojian Chen², Zhongwei Bi¹ and Qingtong Chen¹

- ¹ China Coal Technology and Engineering Group Corp., China Coal Research Institute, Beijing 100013, China
- ² Earth Science and Surveying Engineering Institute, China University of Mining and Technology (Beijing), Ding 11 XueYuan Road, Beijing 100083, China
- * Correspondence: 18810545106@163.com (Z.L.); cdy@cumtb.edu.cn (D.C.)

Abstract: In order to explore the graphitization of inertinite, this paper conducted high-temperature thermal simulation experiments (HTT) and high-temperature high-pressure simulation experiments (HTHP) on isolated samples enriched in inertinite. X-ray diffraction (XRD), Raman spectroscopy, and transmission electron microscopy (TEM) were used to analyze the graphitization process of inertinite. ① Results of HTT: the graphitization of inertinite has a "threshold condition" with the temperature threshold ranging between 2100 °C and 2400 °C. Below this threshold, the d₀₀₂ value of the samples remains above 0.342 nm. ② Results of HTTP: (i) External forces have a significant positive effect on the graphitization of inertinite. Compared to the HTT, the addition of external forces significantly reduces the temperature required for inertinite graphitization. (ii) Proper combinations of temperature and pressure conditions are crucial for efficiently promoting the graphitization of inertinite. Changes in pressure, either increasing or decreasing from the optimal pressure, have a suppressive effect on the graphitization of inertinite. ③ The mechanism of external forces on the graphitization of inertinite was analyzed. Shear stress promotes the rotation and orientation of interlayer spacing in carbon layers.

Keywords: inertinite; coal-derived graphite; high-temperature and high-pressure simulation experiments; high-temperature thermal simulation experiments

1. Introduction

Coal-derived graphite is a product of the transformation of coal during the transition from the coalification stage to the graphitization stage [1]. It is the main component of natural cryptocrystalline graphite [2] and has gained attention from the academic community due to the demand in the graphite market [3,4]. Currently, compared to the abundant research results on the coalification stage, our understanding of the graphitization stage is relatively weak. Franklin (1951) was the first to explore the possibility of graphitizing anthracite coal [5], and Bonijoly (1982) and others discussed the mechanism of coal graphitization [6]. Various scholars have explored the controlling factors of coal-derived graphite formation from both internal factors and external conditions [7–9].

The coal maceral and minerals are internal factors that control the process of coal graphitization. Due to the strong heterogeneity of coal's composition and structure, diverse forms of graphite components are formed under geological conditions [10–12]. Inertinite is one of the main organic components in coal [13], and researchers have recognized that the structure of inertinite differs from that of other components (vitrinite and liptinite) during the coalification stage [14,15], exhibiting inertness compared to other components. Whether inertinite can undergo graphitization during the graphitization stage, its trajectory and mechanism of graphitization remain topics with limited discussion among scholars, hindering a comprehensive understanding of the formation and evolution of coalderived graphite.



Citation: Liu, Z.; Cao, D.; Chen, G.; Bi, Z.; Chen, Q. Experimental Verification for the Graphitization of Inertinite. *Minerals* **2023**, *13*, 888. https://doi.org/10.3390/ min13070888

Academic Editor: Yuri N. Palyanov

Received: 23 May 2023 Revised: 20 June 2023 Accepted: 28 June 2023 Published: 29 June 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/). Once coal enters the graphitization stage, the optical properties of its components tend to become unified, making it difficult to distinguish the original structural characteristics of coal components. Therefore, laboratory simulation experiments have become an important means to study the structural changes of coal during high-evolution stages. Temperature and tectonic stress are the main external conditions that promote coal graphitization. Simulation experiments recreate the graphitization process of coal by controlling temperature and pressure conditions. Wilks (1993) and Bustin (1995) were the first to conduct high-temperature and high-pressure simulation experiments on coal [16,17], confirming the significant role of tectonic stress in coal graphitization. The experiments used mixed samples dominated by vitrinite as the precursor, without considering the significant differences between the components of coal itself. The demanding requirements of high-temperature and high-pressure experimental conditions have led subsequent researchers to opt for low-pressure thermal simulations when studying the graphitization process of coal, abandoning the factor of stress [18–20].

Currently, there is limited research on high-temperature and high-pressure experiments focusing on a single component (e.g., inertinite). The effects and mechanisms of stress on the graphitization of inertinite are also scientific questions worthy of further exploration. In this study, component separation was performed on a sample with $R_{max} = 1.7\%$, obtaining a purified inertinite-rich sample with a purity of 92%. The graphitization process of inertinite was reproduced through high-temperature thermal simulations and high-temperature and high-pressure experiments, and an analysis of the graphitization process of inertinite was conducted, exploring the key role of "stress" in the graphitization process.

2. Samples and Methods

2.1. Samples

The coal samples (vitrinite $R_{max} = 1.7\%$) were collected from the Gemudi mining area in Guizhou province. In order to exclude the influence of the vitrinite in the coal on the experiment, the coal samples were hand-selected to obtain inertinite-enriched samples. According to the Chinese standard GB/T 15588-2013 and GB/T 8899-2013, the obtained samples were observed under a microscope, and the samples with 90% or higher inertinite purity were used as the precursor for the simulation experiment. Detailed industrial analysis and elemental analysis can be found in Table 1.

Samula -		Maceral		I	ndustrial	l Analysis	;		Elem	nental Aı	nalysis	
Sample -	Vitrinite	Inertinite	Liptinite	M _{ad}	A _d	\mathbf{V}_{daf}	FCd	$\mathbf{S}_{\mathbf{t}}$	O _{daf}	C _{daf}	H _{daf}	N _{daf}
GMI	8.4%	91.6%	0.0%	0.5%	7.3%	16.0%	81.2%	0.5%	3.2%	91.9%	3.5%	0.8%

Table 1. Basic information of the inertinite-rich sample.

M, moisture; A, ash yield; V, volatile matter; FC, fixed carbon; S_t , total sulfur; C, carbon; H, hydrogen; N, nitrogen; ad, air dry basis; d, dry basis; daf, dry and ash-free basis.

The influence of minerals on the graphitization process of microscopic components is highly complex, and the relative content of minerals in the microscopic components is difficult to control. Therefore, in this study, acid washing was performed to remove the random and uncertain effects of minerals on the coal graphitization process. The acid washing process is as follows:

- (1) The sample was crushed and sieved through a 200-mesh (75 μ m) standard sieve.
- (2) Approximately 15 g of coal powder (proportional to the increase in sample weight) was placed in a plastic beaker and mixed with 80 mL of HCl solution (36% mass fraction).
- (3) The mixture was stirred for 4 h at a constant temperature of 60 $^{\circ}$ C in a water bath.
- (4) The HCl solution was then filtered out, and 80 mL of HF solution (40%) was added to the coal sample.
- (5) The same water bath and acid washing process were repeated.

Finally, the acid-washed coal sample was washed with ultrapure water until no precipitate appeared in the filtrate, filtered using filter paper, and dried in a vacuum oven at 60 °C for 24 h to obtain the mineral-free coal sample.

Powder samples were used for HTT simulation experiments. However, HTHP simulation experiments require solid-state samples of fixed dimensions. Conventional HTHP involves drilling cylindrical samples of a certain size using hollow drill bits. However, coal samples in the high-metamorphism stage are brittle, and it is difficult to obtain enriched samples of a single component (vitrinite or inertinite). This has been a significant obstacle for previous researchers in conducting this type of experiment. In this study, a breakthrough was made by using powder compaction to prepare the required experimental samples (Figure 1). The equipment used includes tungsten carbide molds and a uniaxial hydraulic press. The samples were prepared using powder compaction, resulting in cylindrical samples with dimensions of 7 mm \times 12.5 mm and a density of 1.5 g/cm³.



Figure 1. High-temperature and high-pressure simulation experimental sample.

High-temperature thermal simulation experiments (HTT)

- (1) Take a 10 g sample and place it in a crucible, then put it into an induction furnace for graphitization.
- (2) Vacuum is applied to remove gas from graphitization furnace and then maintain an argon gas atmosphere throughout the process.
- (3) Increase the temperature with controlled ventilation. The pressure inside the furnace is maintained at 20–30 KPa above standard atmospheric pressure.
- (4) The temperature is raised from room temperature to 1000 °C at a rate of 5 °C/min. The sample is held at 1000 °C for 60 min.
- (5) The temperature ramp rate is then changed to 10 $^{\circ}$ C/min until reaching the target temperature point. The sample is held at the target temperature for 90 min.
- (6) Afterward, the furnace is allowed to naturally cool down.
- (7) The graphitization temperature range starts at 1800 °C, with intervals of 300 °C, and the maximum temperature point is set at 3000 °C. A total of five treatment temperature points are used.

High-temperature and high-pressure simulation experiment (HTHP)

A six-faced hydraulic press is used for HTHP simulation experiments [21], which can simulate temperature and pressure conditions of up to 2000 °C and 6 GPa, respectively, meeting the requirements of this study.

The determination of experimental temperature and pressure conditions refers to relevant domestic and international research. For example, Jiang conducted high-temperature and high-pressure experiments with the highest temperature and pressure conditions of 700 °C/0.6 GPa [22,23], and Professor Bustin's team conducted classic high-temperature and high-pressure experiments with the highest temperature and pressure conditions of 900 °C/1 GPa [17]. In this study, the lower limit of the experimental conditions is set at 600 °C/1 GPa, and the upper limit of temperature and pressure conditions is relaxed to 1200 °C/2 GPa. Eight sets of high-temperature and high-pressure simulation experiments are conducted under the following conditions: 600 °C/1 GPa, 600 °C/1.5 GPa, 600 °C/1.5 GPa, and

1200 °C/2 GPa. The experiment under the 1200 °C/1 GPa condition was not conducted due to equipment limitations at high temperature and low pressure.

2.2. X-ray Diffraction

The XRD instrument selection specifications are: SmartLab-9 kW, copper target, acceleration voltage 45 kV, current 200 mA, scanning range 20 from 5° to 70°, scanning rate 2°/min, X-ray wavelength 0.15418 nm. Two diffraction peaks on the XRD pattern (20 ranges of 20° to 30° and 40° to 50°) correspond to the positions of the 002 and 100 peaks in the standard graphite XRD diffraction [24].

MDI Jade 6.0 software was used to process the XRD patterns and calculate the relevant lattice parameters: interlayer spacing d_{002} , crystallite size La, and stacking height Lc, based on the Bragg equation and Scherrer formula.

2.3. Raman Spectroscopy

The experimental instrument used is the Jobin-Yvon Labram HR Evolution high-resolution micro-Raman spectrometer. The experiment measurements employed an argon ion laser as the excitation light source, with an excitation wavelength of 532 nm and laser power of 100 mW. The scanning range was from 800 cm⁻¹ to 3500 cm⁻¹, and the exposure time was 10 s.

The obtained Raman spectra were analyzed using Origin 8.0 software, utilizing Lorentzian functions for fitting and processing. The Raman spectrum exhibited two bands: the first-order Raman (700 cm⁻¹ to 2000 cm⁻¹) and the second-order Raman (2000 cm⁻¹ to 3000 cm⁻¹). The first-order Raman spectrum showed four types of defect peaks, namely D1 to D4 peaks, and an ordered graphite peak G. D1 represents in-plane defects caused by the incorporation of impurities or imperfect structure, which are difficult to eliminate during graphitization. D2 represents interstitial defects in the graphite lattice [25,26]. D3 and D4 are out-of-plane defects in the carbon layers and belong to active sites, which are released and eliminated during the early stages of graphitization [27]. The second-order Raman spectrum initially showed only two peaks, S1 and S2, in the low evolution stage. As the degree of evolution increased, the S1 peak gradually split into two peaks, and the S2 peak disappeared (Figure 2).



Figure 2. Illustration of peak assignment in Raman spectra of carbon materials.

Researchers often use the ratio $R2 = A_{D1}/(A_{(G+D1+D2)})$, where A_{D1} represents the area under the D1 peak, to characterize the degree of structural defects or the degree of order in carbon materials [28]. This parameter can effectively represent the development of graphite structure defects in carbon materials with a high degree of evolution and a single type of defect and fewer defects. However, if the sample has a lower degree of evolution, complex defect types, and a higher proportion of defects, this parameter may not adequately evaluate the development of the sample. Therefore, in addition to using the R2 parameter, this paper proposes the R3 parameter, which represents the ratio of the total area under all types of defect peaks in the first-order Raman spectrum to the total area under all peaks (R3 = $A_{(D1+D2+D3+D4)}/A_{(D1+D2+D3+D4+G)}$).

R2 is referred to as the "in-plane defect parameter" that characterizes the proportion of in-plane defects (D1) and has good evaluation significance for samples with a high degree of evolution, fewer defects, and a dominance of D1-type defects (highly evolved graphite samples), and it can be used for cross-comparison with other relevant studies. R3 is referred to as the "overall defect parameter" that represents the proportion of all types of defects and has significant physical meaning for samples with a lower degree of evolution and more defects.

2.4. Transmission Electron Microscopy

The experiments utilized the Tecnai G2 F30 field emission transmission electron microscope (TEM) with an acceleration voltage of 300 kV. The point resolution was 0.20 nm, the line resolution was 0.10 nm, and the information resolution was 0.14 nm. The magnification ranged from $3000 \times to 500,000 \times$.

The specific procedure involved grinding the sample to 300 mesh and then dispersing it in ethanol using ultrasonic treatment. The dispersed sample was then dropped onto a copper mesh. Subsequently, the sample was searched for on the holes of the copper mesh, and particles that could represent the majority of the particle characteristics within the sample were selected for multiscale observation. High-resolution images and selected area diffraction (SAD) patterns were captured during the observation process.

3. Results

3.1. X-ray Diffraction

3.1.1. Precursors

X-ray diffraction (XRD) has been widely utilized in the study of coal structure [29]. When the sample mainly consists of amorphous carbon, sharp silicon peaks can influence the shape of the carbon peaks. Therefore, silicon powder calibration is not applied to such samples. Instead, an estimation is made for the d_{002} , La, and Lc parameters (Figure 3). The estimated values are as follows: $d_{002} = 0.3494$ nm, La = 2.822 nm, and Lc = 1.529 nm.



Figure 3. XRD pattern of simulated experimental precursor (inertinite-rich sample).

3.1.2. High-Temperature Thermal Simulation Experiments (HTT)

As the processing temperature increases, the carbon peak at $2\theta = 26^{\circ}$ approaches the position of the standard graphite peak at $2\theta = 26.6^{\circ}$ (Figure 4). The peak becomes sharper, and at different processing temperatures the peak shape exhibits an asymmetry, with a steeper slope on the right. The largest change in d₀₀₂ occurs at the temperature intervals of initial state $\rightarrow 1800 \ ^{\circ}$ C and $2100 \ ^{\circ}$ C $\rightarrow 2400 \ ^{\circ}$ C. From $1800 \ ^{\circ}$ C to $2100 \ ^{\circ}$ C, d₀₀₂ remains relatively stable with minimal changes (Table 2).



Figure 4. XRD pattern for the products of HTT simulation experiments.

Table 2. XRD lattice parameter calculations for the products of HTT simulation experiments.

Processing Temperature	2θ ₀₀₂ /°	Lc/nm	La/nm	d ₀₀₂ /nm
1800 °C	25.93	3.18	10.76	0.3433
2100 °C	25.92	3.43	12.06	0.3434
2400 °C	26.21	7.57	17.88	0.3398
2700 °C	26.25	9.12	17.98	0.3393
3000 °C	26.29	17.99	19.84	0.3387

3.1.3. High-Temperature and High-Pressure Simulation Experiments (HTHP)

Under the condition of 600 °C, the peaks around $2\theta = 26^{\circ}$ exhibit a broad and flat shape (opposite to sharp peak shape). At 900 °C, the full width at half maximum (FWHM) of the peaks near $2\theta = 26^{\circ}$ significantly decreases. Under the condition of 1200 °C, the (002) peak becomes sharp and symmetrical, indicating the formation of perfect graphite crystals (Figure 5).



Figure 5. XRD pattern for the products of HTHP simulation experiment.

Using d_{002} as a measure of graphitization degree, the involvement of "force" significantly reduces the initiation temperature of sample graphitization. With the assistance of force, under the condition of 1200 °C, the graphitization degree of the inertinite exceeds

that of the 3000 °C high-temperature simulated experiment (Table 3). Compared to the corresponding samples in the high-temperature simulated experiment, the symmetry of the peaks around $2\theta = 26^{\circ}$ is higher, indicating a more uniform evolution of the HTHP experimental samples.

Processing Temperature /°C	Processing Pressure/Gpa	$2\theta_{002}/^{\circ}$	Lc/nm	La/nm	d ₀₀₂ /nm
	1.0	25.499	1.62	3.95	0.3490
600	1.5	25.405	1.88	1.60	0.3503
	2.0	25.483	1.43	2.70	0.3494
	1.0	26.000	2.72	9.74	0.3424
900	1.5	26.157	3.11	10.57	0.3404
	2.0	25.932	2.30	6.23	0.3433
1200	1.5	26.330	17.68	60.79	0.3382
1200	2.0	26.421	20.73	42.33	0.3371

Table 3. XRD lattice parameter calculations for the products of HTHP simulation experiment.

3.2. Raman Spectroscopy

3.2.1. Precursors

The Raman spectrum of the inertinite-rich precursor (Figure 6) indicates the presence of various types of defects. The predominant defects are of D1 and D2 types, while the presence of D3 and D4 defects suggests the presence of reactive structures such as fatty structures or polyene structures [30]. The secondary Raman spectrum does not show any splitting of the S1 peak, indicating the absence of a three-dimensional structure. Peak fitting analysis yields the following values: R2 = 0.65 and R3 = 0.83.



Figure 6. Raman spectrum of the simulated precursor (inertinite-rich sample).

3.2.2. High-Temperature Thermal Simulation (HTT)

With increasing treatment temperature, the G peak representing the ordered graphite structure gradually intensifies and shifts towards 1580 cm⁻¹, while the intensity of the D peaks representing the disordered structure weakens. Among the defect peaks, the D1 peak is predominantly present, and even in samples with high degrees of graphitization, the D2 peak does not completely disappear. However, other heteroatom-related defect peaks, D3 and D4, disappear completely under high-temperature treatment conditions (Figure 7). Beyond 1800 °C, the D3 defect peak is almost undeveloped (except for a few samples that exhibit weak D4 defect peaks), and beyond 2400 °C, the D4 peak is no longer present.



Figure 7. Raman spectrum for the products of HTT simulation experiments.

As the treatment temperature increases, in the second-order Raman spectrum, the S1 peak gradually splits into S1' and S1'' peaks, while the S2 peak gradually disappears, indicating the progressive formation of a three-dimensional structure.

Quantitative evaluation and comparison of the defect development degree in the products of HTT simulation experiments are performed using the R2 and R3 parameters (Table 4). With increasing treatment temperature, the defect degree (R2 and R3) significantly decreases, but even at a treatment temperature of 3000 °C, it is difficult to reduce the defect degree below 0.1.

Table 4. Raman parameter values for the products of HTT simulation experiments.

Processing Temperature/°C	1800	2100	2400	2700	3000
R2	0.592	0.509	0.409	0.277	0.189
R3	0.658	0.587	0.473	0.291	0.205

3.2.3. High-Temperature and High-Pressure Simulation Experiments (HTHP)

In the HTHP simulation experiment, compared to the high-temperature-treated samples, the HTHP samples exhibit higher defect density under similar d_{002} conditions (Figure 8; Table 5).



Figure 8. Raman spectrum for the products of HTHP simulation experiments.

Processing Temperature/°C	600			900			1200	
Processing pressure/Gpa	1.0	1.5	2.0	1.0	1.5	2.0	1.5	2.0
R2	0.712	0.692	0.689	0.745	0.763	0.760	0.472	0.527
R3	0.867	0.871	0.854	0.826	0.849	0.845	0.541	0.642

Table 5. Raman parameter values for the products of HTHP simulation experiments.

In the HTHP experiment, a clear secondary Raman peak representing the development of a three-dimensional ordered structure is observed only at temperatures above 900 °C. Under the temperature condition of 600 °C, regardless of the variation in pressure, the overall changes in the peak shape of the D and G peaks are minimal.

Similar to the HTT simulation experiments, the Raman characterization parameters of the HTHP samples were calculated (Table 5). We can observe that the HTHP samples exhibit some differences compared to the HTT samples. Under the 600 °C condition, the R2 value of the samples is lower than that of the 900 °C samples. This anomalous phenomenon is caused by the relatively higher proportion of D3 and D4 type defects in the 600 °C samples, resulting in a lower relative proportion of D1 defects, which leads to an abnormal value of the in-plane defect parameter R2.

3.3. Transmission Electron Microscopy

3.3.1. Precursors

TEM reveals that the basic structural units (BSUs) in the large molecular structure of the precursor are small in size and arranged in a disordered manner (Figure 9a). The Selected Area Diffraction (SAD) pattern exhibits an amorphous diffraction ring (Figure 9b).



Figure 9. TEM characteristics of the simulated precursor. (**a**) Aromatic fringe morphology of samples with high magnification, (**b**) The selected area diffraction (SAD) pattern.

3.3.2. High-Temperature Thermal Treatment (HTT)

Transmission electron microscopy (TEM) observations of the products at different processing temperatures reveal a gradual increase in lattice expansion and stacking degree (Figure 10a–e). However, the morphology images show that the graphite lattice development direction varies, resulting in polycrystalline graphite (Figure 10c,d). The Selected Area Diffraction (SAD) pattern consists of concentric diffraction rings with different radii, indicating that the measured sample exhibits a polycrystalline structure (Figure 10f).



Figure 10. TEM characteristics for the products of HTT simulation experiment. (**a**–**e**) Aromatic fringe morphology of sample GMI treated at different temperatures, (**f**) The selected area diffraction (SAD) pattern of sample GMI treated at 3000 $^{\circ}$ C.

3.3.3. High-Temperature and High-Pressure Simulation Experiment (HTHP)

At 900 °C, under a pressure of 1.5 GPa/2 GPa, the formation of graphite structure begins, with carbon layers stacking to about five layers and an extended length of up to 10 nm (Figure 11a,b). Under the condition of 900 °C/2 GPa, an onion-ring concentric microtexture is formed, which is a transitional product of large-sized flat graphite structure (Figure 11b).

At 1200 °C, under the combination of 1.5 GPa/2 GPa, graphite flakes are formed (Figure 11c–e), but the graphite exhibits distinct "rough in-plane, flat interlayer" structural features (Figure 11e). At the same time, it can be observed that the stacking of carbon layers in the high-temperature high-pressure product is relatively low, generally concentrated within 10 layers, but with a significant extension and smooth stacking. The in-plane development is rough, indicating a high degree of defects. The SAD pattern shows a regular arrangement of diffraction spots, indicating that the product is mainly single crystal (Figure 11f).



Figure 11. TEM features for the products of HTHP simulation experiments. (**a**,**b**) Aromatic fringe morphology of 900 °C–1.5 Gpa–GMI and 900 °C–2 Gpa–GMI with high magnification, (**c**) Aromatic fringe morphology of 1200 °C–1.5 Gpa–GMI with low magnification, (**d**) Aromatic fringe morphology of 1200 °C–1.5 Gpa–GMI with high magnification, (**e**) Aromatic fringe morphology of 1200 °C–2 Gpa–GMI with high magnification, (**f**) The selected area diffraction (SAD) pattern of 1200 °C–2 Gpa–GMI.

4. Discussion

4.1. Threshold Conditions for Graphitization of Inertinite

The evolution of a graphite lattice involves two aspects: the construction of a threedimensional lattice and the elimination of lattice defects. High-temperature thermal simulation experiments show that the inertinite exhibits a "inert" state between processing temperatures of 1800 °C and 2100 °C (where d₀₀₂ remains above 0.3420 nm in a disordered state). Once the processing temperature exceeds 2100 °C, the inertinite undergoes a significant change. There exists a graphitization threshold (Critical Temperature) for the inertinite between 2100 °C and 2400 °C where only temperatures above this threshold can achieve rapid graphitization, and the d₀₀₂ value decreases to around 0.3380 nm. From 2400 °C to 3000 °C, the rate of decrease in d₀₀₂ slows down again, approaching the standard graphite lattice value of 0.3354 nm (Figure 12a).





As the processing temperature increases, the defects in the graphite lattice are uniformly eliminated, and the temperature plays an absolute control role in defect elimination. The high-temperature thermal vibration promotes the elimination of defects. At higher processing temperatures, due to the disappearance of D3 and D4 defects, the "in-plane defect parameter" R2 is almost identical to the "total defect parameter" R3 (Figure 12b).

4.2. Catalytic Effect of Structural Stress on Graphitization

In HTHP simulation experiments, the inertinite showed no significant change in d_{002} under all pressure conditions at 600 °C. Only at 900 °C did the d_{002} of the inertinite decrease significantly. Among the different pressure conditions at 900 °C, the product obtained under 900 °C/1.5 GPa exhibited the smallest d_{002} value, falling below 0.3420 nm (the starting point of carbon material graphitization proposed by Oberlin et al., (1984)) [31]. This indicates that the synergistic combination of suitable pressures is required for the manifestation of the temperature effect, as excessively high or low pressure is unfavorable for structural development (Figure 13).



Figure 13. Evolution of structural parameters during the graphitization process of the inertinite.

By comparing HTHP simulation experiments with HTT simulation experiments, the importance of force in the graphitization process is demonstrated. Compared to the pure high-temperature treatment at 3000 °C in the HTT simulation experiments, the sample obtained at 1200 °C/1.5 GPa has a smaller d_{002} value (Table 6).

Experimental Conditions		Samula ID	XRD Parameters			Raman		
Temperature/°C	Ressure/Gpa	Sample ID	d ₀₀₂ /nm	Lc/nm	La/nm	R1	R2	R3
1800 3000	Atmospheric	1800 °C–GMI 3000 °C–GMI	0.3433 0.3387	3.18 17.99	10.76 19.84	1.52 0.13	0.589 0.19	0.663 0.21
1200	1.5	1200 °C-1.5 GPa-GMI-7	0.3382	17.68	60.79	0.6	0.47	0.54

Table 6. Comparison of structural parameters between HTT and HTHP samples.

The role of stress is mainly to promote the stacking of carbon layers in the threedimensional direction and the growth in the two-dimensional direction, while its effect on the elimination of in-plane defects is relatively small. The graphite structure formed under high temperature and high pressure conditions (1.5 GPa, 1200 °C) exhibits a better threedimensional lattice structure (d_{002} , La, Lc) compared to the samples simulated under high temperature (3000 °C). However, its defect level is higher than that of the high-temperature simulation (3000 °C) samples (with higher D peak) but lower than that of the pure hightemperature-treated samples at 1800 °C (Table 6). This indicates that the involvement of stress can indeed reduce the defect level of the samples, but its effect is relatively weak. TEM observations also reveal that the products of HTHP consist of flat graphite layers with significant surface defects (Figure 11d).

4.3. The Mechanism of Stress in the Graphitization Process

In this experiment, hydrostatic pressure was applied, meaning that the sample experienced the same force in all directions. If the sample is highly symmetrical, then any point inside experiences isotropic hydrostatic pressure. However, it should be noted that coal has various types of well-developed pore structures, which inherently exhibit high asymmetry and non-uniformity [32]. In this HTHP experiment, the sample was formed by powder compaction, which also resulted in the formation of numerous pores of different sizes within the sample.

In the HTHP experiment, the introduction of external forces disrupts the arching effect and causes relative movement between particles, resulting in different stress states [33,34] (Figure 14). Although the sample as a whole is subjected to hydrostatic pressure, there still exist differential stresses within the internal structure, and any contact point in the sample may have shear effects [35,36]. The internal structure of the sample responds to external forces by migration or reconstruction in order to release and eliminate shear stress, and this effect of stress can even occur at the nanoscale level [37].



Figure 14. Depicts the displacement of powder particles under compressed conditions in the sample [38]. (a) illustrates the formation of arching effect among powder particles, (b) represents the displacement modes of powder particles.

Static hydrostatic pressure and shear stress play different roles in the construction of a graphite structure. Shear stress promotes the rotation and orientation of aromatic layers. Static hydrostatic pressure has a positive effect on the contraction and reduction of interlayer spacing in carbon layers (Figure 15).



Figure 15. Illustrates the influence of force on the orientation arrangement of aromatic layers and the reduction of interlayer spacing. (**A**) Shear force promotes the rotation and orientation of aromatic layers, (**B**) Pressure has a positive effect on the contraction and reduction of interlayer spacing in carbon layers.

It is important to note that the overall effect of applying hydrostatic pressure to the sample is weaker than the effects of axial compression and shear stress. As the asymmetry of the applied force increases, the differences in the effects of these three forces become smaller. In the case of a perfectly symmetrical object, where the force directions at any point within the sample are isotropic with no differential stress, static hydrostatic pressure will not have any positive effect.

5. Conclusions

- (1) Through HTT and HTHP simulation experiments, it has been demonstrated that the inertinite in coal can undergo graphitization, but there exists a structural transformation threshold. In the HTT simulation experiments, the inertinite remains in an "inert" state (with d_{002} stagnant before reaching 0.3420 nm) within the temperature range of 1800 °C to 2100 °C. However, beyond 2100 °C, the inertinite undergoes transformation.
- (2) The HTHP experiments indicate that at a temperature of 600 °C, the variation in pressure does not lead to any significant structural changes. However, at 900 °C/ 1.5 GPa, the d₀₀₂ value decreases to below 0.3420 nm. There exists an optimal pressure for the development of the graphite lattice.
- (3) Force has a significant promoting effect on the construction of the three-dimensional lattice, while its impact on the elimination of lattice defects is relatively minor. Compared to the high-temperature treatment at 3000 °C (atmospheric pressure), the sample obtained at 1200 °C/1.5 GPa exhibits a smaller d₀₀₂ value but a higher degree of defects (as indicated by the higher D peaks), albeit lower than that of the pure high-temperature treatment at 1800 °C.
- (4) A potential mechanism by which force promotes graphitization is analyzed and summarized. It involves the internal structure of the sample responding to external forces through different modes (migration or reconstruction) to release and eliminate shear and pressure effects, thereby promoting the rotation and orientation of aromatic layers and reducing the interlayer spacing (d₀₀₂).

Author Contributions: Conceptualization, Z.L.; methodology, Z.L.; software, Q.C.; formal analysis, Z.L.; investigation, Q.C.; resources, D.C. and Z.B.; data curation, G.C.; writing—original draft preparation, Z.L. and G.C.; writing—review and editing, Z.L.; supervision, D.C. and Z.B.; funding acquisition, D.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by The National Natural Science Foundation of China (42072197, 41772156), and Special project of Science and Technology Innovation and Entrepreneurship Fund of China Coal Science and Industry Group Co., LTD (2019-ZD004).

Data Availability Statement: All relevant data are within the paper.

Acknowledgments: The National Natural Science Foundation of China (42072197, 41772156) financially support this research.

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

References

- 1. Marqués, M.; Suárez-Ruiz, I.; Flores, D.; Guedes, A.; Rodrigues, S. Correlation between optical, chemical and micro-structural parameters of high-rank coals and graphite. *Int. J. Coal Geol.* **2009**, *77*, 377–382. [CrossRef]
- Cao, D.; Zhang, H.; Dong, Y.; Yang, C. Nanoscale Microscopic Features and Evolution Sequence of Coal-Based Graphite. J. Nanosci. Nanotechnol. 2017, 17, 6276–6283. [CrossRef]
- 3. Rao, J.; Zhang, P.; He, S.; Li, Z.; Ma, H.; Shen, Z.; Miao, S. A review on the utilization of natural graphite and graphite-based materials. *Sci. Sin. Technol.* **2017**, *47*, 13–31. [CrossRef]
- 4. Cao, D.Y.; Zhang, H.; Dong, Y.J.; Wu, G.; Ning, S.; Mo, J.; Li, X. Research status and key directions of geological study on coal-based graphite. *Earth Sci. Front.* **2017**, *24*, 317–327. (In Chinese)
- 5. Franklin, R.E. The structure of graphitic carbon. *Acta Crystallogr.* **1951**, *4*, 253–261. [CrossRef]
- 6. Bonijoly, M.; Oberlin, M.; Oberlin, A. A possible mechanism for natural graphite formation. *Int. J. Coal Geol.* **1982**, *1*, 283–312. [CrossRef]
- 7. Wang, L.; Dong, Y.J.; Zhang, H.; Cao, D.Y. Factors influencing coal graphitization and their experimental verification. *J. Mineral. Sci.* **2018**, *3*, 9–19. (In Chinese)
- 8. Nyathi, M.S.; Clifford, C.B.; Schobert, H.H. Characterization of graphitic materials prepared from different rank Pennsylvania anthracites. *Fuel* **2013**, *114*, 244–250. [CrossRef]
- 9. Beyssac, O.; Rouzaud, J.N.; Goffe, B.; Brunet, F.; Chopin, C. Graphitization in a high-pressure, low-temperature metamorphic gradient: A Raman microspectroscopy and HRTEM study. *Contrib. Mineral. Petrol.* **2002**, *143*, 19–31. [CrossRef]
- 10. Diessel, C.F.K.; Brothers, R.N.; Black, P.M. Coalification and graphitization in high-pressure schists in New Caledonia. *Contrib. Mineral. Petrol.* **1978**, *68*, 63–78. [CrossRef]
- 11. Rodrigues, S.; Suárez-Ruiz, I.; Marques, M.; Flores, D. Catalytic role of mineral matter in structural transformation of anthracites during high temperature treatment. *Int. J. Coal Geol.* **2012**, *93*, 49–55. [CrossRef]
- 12. Li, J.; Qin, Y.; Chen, Y.; Luo, Q.; Deng, R.; Guo, S.; Chen, Q. Differential graphitization of organic matter in coal: Some new understandings from reflectance evolution of meta-anthracite macerals. *Int. J. Coal Geol.* **2021**, 240, 103747. [CrossRef]
- 13. Dai, S.F.; Bechtel, A.; Eble, C.F.; Flores, R.M.; French, D.; Graham, I.T.; Madison, M.; Hood, M.M.; Hower, J.C.; Korasidis, V.A.; et al. Recognition of peat depositional environments in coal: A review. *Int. J. Coal Geol.* **2020**, *219*, 103383. [CrossRef]
- 14. Niekerk, D.V.; Jonathan, P.; Mathews, J.P. Molecular representations of Permian-aged vitrinite-rich and inertinite-rich South African coals. *Fuel* **2010**, *89*, 73–82. [CrossRef]
- 15. Li, J.; Feng, J.; Wen-Ying, L.I. Thermochemical Reaction Representation of Shenfu Dongshen Inertinite and Vitrinite. *Acta Phys. Chim. Sin.* 2009, 25, 1311–1319.
- 16. Wilks, K.R.; Mastalerz, M.; Ross, J.V.; Bustin, R.M. The effect of experimental deformation on the graphitization of Pennsylvania anthracite. *Int. J. Coal Geol.* **1993**, *24*, 347–369. [CrossRef]
- 17. Bustin, R.M.; Ross, J.V.; Rouzaud, J.N. Mechanisms of graphite formation from kerogen: Experimental evidence. *Int. J. Coal Geol.* **1995**, *28*, 1–36. [CrossRef]
- 18. Pappano, P.J. A Mechanism of Pennsylvania Anthracite Graphitization Involving Carbide Formation and Decomposition; The Pennsylvania State University: State College, PA, USA, 2003.
- 19. Atria, J.V.; Rusinko, F.; Schobert, H.H. Structural Ordering of Pennsylvania Anthracites on Heat Treatment to 2000–2900 °C. *Energy Fuels* **2002**, *16*, 1343–1347. [CrossRef]
- 20. Pappano, P.J.; Schobert, H.H. Effect of Natural Mineral Inclusions on the Graphitizability of a Pennsylvania Anthracite. *Energy Fuels* **2009**, *23*, 422–428. [CrossRef]
- 21. He, Q.; Tang, J.J.; Wang, F.; Liu, X. An assembly of six-face top-pressure machines suitable for extreme high-temperature conditions. *Chin. J. High Press. Phys.* 2014, *28*, 145–151. (In Chinese)
- 22. Jiang, B.; Qin, Y. Experimental study on coal deformation under high temperature and high pressure. *J. China Coal Soc.* **1997**, *22*, 82–86. (In Chinese)

- 23. Jiang, B.; Qin, Y.; Jin, F.L. Deformation characteristics of coal macerals under high temperature and high pressure. *Geol. Sci.* **1998**, 21, 17–24. (In Chinese)
- 24. Zhao, F.H. Composition and Structure of Coal—Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD) Study on Coal Structure; China University of Mining and Technology: Beijing, China, 1994. (In Chinese)
- 25. Beny-Bassez, C.; Rouzaud, J.N. Characterization of carbonaceous materials by correlated electron and optical microscopy and Raman microspectroscopy. *Scanning Electron Microsc.* **1985**, 1985, 119–132.
- Beyssac, O.; Goffé, B.; Chopin, C.; Rouzaud, J.N. Raman spectra of carbonaceous material in metasediments: A new geothermometer. J. Metamorph. Geol. 2002, 20, 859–871. [CrossRef]
- Beyssac, O.; Goffé, B.; Petitet, J.P.; Froigneux, E.; Moreau, M.; Rouzaud, J.N. On the characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 2003, *59*, 2267–2276. [CrossRef]
- 28. Rantitsch, G.; Lämmerer, W.; Fisslthaler, E.; Mitsche, S.; Kaltenböck, H. On the discrimination of semi-graphite and graphite by Raman spectroscopy. *Int. J. Coal Geol.* 2016, 159, 48–56. [CrossRef]
- 29. Harris, L. Quantitative X-ray diffraction analysis and its application to various coals. Carbon 2001, 39, 1821–1833.
- 30. Su, X.B.; Si, Q.; Song, J.X. Raman spectroscopic characteristics of coal. J. China Coal Soc. 2016, 41, 1197–1202. (In Chinese)
- 31. Oberlin, A. Carbonization and graphitization. Carbon 1984, 22, 521–541. [CrossRef]
- 32. Zhou, H. Study on Microcrystal Structure and Pore Structure Characteristics of Organic Microscopic Components in Coal; Henan Polytechnic University: Zhengzhou, China, 2018. (In Chinese)
- 33. Chen, Y.X.; Du, J.G.; Liu, H. Distribution of boundary stress of mineral particles under high temperature and high static pressure. *J. Cent. South Univ.* **2010**, *41*, 286–292. (In Chinese)
- 34. Ciz, R.; Siggins, A.F.; Gurevich, B.; Dvorkin, J. Influence of microheterogeneity on effective stress law for elastic properties of rocks. *Geophysics* 2007, 73, 7–14. [CrossRef]
- 35. Liu, L.M.; Wu, Y.Z. Chemical behavior of crystalline minerals under shear stress and its geological significance. *Geol. Explor.* **1996**, *31*, 26–31. (In Chinese)
- Feng, Z.C.; Zhao, D.; Wang, J.F. Stress distribution characteristics of rocks under static water pressure. In Proceedings of the 11th National Conference on Rock Mechanics and Engineering, Wuhan, China, 19–21 November 2011; Chinese Society for Rock Mechanics and Engineering: Beijing, China, 2011. (In Chinese).
- 37. Sun, J. In-Situ Transmission Electron Microscopy Study on Structural Evolution of Materials under External Fields; Southeast University: Nanjing, China, 2016. (In Chinese)
- 38. Wang, M.B. Study on Powder Compaction; Jilin University: Changchun, China, 2007. (In Chinese)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.


Article



Preparation and Characterization of Asphalt Pitch-Derived Activated Carbons with Enhanced Electrochemical Performance as EDLC Electrode Materials

Ju-Hwan Kim^{1,2}, Young-Jun Kim^{1,3}, Seok-Chang Kang⁴, Hye-Min Lee^{1,*} and Byung-Joo Kim^{5,*}

- ¹ R&BD Group 1, Industrialization Division, Korea Carbon Industry Promotion Agency, Jeonju 54853, Republic of Korea; bear9601@kcarbon.or.kr (J.-H.K.)
- ² Department of Polymer Engineering, Chonnam National University, Gwangju 611186, Republic of Korea

³ Department of Carbon Materials and Fiber Engineering, Chonbuk National University, Jeonju 54896, Republic of Korea

- ⁴ Chemical & Process Technology Division, Korea Research Institute of Chemical Technology (KRICT), Daejeon 34114, Republic of Korea; sckang@krict.re.kr
- ⁵ Department of Advanced Materials and Chemical Engineering, Jeonju University, Jeonju 55069, Republic of Korea
- * Correspondence: leehm@kcarbon.or.kr (H.-M.L.); kimbyungjoo@jj.ac.kr (B.-J.K.)

Abstract: This study used a physical activation method to prepare asphalt-pitch-derived activated carbon (Pitch AC) for an electric double-layer capacitor (EDLC) electrode. X-ray diffraction analysis and Raman spectroscopy were used to estimate the change in the crystal structure of Pitch AC with activation time. In addition, the textural properties of Pitch AC were studied by Brunauer-Emmett-Teller (BET), Dubinin-Radushkevich (DR) and non-localized density functional theory (NLDFT) equations with N2/77K isotherm adsorption-desorption curves. The electrochemical performance of the Pitch AC was analyzed using a coin-type EDLC with 1 M SBPBF₄/PC via galvanostatic charge/discharge, cyclic voltammetry and electrochemical impedance spectroscopy. The specific surface area and total pore volume were 990–2040 m^2/g and 0.42–1.51 cm³/g, respectively. The pore characteristics of the Pitch AC varied according to the activation time and changed from a microporous structure to a micro-mesoporous structure as the activation time increased. The electrochemical performance analysis also found that the specific capacity was increased from 43.6 F/g to 84.5 F/g at 0.1 A/g as activation time increased. In particular, Pitch AC-9 exhibited the best electrochemical performance (rectangular CV curve, reversible GCD, lowest ion charge transfer resistance and Warburg impedance). In addition, Pitch AC-9 was confirmed to have a specific capacitance similar to commercial activated carbon for EDLC (YP-50F). Therefore, it was considered that Pitch AC could replace commercial activated carbon for EDLC because it has excellent pore characteristics and electrochemical performance despite being manufactured through a very low-cost precursor and a simple process (physical activation method).

Keywords: asphalt pitch; activated carbon; physical activation; pore characteristics; EDLC

1. Introduction

Electric double-layer capacitors (EDLC) have an energy storage mechanism involving a surface charge adsorption reaction (non-Faradic process) and have been the most attention-grabbing energy storage devices in recent years, along with Li-ion batteries [1–3]. EDLCs have been primarily used in portable electronics and power backup applications (Uninterruptible Power) owing to their high output characteristics [4]. However, in recent years, the demand for and importance of EDLCs has increased because of the rapid development of industries that require high-power-density characteristics, such as robotics [5,6], renewable energy [7,8] and eco-friendly automobiles [9,10].



Citation: Kim, J.-H.; Kim, Y.-J.; Kang, S.-C.; Lee, H.-M.; Kim, B.-J. Preparation and Characterization of Asphalt Pitch-Derived Activated Carbons with Enhanced Electrochemical Performance as EDLC Electrode Materials. *Minerals* 2023, *13*, 802. https://doi.org/ 10.3390/min13060802

Academic Editors: Qinfu Liu, Kuo Li and Shuai Zhang

Received: 30 April 2023 Revised: 5 June 2023 Accepted: 7 June 2023 Published: 12 June 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/). The active electrode material for EDLC requires a high specific surface area and good electrical conductivity to store large amounts of ions; therefore, activated carbon is commonly used [11,12]. Currently, activated carbon for EDLC is manufactured by the steam activation method using a coconut-shell precursor for high energy density. In addition, coconut-derived activated carbon has microporous characteristics and is easy to process owing to its high hardness; therefore, it is used in various industries, such as water purification [13,14] and air filtration (including VOC abatement) [15,16]. Recently, as environmental pollution has accelerated, the demand for health-improving products, such as air and water purifiers, has increased; thus, the demand for coconut-derived activated carbon is also increasing. However, coconut shells are only produced in subtropical climates with high levels of sunlight. As a result, there is a shortage of activated carbon, which is increasing in use.

In the past, research on activated carbon has focused on developing biomass-derived activated carbon to replace coconut shell-derived activated carbon. As a result, various biomass precursors, such as husks [17], bamboo [18], kenaf [19], wood tar [20] and chitin [21], have been manufactured as activated carbon for EDLC [22,23]. However, most biomass precursors have the disadvantages of a limited growth rate and limited growing area. In addition, biomass requires an extra stabilization process in order to develop the cellulose structure into a carbon crystal structure [18,19], and it has a high ash content [24].

Asphalt pitch is a by-product of the petroleum industry and has a high carbonization yield owing to its low ash content and developed polycrystalline (aromatic) structure [25]. In particular, asphalt pitch is a by-product of the petroleum industry, so the precursor price is very low. Furthermore, unlike biomass, it is less affected by climate or the environment, so it provides a stable and smooth supply as an activated carbon precursor.

Production of activated carbon is divided into physical and chemical activation methods [26–28]. Generally, pitch has a more developed crystalline structure than biomass because of its polycrystalline structure. Therefore, pitch-derived activated carbon is prepared using chemical activation methods to destroy sp2 hybridized carbon bonds and develop them into pores [29]. The chemical activation method can convert highly crystalline precursors into activated carbon with a high specific surface area, owing to its higher activation energy than the physical activation method. However, activated carbon production costs increase because of chemical activation agents (KOH, H₃PO₄, ZnCl₂, among others). In addition, chemical activation presents challenges, such as equipment corrosion and wastewater generation, making it difficult to apply it in industry. In other words, even if activated carbon is manufactured from low priced asphalt pitch by the chemical activation method, it would be uneconomical and difficult to apply in industry. Therefore, research is needed to prepare activated carbon for EDLC through physical activation using asphalt pitch to achieve high economic efficiency.

This study prepared asphalt-pitch-derived activated carbon (Pitch AC) with excellent pore characteristics to replace commercial coconut-shell-derived activated carbon (YP-50F) in EDLC. Asphalt pitch, a by-product of the oil refining industry, was selected as the activated carbon precursor because of its low precursor price. In addition, the steam activation method was selected as the activation method for manufacturing Pitch AC with high economic efficiency and excellent pore characteristics. Finally, the electrochemical performance of the pitch AC was evaluated based on its pore characteristics after manufacturing a CR2032 type EDLC with a 1 M SBPBF₄/PC electrolyte.

2. Materials and Methods

2.1. Sample Preparation

The Korea Petroleum Industries Company provided asphalt pitch manufactured from vacuum residue, which was used as a precursor for activated carbon in this study. The asphalt pitch was crushed to a particle size of less than 250 μ m. Then, it was placed in an alumina boat and stabilized in a custom-made cylindrical tubular furnace (SIC heater: 80 \times 800 mm). The asphalt pitch was heated to 270 °C at a 0.2 °C/min rate under air

atmosphere and held at stabilization temperature for 2 h. After stabilization, the gas flow was switched to an N₂ atmosphere (99.999%), and the stabilized asphalt pitch was carbonized for 1 h after heating up to 700 °C at a 10.0 °C /min rate. The stabilization and carbonization yields of the asphalt pitch were 102% and 67%, respectively.

Carbonized asphalt pitch (3 g) was placed in an alumina boat and inserted into a self-made cylindrical tubular furnace (SIC heater, 120×670 mm). Then, it was heated to 900 °C under an N₂ atmosphere at a rate of 10.0 °C /min. After reaching the activation temperature, the gas flow was switched to steam (flow rate of 0.5 mL/min) and activated for 60–120 min. The sample names of the asphalt pitch-derived activated carbon were labeled based on the regulation of the Pitch-activated carbon activation time (Pitch AC-6, 7, 8, 9 and 12). In addition, pitch AC was compared with commercial steam-activated coconut shell-based activated carbon (YP-50F, Kuraray Chemical Corporation, Tokyo, Japan).

2.2. Characterization

The change in the nanocrystal structure of the Pitch AC was analyzed by X-ray diffraction (XRD) spectroscopy (MiniFlex 600, Rigaku, Japan) and Raman spectroscopy (Raman spectroscope, HEDA, NOST, KOREA). The XRD curve was measured using CuK α (1.5406 Å) in the 10–60° range at 2°/min. To observe the change in the crystal structure of the Pitch AC, according to the activation time, the XRD curve was fitted through Gaussian calculations, and the central diffraction angle and full width at half maximum (FWHM) of each crystalline peak were calculated. In addition, the interplanar distances (d₀₀₂ and d_{10l}) of the Pitch AC were calculated using the Bragg equation (Equation (1)). Furthermore, crystal size (La) and crystal height (Lc) were calculated from the XRD pattern using the Scherrer equation (Equation (2)) [30].

$$d(\text{\AA}) = \frac{\lambda}{2\sin\theta} \tag{1}$$

$$L(\text{\AA}) = \frac{K\lambda}{B\cos\theta}$$
(2)

where λ indicates the wavelength of the applied X-ray (1.5406 Å), B indicates the FWHM, θ indicates the center diffraction angles and *K* indicates the constant lattice Lc (0.91) and La (1.84). Raman spectrum was measured using green raiser wavelength (532 nm) and ×100 magnification in the 800–2000 cm⁻¹ range. The Raman spectra were normalized based on the G peak and then fitted using Gaussian calculations to four peaks (G1, G2, D1 and D2) with an r-squared value of 0.999 or greater [31].

Textural properties of Pitch AC were measured after 12 h of drying at 300 °C under 0.133 Pa residual pressure using an isotherm gas adsorption analyzer (BELSORP-max, BEL Japan, Osaka, Japan). The specific surface area was calculated from the isotherm adsorption-desorption curves using the Brunauer-Emmett-Teller (BET) equation [32]. The micropore volume was calculated using the Dubinin-Radushkevich (DR) equation [33]. Moreover, pore size distribution (PSD) was calculated using the non-localized density functional theory (NLDFT) [34].

The morphologies and chemical composition of the Pitch AC were observed by fieldemission scanning electron microscopy (FE-SEM, ZEISS sigma500, ZEISS, Jena, Germany) and energy dispersive X-ray spectrometer (EDX, XFlash 6-60, BRUKER, Billerica, MA, USA), respectively. Before imaging their surfaces, the prepared Pitch AC and YP-50F were coated with platinum to minimize the charging effects that occur during SEM analysis. The SEM-EDX analysis was performed under the conditions of 5.0×10^{-5} Pa of pressure and 5 kV of accelerating voltage.

2.3. Electrochemical Tests

The EDLC electrode was manufactured as a slurry that included activated carbon (85 wt%), a binder (7.5 wt%) and a conductive material (7.5 wt%). The binders used

were carboxymethylcellulose (CMC; Dai-Inci Kogyo Seiyaku Co., Ltd., Kyoto, Japan), styrene-butadiene rubber (SBR; BM400B; Zeon, Japan) and polytetrafluoroethylene (PTFE; 9002-84-0; Sigma Aldrich, St. Louis, MO, USA). In addition, carbon black (Super P, Timcal Ltd., Bodio, Switzerland) was used as the conductive material.

The slurry, consisting of activated carbon, a conductive agent and a binder, was coated on an aluminum foil to a thickness of 0.152 mm using a laboratory-scale doctor blade coater. The coated electrode was dried at 100 °C for 24 h and then pressed using a heat-roll press until the electrode thickness was 0.13 mm (about 85% of the coating thickness). For the EDLC, a punched electrode (12 mm in diameter), 1 M spirobipyrrolidinium tetrafluoroborate (SBPBF₄) in propylene carbonate (PC) and a cellulose-based separator (NKK, Kawasaki, Japan) were assembled according to the CR2032 standard.

The electrochemical performance of EDLCs were tested in symmetrical two-electrode systems with 1M SBPBF₄/PC. The galvanostatic charge-discharge (GCD) test was performed using a MACCOR 4300 battery tester (Maccor Inc., Tulsa, OK, USA). The cycle voltammetry (CV) and impedance measurements were performed using a VSP electrochemical workstation (Bio-Logic Science Instruments, Grenoble, France). The GCD was measured with a current density of 0.1-10.0 A/g at a voltage between 0.1-2.5 V. CV was measured at a scan rate of 5–400 mV and a 0.1-2.5 V voltage range, and the impedance was measured within the 10–300 MHz frequency range. The test was performed 10 times to ensure the reliability of the analysis, and the 10th dataset was used. The specific capacitance (F/g) of the symmetric electrodes was calculated using Equation (3), the discharge curve of the GCD.

$$C_g = \frac{2i\Delta t}{m\Delta v} \tag{3}$$

where *i* indicates discharge current (A), Δt indicates discharge time (s), *m* indicates an electrode mass and Δv indicates voltage.

3. Results and Discussions

3.1. X-ray Diffraction Analysis

X-ray diffraction (XRD) is a useful analytical method for observing the crystal structure of carbon materials. This study used XRD to investigate the crystal structure characteristics concerning the activation time. Figure 1 shows the XRD pattern of the Pitch AC.



Figure 1. X-ray diffraction of pitch-derived activated carbons as a function of various activation conditions.

It is generally known that, as the crystal structure of carbon materials develops, the C(002) peak becomes sharper, and the diffraction angle is close to 26.5° [35]. However, as shown in Figure 1, the XRD curves of Pitch AC were observed to have a very broad shape. In other words, the crystal structure of Pitch AC was confirmed to be isotropic rather than anisotropic. As the activation time increased, the intensity of the XRD curve decreased because of increased burn-off. Additionally, the shape of the XRD curve changed from sharp to broad. In particular, the XRD pattern of Pitch AC-12 showed ash peaks other than

the C(002) and C(10*l*) peaks. The ash content relatively increased with increase in burn-off and was the highest for Pitch AC-12.

Table 1 and Figure 2 show the interplanar distance (d_{002}, d_{10l}) , crystal height (La) and crystal size (La) calculated using Bragg's and Scherrer's equations. The interplanar distance changes, and the AC pitch crystal size were more significant for C(10l) than for C (002) because, in the crystal structure of activated carbon, the layers of the C (002) plane consist of strongly hybridized sp² bonds, and the vertical π bond on the C(002) plane results in a weak interlayer bond. Therefore, the oxidation reaction of activated carbon occurred at the crystal edge rather than at the basal plane via physical activation. As a result, a significant change was observed in C(10l) compared to C(002).

Table 1. Structural parameters of pitch-derived activated carbons as a function of various activation conditions.

Sample –	002 Peak								
	20	FWHM	d ₀₀₂	L _c (Å)	20	FWHM	d _{10<i>l</i>}	L _a (Å)	Burn Off (%)
As-received	23.05	8.06	3.86	10.06	43.4	5.99	2.08	29.17	0
Pitch AC-6	23.26	8.7	3.82	9.32	43.52	4.46	2.08	39.2	38
Pitch AC-7	23.48	8.47	3.79	9.58	43.52	4.14	2.08	42.25	55.7
Pitch AC-8	23.41	8.5	3.8	9.54	43.45	4.1	2.08	42.59	62.7
Pitch AC-9	23.48	8.4	3.79	9.66	43.52	4.01	2.08	43.59	78.3
Pitch AC-12	23.24	9.12	3.82	8.89	43.39	4.03	2.08	43.34	94



Figure 2. Structural characteristics of the pitch-derived activated carbons as a function of the various activation time; (**a**) structure parameters and (**b**) interplanar distance.

The crystal structure oxidation of Pitch AC was divided into three stages according to the changed behavior of d_{002} : initial-stage activation (\leq burn-off 55%), middle-stage activation (burn-off 55%–burn-off 90%) and final-stage activation (>burn-off 90%). Figure 2a shows that d_{10l} was maintained without a significant change, regardless of the burn-off. However, d_{002} decreased from 3.86 Å to 3.79 Å in the initial-stage activation. It was maintained in the middle-stage activation. After the final stage of activation, d_{002} increased to 3.82 Å.

In Figure 2b, Lc shows a slight decrease with increasing burn-off time. In contrast, La linearly increased from 29.17 Å to 42.25 Å at initial activation (\leq burn-off 55%); the increasing rate decreased significantly from middle-stage activation. In other words, d₀₀₂ and La exhibited opposite behaviors. The XRD results showed changes in the crystal structure of the activated carbon as statistical data. The oxidation of the amorphous and crystal edges affects the interplanar distance and crystal size change of activated carbon by physical activation [36,37]. In addition, amorphous preferential oxidation occurs more often than at crystal edges [36,37]. Accordingly, by the physical activation mechanism, the oxidation reaction of the Pitch AC was dominant in the amorphous phase at the initial

activation stage; thus, d_{002} decreased owing to the decrease in the distance between the crystallites. On the other hand, La increased owing to the relative increase in the crystallite ratio due to the oxidation of the amorphous phase.

During the middle-stage activation, d_{002} and La were maintained without significant changes, even when the burn-off increased. It was confirmed that the Pitch AC oxidation reaction occurred simultaneously at the amorphous and crystalline edges. This result is due to the simultaneous oxidation of the amorphous and crystalline edges during middle-stage activation. Carbon domains composed of crystalline and amorphous phases are oxidized from the outside by the diffusion of an activation agent (Steam, H₂O) [38]. During this process, the crystal edge of the outer domain and the amorphous structure of the new inner domain were simultaneously oxidized. In other words, based on statistical changes, changes in d_{002} and La were not observed because the amorphous and crystal edges were simultaneously oxidized.

Finally, in the final-stage activation, d_{002} was increased to 3.82 Å with increasing burnoff. Pitch AC-12 exhibited a 94% burn-off. In other words, the amorphous and crystal edges of Pitch AC were mainly oxidized during the long activation time. Only d_{002} increased, owing to the skeleton forming the remaining pore structure.

3.2. Raman Spectroscopy Analysis

Raman spectroscopy is frequently used to study individual changes in the crystal structure of porous carbon materials. Figure 3a shows the Raman spectra of Pitch AC. The Raman spectrum of Pitch AC showed two characteristic peaks at 1590 cm⁻¹ and 1330 cm⁻¹ assigned to the G-band (sp² hybridized graphitic lattice vibration mode, amorphous carbon or small crystallites) and D-band (disordered graphitic lattice or defects/disorder), respectively. The valley between the G- and D-bands gradually deepened with activation time until 80 min (Pitch AC-8). In Figure 2, until 55% burn-off, it was confirmed that the oxidation of Pitch AC occurred predominantly in the amorphous phase. In other words, until 55% burn-off, the amorphous phase was continuously oxidized, and as a result, the G-and D-bands changed narrowly.



Figure 3. (a) Raman spectra of pitch-derived activated carbons as a function of various activation conditions, (b) band parameters derived from raw spectra decompositions.

The first-order Raman spectral bands were deconvoluted into four Lorenz sub-bands (G1, G2, D1 and D2). Figure 4 shows the results of the peak fitting of the Raman spectra to observe the changes in the crystalline structure according to the activation time. For example, G1 is the in-plane bond-stretching motion of pairs of sp² hybridized carbon atoms; D1 indicates disorder and edges in crystallite; G2 indicates amorphous carbon; and D2 indicates a disordered graphitic lattice [31].

As shown in Figure 3b, the FWHM of G1 did not significantly change, but the FWHM of D1 decreased from an activation time of 80 min. The physical activation method involves a pore development mechanism in which amorphous activated carbon is preferentially oxidized, followed by oxidation of the disordered graphitic lattice or crystal edge [36–38].

Therefore, by the physical activation mechanism, G1 did not change because the basal plane of the crystallite was not oxidized by steam, even when 94% was burned off. In addition, the FWHM of D1 decreased due to the oxidation of the disorders and edges in the crystallite after an activation time of 80 min (middle-stage activation). However, unlike G1 and D1, the FWHM of G2 and D2 decreased until Pitch AC-8 and then significantly increased at Pitch AC-12. As shown in Figure 2a, Pitch AC-12 was confirmed to leave only the skeleton of the pore structure (increase in d_{002}) owing to the longest activation time. In other words, the FWHM of G2 and D2 decreased owing to the continuous oxidation of the amorphous and disordered graphitic lattices. However, when the activation time was increased to 120 min, the FWHM of G2 and D2 significantly increased because most amorphous and disordered graphitic lattices were oxidized, and only approximately 6% of the carbon skeleton remained.



Figure 4. Raman spectra peak intensity ratio in the pitch-derived activated carbons as a function of the various activation time.

Figure 4 presents the change in the intensity ratio of the deconvoluted Raman peak as a function of activation time. Initially, I_D/I_G and I_{D1}/I_{G1} increased linearly with increasing activation time. Then, however, I_{G2}/I_{G1} was constantly decreased with increasing activation time. These results indicate that the amorphous structure (G2) of Pitch AC is preferentially oxidized compared to the in-plane bond stretching motion of the pairs of sp² hybridized carbon atoms (G1) structures, disorders and edges in crystallite (D1).

As mentioned earlier, the physical activation method involves a pore development mechanism based on the crystal structure oxidation of the activated carbon. For example, in Figure 2b, the La of Pitch AC increased with the activation time due to the amorphous phase's constant oxidation. In other words, I_{G2}/I_{G1} decreases with increasing activation time because of the constant oxidation of the amorphous phase. However, as the activation time increased, the amount of exposed crystal edges increased as the amorphous phase was oxidized, and it was considered that I_D/I_G and I_{D1}/I_{G1} increased because of the relative increase in the crystal edge content.

Finally, I_{D2}/I_{D1} exhibited a significant decrease up to a 55% burn-off, after which it tended to remain constant. As shown in Figure 2a, d_{002} was significantly decreased to a 55% burn-off and then increased to 94%, owing to the oxidation of edges in the crystal grain. Accordingly, I_{D2}/I_{D1} decreased to a 55% burn-off due to amorphous and disordered graphitic lattice oxidation and was then considered to be constant, owing to the oxidation of edges in crystal grain.

As a result, it was confirmed that the oxidation reaction of Pitch AC by the steam activation method mainly occurred in the amorphous and disordered graphitic lattice, and the oxidation of edges in crystal grain occurred with increased activation time.

3.3. N₂/77K Isotherm Adsorption-Desorption Analysis

 $N_2/77K$ isotherm adsorption-desorption analysis is a very useful method for analyzing the pore characteristics of activated carbon. In this study, $N_2/77K$ isotherm adsorption-desorption analysis was used to analyze the change in the pore characteristics of Pitch AC with activation time.

Figure 5 shows the Pitch AC's $N_2/77K$ isotherm adsorption-desorption curves. The isotherm adsorption-desorption curves of the Pitch AC showed that the amount of N_2 adsorption increased with increasing activation time, and the shape of the curve changed in the order of Type I (a) < Type I (b) < Type II, according to the International Union of Pure and Applied Chemistry (IUPAC) [39]. The adsorption-desorption curve of Type I (a) was observed when single-layer adsorption occurred because of the strong interaction between the pore wall of the activated carbon and the adsorbent (N_2), and it was mainly observed on activated carbons with microporous pore characteristics [39]. In addition, the adsorption-desorption curve of Type I (b) was observed in microporous activated carbon with a wider pore size distribution [39]. The type II adsorption-desorption curve was observed for single-layer adsorption and multilayer adsorption between the pore wall and the adsorbent, which was observed in activated carbon with the simultaneous development of micropores and mesopores [39]. In other words, the mesopore ratio of the Pitch AC changed from microporous to micro-mesoporous.



Figure 5. $N_2/77K$ isotherm adsorption-desorption curves of pitch-derived activated carbons as a function of various steam activation conditions.

The shape of the hysteresis loop observed in the N₂/77K isotherm adsorption-desorption curve was classified into six types by IUPAC according to the activated carbon's pore shape [39]. The hysteresis of Pitch AC-6–Pitch AC-9 was observed to be H4-type, and then Pitch AC-12 was observed to be H3-type by IUPAC classification. In addition, the hysteresis area increased with increasing activation time. Crystal structure analysis (XRD and Raman analysis) confirmed that the oxidation reaction of Pitch AC by the steam activation method mainly occurred in the amorphous and disordered graphitic lattice, and the oxidation of edges in crystal grain occurred with increased activation time. In particular, Pitch AC-6–Pitch AC-9 developed silt-type micropores upon the oxidation of amorphous and disordered graphitic lattices, while Pitch AC-12 showed groove pores of a nonrigid generation formed by flaky particles upon the oxidation of edges in polycrystalline graphite with increasing activation time. Commercial activated carbon (YP-50F, coconut shell-derived activated carbon) was confirmed to have a Type I (a) and a hysteresis loop of H4-type. Therefore, it was considered that YP-50F has microporous pore characteristics and a slit-type pore structure similar to that of Pitch AC-6–Pitch AC-9.

Table 2 lists the textural properties of the Pitch AC as a function of activation time. The pore development behavior of activated carbon using the physical activation method is determined by the oxidation of the crystal structure; therefore, the pore characteristics and crystal structure are highly correlated [36,37]. Therefore, the textural properties of Pitch AC were analyzed based on the oxidation behavior of the crystal structure, as shown in Figures 2 and 3. As shown in Table 2, the specific surface area and total pore volume were observed to be 990–2040 m²/g and 0.42–1.51 cm³/g, respectively. In addition, the micropore and mesopore volumes increased with increasing activation time. However, the rate of increase in the micropore volume gradually decreased, and the increase in the mesopore volume gradually increased, with the highest rate of increase observed in Pitch AC-12.

Table 2. Textural properties of the pitch-derived activated carbons as a function of various activation conditions.

Sample	S _{BET} (m²/g)	V _{Total} (cm ³ /g)	V _{Micro} (cm ³ /g)	V _{Meso} (cm ³ /g)	R _{Meso} (%)	Yield (%)
Pitch AC-6	990	0.42	0.38	0.04	9.5	62
Pitch AC-7	1340	0.6	0.51	0.09	15	44.3
Pitch AC-8	1500	0.7	0.53	0.17	24.3	37.3
Pitch AC-9	1820	0.98	0.62	0.36	36.7	21.7
Pitch AC-12	2040	1.51	0.67	0.84	55.6	6
YP-50F	1710	0.79	0.62	0.17	21.5	-

As shown in Figures 2 and 4, the oxidation reaction of Pitch AC can be classified into three steps. In the initial-stage activation (\leq 55% burn-off), the oxidation reaction of Pitch AC mainly occurred at amorphous phase, and in the middle-stage activation (55% burn-off–90% burn-off), oxidation of the disordered graphitic lattice occurred in addition to amorphous oxidation. Finally, oxidation of the edges in the crystal grain occurred in the final activation stage (>90% burn-off). In a previous study, the micropore and mesopore volumes of activated carbon were confirmed to be affected by amorphous oxidation, disordered graphitics and oxidation of edges in crystal grain [36–38]. In other words, in the initial stage of activation, the pore characteristics of Pitch AC mainly developed into micropores by amorphous oxidation, but as the activation time increased, mesopores were developed by disordered graphitics and oxidation of edges in crystal grain owing to the longest activation time, resulting in the highest mesopore volume (0.84 cm³/g).

Figure 6a,b shows the pore size distribution (PSD) curves of pitch AC obtained using NLDFT and BJH equations, respectively. In Figure 6a, the PSD curves of the Pitch AC show change from a narrow peak to a broad peak with increasing activation time. Pitches AC-6 and -7 had PSD curves mainly developed with micropores of 1–2 nm pore diameters. As the activation increased, Pitch AC-8 had a 2–3 nm pore diameter PSD curve of mesopore with micropores of 1–2 nm pore diameters. Finally, in Pitch AC-9 and -12, the micropore and mesopore PSD merged, and the development of mesopores with diameters of 3 nm or more was observed. The increase in the pore volume in activated carbon induced by physical activation occurs in two ways: pore drilling (which results in a steady increase in the pore diameter) and pore deepening (which has virtually no effect on the pore diameter). As can be seen in Table 2, the total pore volume of Pitch AC increased from $0.42 \text{ cm}^3/\text{g}$ to $1.51 \text{ cm}^3/\text{g}$ with increasing activation time. In addition, as shown in Figure 4, the oxidation reaction of Pitch AC mainly occurred in the amorphous state, and as the activation time increased, the oxidation reaction occurred at the disordered graphitic lattice and edges in crystal grain. In other words, the pores of Pitch AC-6 and Pitch AC-7 were developed by pore deepening, and as the activation time increased, the pores of Pitch AC-8–Pitch AC-12 were developed by pore drilling. In Figure 6b, Pitch AC-6–Pitch AC-8 were observed to

develop mesopores with a pore diameter of less than 10 nm. However, as the activation time increased, the PSD curves of Pitch AC-9 and -12 were expanded to pore diameters greater than 10 nm. In particular, Pitch AC-12 developed macropores with pore diameters greater than 50 nm. That is, the change in the PSD curve of the Pitch AC was influenced by pore deepening in the initial stage of activation; however, as the activation time increased, the PSD curve was influenced by pore drilling. Therefore, Pitch AC exhibited macropore development owing to the collapse of micropores and mesopores due to a 94% burn-off.



Figure 6. Pore size distribution of the pitch-derived activated carbons as a function of various activation conditions; (**a**) NLDFT method and (**b**) BJH equation.

Figure 6a shows that YP-50F has a PSD with less than 2 nm pore diameter. In Figure 6b, YP-50F is observed to have a PSD very similar to that of Pitch AC-8. However, as shown in Table 2, the specific surface area of YP-50F was 1710 m^2/g , which was higher than that of Pitch AC-8 (1500 m^2/g). In other words, YP-50F is considered to have microporous pore characteristics, despite its higher specific surface area than that of Pitch AC-8; this is because Pitch AC has a crystal structure developed from aromatic polycrystals, whereas YP-50F has a crystal structure developed from cellulose. Thus, despite having the same specific surface area, YP-50F and Pitch AC are considered to have different pore properties because they were prepared using different precursors.

3.4. SEM and EDX Analysis

Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometer (EDX) were used to observe the morphology and chemical composition, respectively. Figure 7 shows the SEM images of the Pitch AC and YP-50F. The SEM images of the Pitch AC show that the steam activation process produced extensive very rough and irregular morphology voids. As mentioned above, the oxidation reaction of pitch AC by steam activation mainly occurred at amorphous and the edges of crystalline grains, and the mesopore volume increased as the activation time increased (in Table 2). Also, the hysteresis loop area of Pitch AC was increased with increasing activation time (in Figure 6). Therefore, as the

activation time increased, the void of the Pitch AC increased due to the oxidation of grain edges and the increase in the hysteresis loop area. Pitch AC-12 had the largest void due to the lowest yield and high mesopore volume. YP-50F has a microporous pore structure than Pitch AC, so it is decided that smaller voids were observed in the same specific surface area. The morphology of Pitch AC and YP-50F is considered by the effect of pore development behavior, according to the difference in the crystal structure of the precursor.

The elemental composition of the sample was measured using the energy dispersive X-ray (EDX) analysis. Table 3 shows the presence of the main elements of Pitch AC and YP-50F. The elemental composition of the Pitch AC was observed in the order of C > O > S. In addition, as the activation time increased, the O elemental of the Pitch AC was observed to increase, while the S elemental was observed to decrease. The steam activation has a mechanism in which pores are formed by oxidation of crystals by high-temperature steam. Therefore, as the activation time increases, the content of element O is determined to increase due to the formation of oxygen functional groups at the edges of the crystal grains. On the other hand, it is decided that the content of S element was reduced by the high-temperature oxidation reaction. In addition, Pitch AC-12 was observed to have Zr elemental (1.16%) differently from the other Pitch AC. This is considered that the ash content relatively increased with increase in burn-off. YP-50F has a slightly different elemental composition (C > O > N) from Pitch AC. This is because the YP-50F was manufactured with a different precursor (coconut shell) than the Pitch AC [40].



Figure 7. Cont.



Figure 7. Scanning electron microscopy (SEM) images for (**a**) Pitch AC-6, (**b**) Pitch AC-7, (**c**) Pitch AC-8, (**d**) Pitch AC-9, (**e**) Pitch AC-10 and (**f**) YP-50F.

Sample	C (Weight %)	O (Weight %)	S (Weight %)	N (Weight %)	Zr (Weight %)	Total (Weight %)
Pitch AC-6	88.71	6.38	4.91	0	0	100
Pitch AC-7	89.11	8.9	1.99	0	0	100
Pitch AC-8	90.65	7.4	1.95	0	0	100
Pitch AC-9	86.76	12.07	1.17	0	0	100
Pitch AC-12	83.76	14.78	0.3	0	1.16	100
YP-50F	84.51	10.08	0	5.41	0	100

Table 3. Elemental composition of the pitch-derived activated carbon from EDX analysis.

3.5. Electrochemical Performance

The Pitch AC electrode was prepared using activated carbon with an activation yield of more than 10% for economic feasibility, and the electrochemical performance of Pitch AC was analyzed using CV, GCD and impedance analysis. The measurements were performed in 1 M SBPBF₄/PC. Figure 7 shows the GCD curve of the Pitch AC measured at various current densities (0.1 A/g and 10.0 A/g) in the 0–2.5 voltage range. The GCD curve is the most commonly used method for analyzing the charge and discharge behaviors of EDLC. EDLC using activated carbon as the active electrode material is generally charged and discharged using a non-Faradaic process. Therefore, the GCD curve of an ideal EDLC is observed to be a reversible isosceles triangle with symmetrical charge-discharge curves.

In Figure 8a, the GCD curve of Pitch AC-6 is observed to be irreversible in shape, and the charge and discharge curves are not symmetrical. The sizes of the solvated electrolyte

ions in 1 M SBPBF₄/PC are 1.35 to 1.40 nm [41]. As shown in Figure 6a, Pitch AC-6 has a very narrow PSD curve with a pore diameter of 1 nm. In other words, Pitch AC-6 had a smaller PSD curve than that of the solvated ions. Accordingly, Pitch AC-6 was considered to have an irreversible GCD curve due to its higher ion charge transfer resistance than the other samples.



Figure 8. Charge-discharge curves of the pitch-derived activated carbons at various current densities; (**a**) 0.1 A/g and (**b**) 10.0 A/g.

On the other hand, as the activation increased, Pitch AC-7–Pitch AC-9 were confirmed to have a PSD curve with pore diameters larger than the solvated ion. Therefore, pitch AC-7–pitch AC-9 had a reduced ion charge transfer resistance due to the PSD curve of a larger pore diameter than the solvated ions and were considered to have reversible charge and discharge behavior. In Figure 8b, all GCD curves of the Pitch AC are observed to have an irreversible shape with charge and discharge curves. In particular, the IR drop was not observed at 0.1 A/g (except for Pitch AC-6) but at a very large value of 10.0 A/g. In general, the IR drop in the GCD discharge curve represents a voltage charge arising from the internal resistance of the electrode (contact resistance between the electrodes and collectors, electrolyte resistance and distance between electrodes, amongst others) and ion diffusion resistance in the nanopore. Therefore, it was considered that the irreversible GCD curve and the large IR-drop observed in Figure 8b were due to the increased ohmic resistance with increasing current density. However, the size of the IR drop was in the order of Pitch AC-6 > Pitch AC-7 > Pitch AC-8 > Pitch AC-9. Our previous study confirmed that the ion diffusion resistance decreased because of the increased mesopore volume [18]. As shown in Table 2, the mesopore volume of Pitch AC increased from $0.04 \text{ cm}^3/\text{g}$ to $0.36 \text{ cm}^3/\text{g}$ with increasing activation time. In other words, the increase in the mesopore volume positively affected the ion diffusion resistance; therefore, the IR drop decreased as the activation time increased.

Figure 9 shows the specific capacitance of the Pitch AC calculated from the GCD discharge curves at various current densities (0.1-10.0 A/g). The specific capacitance of Pitch AC was observed to be 43.6–84.6 F/g at a current density of 0.1 A/g and 7.5–66.4 F/g at 10.0 A/g. At 0.1 A/g, the specific capacitance of Pitch AC increased with increasing activation

time. Especially, Pitch AC-9 was observed to have the largest specific capacitance and lowest specific capacitance decrease rate. In our previous study, the specific capacitance of activated carbon at low current densities was confirmed to be affected more by the micropore volume with pore diameters similar to the size of the solvated ions than by the specific surface area [18]. Also, the ion diffusion resistance of AC at high current densities was confirmed to be affected more by the mesopore volume (pore diameter 3–5 nm) [18]. In Figure 6a, in Pitch AC-9, the micropore and mesopore PSD merged, and the development of mesopores with a diameter of 3 nm or more was observed. In other words, the specific capacitance decrease rate of the Pitch AC decreased due to ion diffusion resistance decreasing as the mesopore volume increased.



Figure 9. The specific capacitance of Pitch AC as a function of discharge current density.

The specific capacitance of the YP-50F was observed to be 87.2 F/g at 0.1 A/g and 63.2 F/g at 10.0 A/g. Especially, YP-50F was observed to have a slightly higher specific capacitance than Pitch AC-9 at 0.1 A/g, but at 10.0 A/g, approximately 5% lower than that of Pitch AC-9. In Figure 6a, YP-50F was observed to have mostly PSD with less than 2 nm pore diameter. In other words, YP-50F has microporous pore structure, it was observed that the ion diffusion resistance was higher than that of Pitch AC-9. In conclusion, to achieve high energy and power densities in EDLCs, large micropore and mesopore volumes are required.

CV is a very useful method for analyzing the charge-discharge characteristics of EDLC in conjunction with GCD. Figure 9 shows the CV curves of the Pitch AC measured at various scan rates (5 and 400 mV/s). The CV curve of an ideal EDLC has a rectangular shape, and the area of the curve represents the specific capacitance of the EDLC.

The CV curve of Pitch AC-6 was observed to be leaf-shaped instead of rectangular, regardless of the scan rate; this is consistent with previous GCD results. These results can be attributed to the difficulty of ion transfer in the pores of Pitch AC-6. As shown in Figure 10a, all CV curves of Pitch AC-7–Pitch AC-9 were rectangular. In particular, the area of the CV curve increased with increasing activation time. As shown in Table 2, this is because the specific surface area of the pitch AC increases as the activation time increases; as a result, more electrolyte ions can be stored. However, as shown in Figure 10b, the CV curves of pitch AC-7–pitch AC-9 showed a change from rectangular to leaf shapes as the scan rate increased. The CV curve changed because the ion diffusion resistance increased as the scan rate increased. However, the CV curve of Pitch AC-9 exhibited less deformation than those of the other pitch ACs, and a larger area was observed. As mentioned earlier, Pitch AC-9 had the lowest ion-diffusion resistance, owing to its highest mesopore volume (0.36 cm³/g). Therefore, Pitch AC-9 was considered to have excellent electrochemical performance (e.g., rectangular-shaped CV curve, larger CV curve area) despite a high scan rate of 400 mV/s.

Electrochemical impedance spectroscopy (EIS) is commonly used for analyzing the impedance of EDLCs. Figure 11 presents the Nyquist plots for the Pitch AC obtained in the frequency range of 10 MHz to 300 kHz using EIS. Nyquist plots are generally separated into three types of resistances (bulk solution electrolyte resistance, charge transfer resistance, and Warburg impedance) [42]. First, the bulk solution electrolyte resistance (R_S) can be easily verified from the x-intercept at high frequencies. In additions, Rs may vary according to the electrolyte properties used in the EDLC [42]. In this study, the Rs values of the samples were the same because all samples were prepared using 1 M SBPBF₄/PC.







Figure 11. Nyquist plots of the pitch-derived activated carbons as a function of various activation conditions.

Second, the charge transfer resistance (R_{CT}) was observed as a semicircle on the Nyquist plot in the mid-frequency range. The R_{CT} is the resistance that occurs when an electric double layer (EDL) is formed and includes the interface resistance between the current collector and electrode active material, the interface resistance between the

electrode active material and electrolyte ions, the electrical conductivity of the electrode, and the electrolyte ion resistance inside the pores [42]. As shown in Figure 10, the R_{CT} of Pitch AC-6 did not exhibit a semicircular shape; this is consistent with previous GCD results. Therefore, it was considered that Pitch AC-6 had a larger ion charge transfer resistance owing to a pore structure that was unfavorable for EDL formation (PSD of pore diameter smaller than that of solvated ions). In contrast, R_{CT} of Pitch AC-7–Pitch AC-9 were observed to exhibit a semicircle shape, and the diameter of the semicircle decreased with increasing activation time. Furthermore, as shown in Figure 6a, the pore diameter of Pitch AC increased with increasing activation time. It was considered that the increased pore diameter positively affects the ion charge transfer resistance, which results in a decrease in R_{CT} with activation time.

Finally, the Warburg impedance (R_W) was observed as a straight line with a 45° slope at low frequency. As shown in Figure 10, R_W was observed in the following order: Pitch AC-6 > Pitch AC-7 > Pitch AC-8 > Pitch AC-9. In our previous study, ion diffusion resistance was highly correlated with the mesopore volume ratio of activated carbon [18]. Accordingly, in this study, R_W consistently decreased as the mesopore volume ratio of the Pitch AC increased from 9.5% to 36.7%.

Table 4 lists the specific surface areas and capacitances of the Pitch AC and biomassderived activated carbons for EDLC. As shown in Table 4, Pitch AC-9 prepared by the physical activation method had a specific surface area similar to that of the biomass-derived activated carbon prepared by the chemical activation method. Furthermore, Pitch AC-9 was confirmed to have a relatively high specific capacitance (81.8 F/g at 1.0 A/g), owing to its excellent pore characteristics, even though it was prepared by physical activation. Moreover, pitch AC had the advantages of low cost and high efficiency because it was manufactured via physical activation from a relatively inexpensive asphalt pitch.

Precursor	S _{BET} (m²/g)	Activation Agent	Electrolyte	Specific Capacitance (F/g)	Reference No.
Asphalt pitch	1820	Steam	1 M SBPBF ₄ /PC	81.8 at 1.0 A/g	This work
Jujube fruit	1135	NaOH	1 M Et ₄ BF ₄ /AN	43.8 at 1.0 A/g	[43]
Miscanthus	3024	KOH	1 M TEABF ₄ /PC	52.3 at 1.0 A/g	[44]
Sweet corn husk	1378	KOH	1 M TEABF ₄ /AN	64.0 at 1.0 A/g	[45]
The bark of Platanus	1587	ZnO	1 M TEABF ₄ /AN	92.5 at 0.5 A/g	[46]

Table 4. Comparison of the specific capacitance of EDLC using different biomass-derived activated carbon electrodes with organic electrolyte.

4. Conclusions

In this study, asphalt pitch-derived activated carbon (Pitch AC) was prepared via steam activation to replace coconut-derived activated carbon. The activation time was varied during the activation step to control the pore size. The specific surface area and mesopore volume of Pitch AC increased to 990–2040 m²/g and 0.04–0.84 cm³/g, respectively, with increased activation time. In particular, the pore characteristics of the Pitch AC developed from a microporous structure to a micro-mesoporous structure, according to the activation time. This study showed that asphalt pitch is a suitable precursor for producing activated carbon because it satisfies the ratio of specific surface area to mesopore volume.

The electrochemical performance of Pitch AC was confirmed to be influenced by its crystal structure and pore properties of Pitch AC, which changed with activation time. The micropore and mesopore volumes of the Pitch AC developed with activation time positively affected the specific capacitance and ion diffusion resistance, respectively. The micropore and mesopore volumes of the Pitch AC-9 were 0.62 cm³/g and 0.36 cm³/g, respectively. The specific surface area and micropore volume of Pitch AC-9 were similar to those of commercial activated carbon (YP-50F); however, the mesopore volume was two times higher than that of YP-50F. Accordingly, the specific capacitance of Pitch AC-9 was similar to that of YP-50F. In addition, the high mesopore volume of Pitch AC-9 lowered the

ion diffusion resistance, exhibiting the highest output characteristics compared with the other Pitch AC. As a result, Pitch AC has low cost and high efficiency compared to other biomass-derived activated carbons prepared by chemical activation. Therefore, Pitch AC is expected to replace commercial activated carbon in EDLC, owing to its excellent pore and electrochemical properties.

Author Contributions: Conceptualization, H.-M.L. and B.-J.K.; methodology, Y.-J.K., S.-C.K. and H.-M.L.; software, J.-H.K. and Y.-J.K.; validation, S.-C.K. and Y.-J.K.; formal analysis, J.-H.K., Y.-J.K. and H.-M.L.; investigation, Y.-J.K. and H.-M.L.; resources, S.-C.K. and H.-M.L.; data curation, J.-H.K. and H.-M.L.; writing—original draft preparation, J.-H.K. and H.-M.L.; writing—review and editing, H.-M.L. and B.-J.K.; visualization, J.-H.K., Y.-J.K. and H.-M.L.; supervision, H.-M.L. and B.-J.K.; project administration, H.-M.L.; funding acquisition, H.-M.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Technology Innovation Program (20016795, Development of manufacturing technology independence of advanced activated carbons and application for high performance supercapacitors) and the Technology Innovation Program (20016789, Development of manufacturing and application technology of carbon molecular sieve for high-purity gas separation module) funded by the Ministry of Trade, Industry and Energy (MOTIE, Korea) and the Nano-Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (NRF-2019M3A7B9071501).

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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

References

- 1. Li, T.; Ma, R.; Lin, J.; Hu, Y.; Zhang, P.; Sun, S.; Fang, L. The synthesis and performance analysis of various biomass-based carbon materials for electric double-layer capacitors: A review. *Int. J. Energy Res.* **2019**, *44*, 2426–2454. [CrossRef]
- Liu, S.; Wei, L.; Wang, H. Review on reliability of supercapacitors in energy storage applications. *Appl. Energy* 2020, 278, 115436. [CrossRef]
- 3. Khan, K.; Tareen, A.K.; Aslam, M.; Mahmood, A.; Khan, Q.; Zhang, Y.; Ouyang, Z.; Guo, Z.; Zhang, H. Going green with batteries and supercapacitor: Two dimensional materials and their nanocomposites based energy storage applications. *Prog. Solid State Chem.* **2020**, *58*, 100254. [CrossRef]
- 4. Schütter, C.; Pohlmann, S.; Balducci, A. Industrial Requirements of Materials for Electrical Double Layer Capacitors: Impact on Current and Future Applications. *Adv. Energy Mater.* **2019**, *9*, 1900334. [CrossRef]
- Hartmann, F.; Baumgartner, M.; Kaltenbrunner, M. Becoming Sustainable, The New Frontier in Soft Robotics. *Adv. Mater.* 2020, 33, 2004413. [CrossRef] [PubMed]
- Liang, Z.; He, J.; Hu, C.; Pu, X.; Khani, H.; Dai, L.; Fan, D.; Manthiram, A.; Wang, Z.L. Next-Generation Energy Harvesting and Storage Technologies for Robots Across All Scales. *Adv. Intell. Syst.* 2022, *5*, 2200045. [CrossRef]
- Lim, J.M.; Jang, Y.S.; Nguyen, H.V.T.; Kim, J.S.; Yoon, Y.; Park, B.J.; Seo, D.H.; Lee, K.K.; Han, Z.; Ostrikov, K.; et al. Advance in high-voltage supercapacitors for energy storage systems: Materials and electrolyte tailoring to implementation. *Nanoscale Adv.* 2023, 5, 615–626. [CrossRef]
- 8. Kebede, A.A.; Kalogiannis, T.; Mierlo, J.V.; Berrecibar, M. A comprehensive review of stationary energy storage devices for large scale renewable energy sources grid integration. *Renew. Sust. Energy Rev.* **2022**, *159*, 112213. [CrossRef]
- Ahsan, M.B.F.; Mekhilef, S.; Soon, T.K.; Mubin, M.B.; Shrivastava, P.; Seyedmahmoudian, M. Lithium-ion battery and supercapacitor-based hybrid energy storage system for electric vehicle applications: A review. *Int. J. Energy Res.* 2022, 46, 19826–19854. [CrossRef]
- 10. Rajagopal, S.; Vallikkattil, R.P.; Ibrahim, M.M.; Velev, D.G. Electrode Materials for Supercapacitors in Hybrid Electric Vehicles: Challenges and Current Progress. *Condens. Matter* **2022**, *7*, 6. [CrossRef]
- 11. Luo, L.; Lan, Y.; Zhang, Q.; Deng, J.; Luo, L.; Zeng, Q.; Gao, H.; Zhao, W. A review on biomass-derived activated carbon as electrode materials for energy storage supercapacitors. *J. Energy Storage* **2022**, *55*, 105839. [CrossRef]
- 12. Faisal, M.S.S.; Abedin, F.; Asmatulu, R. Activated carbons of pistachio and acorn shells for supercapacitor electrodes with TEABF₄/PC solutions as electrolytes. *Carbon Lett.* **2020**, *30*, 509–520. [CrossRef]
- Reza, M.S.; Yun, C.S.; Afroze, S.; Radenahmad, N.; Bakar, M.S.A.; Saidur, R.; Taweekun, J.; Azad, A.K. Preparation of activated carbon from biomass and its' applications in water and gas purification, a review. *Arab. J. Basic Appl. Sci.* 2020, 27, 208–238. [CrossRef]
- 14. Packialakshmi, S.; Anuradha, B.; Nagamani, K.; Devi, J.S.; Sujatha, S. Treatment of industrial wastewater using coconut shell based activated carbon. *Mater. Today Proc.* 2021, *81*, 1167–1171. [CrossRef]

- Gao, F.; Tang, X.; Yi, H.; Zhang, B.; Zhao, S.; Wang, J.; Gu, T.; Wang, Y. NiO-Modified Coconut Shell Based Activated Carbon Pretreated with KOH for the High-Efficiency Adsorption of NO at Ambient Temperature. *Ind. Eng. Chem. Res.* 2018, 57, 16593–16603. [CrossRef]
- 16. Deng, Z.; Deng, Q.; Wang, L.; Xiang, P.; Lin, J.; Murugadoss, V.; Song, G. Modifying coconut shell activated carbon for improved purification of benzene from volatile organic waste gas. *Adv. Compos. Hybrid Mater.* **2021**, *4*, 751–760. [CrossRef]
- 17. Arkhipova, E.A.; Novotortsev, R.Y.; Ivanov, A.S.; Maslakov, K.I.; Savilov, S.V. Rice husk-derived activated carbon electrode in redox-active electrolyte-New approach for enhancing supercapacitor performance. J. Energy Storage 2022, 55, 105699. [CrossRef]
- 18. Kim, J.H.; Lee, H.M.; Jung, S.C.; Chung, D.C.; Kim, B.J. Bamboo-Based Mesoporous Activated Carbon for High-Power-Density Electric Double-Layer Capacitors. *Nanomaterials* **2021**, *11*, 2750. [CrossRef]
- Bang, J.H.; Lee, B.H.; Choi, Y.C.; Lee, H.M.; Kim, B.J. A Study on Superior Mesoporous Activated Carbons for Ultra Power Density Supercapacitor from Biomass Precursors. *Int. J. Mol. Sci.* 2022, 23, 8537. [CrossRef]
- 20. Wu, J.; Xia, M.; Zhang, X.; Chen, Y.; Sun, F.; Wang, X.; Yang, H.; Chen, H. Hierarchical porous carbon derived from wood tar using crab as the template: Performance on supercapacitor. *J. Power Sources* **2020**, *455*, 227982. [CrossRef]
- 21. Zheng, S.; Zhang, J.; Deng, H.; Du, Y.; Shi, X. Chitin derived nitrogen-doped porous carbons with ultrahigh specific surface area and tailored hierarchical porosity for high performance supercapacitors. *J. Bioresour. Bioprod.* **2021**, *6*, 142–151. [CrossRef]
- 22. Zhang, Q.; Yan, B.; Feng, L.; Zheng, J.; You, B.; Chen, J.; Zhao, X.; Zhang, C.; Jiang, S.; He, S. Progress in the use of organic potassium salts for the synthesis of porous carbon nanomaterials: Microstructure engineering for advanced supercapacitors. *Nanoscale* **2022**, *14*, 8216. [CrossRef] [PubMed]
- 23. Yan, B.; Zheng, J.; Feng, L.; Zhang, Q.; Zhang, C.; Ding, Y.; Han, J.; Jiang, S.; He, S. Pore engineering: Structure-capacitance correlations for biomass-derived porous carbon materials. *Mater. Des.* **2023**, *229*, 111904. [CrossRef]
- 24. Wu, R.; Beutler, J.; Baxter, L.L. Biomass char gasification kinetic rates compared to data, including ash effects. *Energy* **2023**, *266*, 126392. [CrossRef]
- Lee, S.H.; Lee, S.M.; Im, U.S.; Kim, S.D.; Yoon, S.H.; Lee, B.R.; Peck, D.H.; Shul, Y.G.; Jung, D.H. Preparation and characterization of high-spinnability isotropic pitch from 1-methylnaphthalene-extracted low-rank coal by co-carbonization with petroleum reside. *Carbon* 2019, 155, 186–194. [CrossRef]
- 26. Yahya, M.A.; Qadah, Z.A.; Ngah, C.W.Z. Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production: A review. *Renew. Sustain. Energy Rev.* **2015**, *46*, 218–235. [CrossRef]
- 27. Mamaní, A.; Sardella, M.F.; Giménez, M.; Deiana, C. Highly microporous carbons from olive tree pruning: Optimization of chemical activation conditions. *J. Environ. Chem. Eng.* **2019**, *7*, 102830. [CrossRef]
- 28. Nowicki, P.; Kazmierczak, J.; Pietrzak, R. Comparison of physicochemical and sorption properties of activated carbons prepared by physical and chemical activation of cherry stones. *Powder Technol.* **2015**, *269*, 312–319. [CrossRef]
- 29. Guan, T.; Zhao, J.; Zhang, G.; Zhang, D.; Han, B.; Tang, N.; Wang, J.; Li, K. Insight into controllability and predictability of pore structures in pitch-based activated carbons. *Microporous Mesoporous Mater.* **2018**, *271*, 118–127. [CrossRef]
- 30. Biscoe, J.; Warren, B.E. An X-ray Study of Carbon Black. J. Appl. Phys. 1942, 13, 364–371. [CrossRef]
- 31. Shimodaira, N.; Masui, A. Raman spectroscopic investigations of activated carbon materials. *J. Appl. Phys.* 2002, 92, 902. [CrossRef]
- 32. Brauneur, S.; Emmet, P.; Telle, E. Adsorption of Gases in Multimolecular Layer. J. Am. Chem. Soc. 1938, 60, 309–319. [CrossRef]
- 33. Dubinin, M.M.; Zaverina, E.D.; Radushkevich, L.V. Sorption and structure of active carbons I. Adsorption of organic vapors. *Zhurnal Fiz. Khimii* **1947**, *21*, 1351–1362.
- 34. Kierlik, E.; Rosinberg, M.L. Free-energy density functional for the inhomogeneous hard-sphere fluid: Application to interfacial adsorption. *Phys. Rev. A* **1990**, *42*, 3382. [CrossRef]
- 35. Li, K.; Liu, Q.; Cheng, H.; Hu, M.; Zhang, S. Classification and carbon structural transformation from anthracite to natural coaly graphite by XRD, Raman spectroscopy, and HRTEM. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2021**, 249, 119286. [CrossRef]
- Baek, J.; Lee, H.M.; Roh, J.S.; Lee, H.S.; Kang, H.S.; Kim, B.J. Studies on preparation and applications of polymeric precursor-based activated hard carbons: I. Activation mechanism and microstructure analyses. *Microporous Mesoporous Mater.* 2016, 219, 258–264. [CrossRef]
- Baek, J.; Shin, H.S.; Chung, D.C.; Kim, B.J. Studies on the correlation between nanostructure and pore development of polymeric precursor-based activated hard carbons: II. Transmission electron microscopy and Raman spectroscopy studies. *J. Ind. Eng. Chem.* 2017, 54, 324–331. [CrossRef]
- 38. Yi, H.; Nakabayashi, K.; Yoon, S.H.; Miyawaki, J. Pressurized physical activation: A simple production method for activated carbon with a highly developed pore structure. *Carbon* **2021**, *183*, 735–742. [CrossRef]
- Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K.S.W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* 2015, *87*, 1051–1069. [CrossRef]
- 40. Sarkar, J.K.; Wang, Q. Different Pyrolysis Process Conditions of South Asian Waste Coconut Shell and Characterization of Gas, Bio-Char, and Bio-Oil. *Energies* **2020**, *13*, 1970. [CrossRef]
- Lin, R.; Taberna, P.L.; Chmiola, J.; Guay, D.; Gogatsi, Y.; Simon, P. Microelectrode Study of Pore Size, Ion Size, and Solvent Effects on the Charge/Discharge Behavior of Microporous Carbons for Electrical Double-Layer Capacitors. J. Electrochem. Soc. 2009, 156, A7–A12. [CrossRef]

- 42. Mei, B.A.; Munteshari, O.; Lau, J.; Dunn, B.; Pilon, L. Physical Interpretations of Nyquist Plots for EDLC Electrodes and Devices. *J. Phys. Chem. C* 2018, 122, 194–206. [CrossRef]
- 43. Yang, V.; Senthil, R.A.; Pan, J.; Kumar, T.R.; Sun, Y.; Liu, X. Hierarchical porous carbon derived from jujube fruits as sustainable and ultrahigh capacitance material for advanced supercapacitors. *J. Colloid Interface Sci.* 2020, 579, 347–356. [CrossRef] [PubMed]
- 44. You, X.; Misra, M.; Gregori, S.; Mohanty, A.K. Preparation of an Electric Double Layer Capacitor (EDLC) Using Miscanthus-Derived Biocarbon. *ACS Sustain. Chem. Eng.* **2018**, *6*, 318–324. [CrossRef]
- 45. Rani, M.U.; Nanaji, K.; Rao, T.N.; Deshpande, A.S. Corn husk derived activated carbon with enhanced electrochemical performance for high-voltage supercapacitors. *J. Power Sources* 2020, 471, 228387. [CrossRef]
- 46. Yu, F.; Ye, Z.; Chen, W.; Wang, Q.; Wang, H.; Zhang, H.; Peng, C. Plane tree bark-derived mesopore-dominant hierarchical carbon for high-voltage supercapacitors. *Appl. Surf. Sci.* **2020**, *507*, 145190. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.





Article Investigation on the Mineral Catalytic Graphitization of Anthracite during Series High Temperature Treatment

Haiyue Cao, Kuo Li *, Hao Zhang and Qinfu Liu



Citation: Cao, H.; Li, K.; Zhang, H.; Liu, Q. Investigation on the Mineral Catalytic Graphitization of Anthracite during Series High Temperature Treatment. *Minerals* 2023, *13*, 749. https://doi.org/ 10.3390/min13060749

Academic Editor: Yuri N. Palyanov

Received: 29 March 2023 Revised: 22 May 2023 Accepted: 29 May 2023 Published: 31 May 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/). School of Geosciences and Surveying Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China; chy@student.cumtb.edu.cn (H.C.); zhh199175@outlook.com (H.Z.) * Correspondence: likuo0818@gmail.com or kuo.li@cumtb.edu.cn

Abstract: Graphite can be artificially converted from anthracites under high temperatures; however, the exact mechanism through which inorganic minerals contribute to the graphitization process is still unknown. In light of this, several selected minerals in different amounts were added to demineralized anthracite coal. The anthracite-mineral mixtures were subjected to artificial graphitization experiments under temperatures ranging from 1700 to 2900 °C in the laboratory. The obtained series of coal-based graphites with various levels of graphitization were characterized by X-ray diffraction (XRD), and the derived structural parameters, such as d_{002} and FWHM (002), La, and Lc were used to compare the carbon structural evolution during the high temperature treatment and mineral catalytic graphitization. Moreover, the amorphous carbon of anthracite is eventually transformed into the highly ordered crystalline carbon of coal-based graphite. The five added minerals show interesting structural variation during the graphitization process, in which pyrite is decomposed into iron (Fe), illite, quartz, and kaolinite, which can react with disordered carbon in organic matter to form moissanite (SiC), while dolomite seems to react with sulfur to form oldhamite (CaS). At temperatures less than 2300 °C, the minerals could significantly enhance the catalytic effect. There is a clear difference in the catalytic effect of different minerals on graphitization. Kaolinite exhibits the strongest catalytic effect. The minerals dolomite, illite, and quartz only show a certain degree of catalysis. Pyrite, however, only has a limited effect on improving the degree of graphitization at a temperature of 1700 °C. However, once the temperature exceeds 2300 °C, the dominant factor controlling the graphitization of anthracite appears to be the temperature. According to the growth pattern at microcrystalline sizes (La and Lc), the minerals' catalytic effects can be classified into three groups. The first group includes minerals that preferentially promote La growth, such as pyrite, illite, and quartz. The second group includes minerals that preferentially promote Lc growth, such as dolomite. Finally, kaolinite is in a separate group that promotes microcrystal growth in both the lateral and vertical directions simultaneously. The mechanisms of the minerals' catalytic graphitization are discussed in this paper. The promotion role of minerals in the artificial graphitization process may help to optimize the graphitization process and reduce the process cost in the future.

Keywords: coal-based graphite; minerals; catalytic graphitization; high-temperature treatment; XRD

1. Introduction

Synthetic graphite is a highly valuable material with many applications, such as metal smelting, rechargeable batteries, steel-making carburizers, etc. Recently, coal-based artificial graphite has been attracting extensive attention as an anode material for lithium-ion batteries (LIBs) [1–9]. In the synthetic graphite industry, readily graphitized carbons are selected as the raw materials. Currently, petroleum coke is used as the primary filler material in the manufacturing of synthetic graphite. However, as the demand for synthetic graphite has grown, the price of petroleum coke has risen significantly, and the performance of synthetic graphite made from coke is unpredictable, which greatly impedes the industrialization of petroleum coke in order to make artificial graphite materials [3,6,7,10]. Seeking low-cost

and easily available graphitizable carbon materials as replacement for petroleum coke can benefit the synthetic graphite industry's sustainable development.

As a type of high-ranking coal and a natural resource with abundant reserves, anthracite should be considered as an attractive feedstock to produce carbon materials rather than as a fuel [11]. First, most anthracites contain 92%–98% carbon, virtually all of which is present as aromatic carbon molecules in large polycyclic aromatic sheets, resulting in extraordinary properties such as a highly aromatic nature, a low proportion of aliphatic sidechains, and a high ultra-microporosity pore volume [3,6,7,10,12,13]. Second, anthracites are widely recognized as being more highly graphitizable than any other graphitizing carbon investigated at heating to temperatures above 2000 °C [11,12,14]. Additionally, anthracite's relatively low cost, compared to petroleum coke, endows it with a great economic advantage [10].

The fact is that not all anthracites, even those of similar ranks, exhibit the same level of graphitization when heated under the same circumstances [15]. This is mainly related to the organic characteristics of anthracite, such as its microstructure, elemental composition, coalification degree, etc., [6,7,10,12,13,16–26]. Coal itself is a complex geological substance, and it also contains varying proportions of minerals in addition to the main organic matter of the coal body. Minerals are common components in coal, yielding ash when coal is used as fuel, thus contributing to air pollution. Nevertheless, in recent years, coal-based minerals have gained recognition as a potentially valuable source of critical metals [27–29]. The major non-organic elements in the mineral components of coal, such as Fe, Mg, Mn, Si, Al, and Ti, are used as catalysts for graphitization in the production of various carbon materials [30–35].

Previous studies on the role of mineral matter during the graphitization of anthracites have demonstrated that certain minerals have a positive impact on the graphitization of these high-rank coals under high-temperature treatment [12,18,28,36–40]. For instance, González et al. showed that the degree of crystalline organization attained by heat-treated anthracites increases with the amount of mineral content included. The clay mineral illite and iron-containing minerals such as ankerite and siderite usually show good catalytic effects [18]. Pappano et al. further considered that anthracite is graphitizable only if mineral matter is present, and the authors proposed that carbides aid in the graphitization of anthracite [36]. Moreover, it was discovered by Rodrigues et al. that carbide can not only promote the coalescence of crystallites in the La direction but also serve as a catalyst and/or a template for the formation of graphite-like structures [28]. In addition, Tang et al. investigated the catalytic mechanism of Fe on the graphitization of coal via a computer simulation using the ReaxFF force field. These authors believe that catalytic graphitization is explained by the metal-carbide formation-decomposition mechanism and the dissolution-precipitation mechanism [31]. However, some reports have asserted that the catalytic impact of minerals in coal is negligible and even impedes the graphitization of organic matter. Nyathi et al. indicate that aluminum compounds found in anthracite serve as a physical obstacle instead of as a catalyst in the graphitization process [19]. According to Huan et al., the existence of minerals leads to many irregular pore defects in anthracitebased graphene during the high-temperature synthesis of graphite from coal [17]. So, up to now, there has been no unified understanding of how minerals affect the high-temperature graphitization of coal, especially the catalytic graphitization effects of different materials at several controlled graphitization stages.

In this paper, five kinds of minerals (quartz, kaolinite, illite, dolomite, and pyrite) that are commonly contained in coal-bearing strata were chosen as the target minerals. Demineralized anthracite samples with the addition of different amounts of the above-mentioned minerals were heated under high temperatures ranging from 1700 to 2900 °C. The purposes of this paper were to (1) evaluate the catalytic graphitization effects of different minerals on anthracite at different temperatures and (2) uncover the catalytic graphitization reaction process of anthracite by the selected minerals under high-temperature treatment.

2. Samples and Analytical Methods

2.1. Sampling and Demineralizing

The samples used in this study were obtained from the underground Jinzhushan coal mine (JZS) in the Hanpo'ao mining area, which is located in central Hunan Province, China [41,42]. The samples were demineralized following an experimental protocol reported previously [17,19,36,41–43]. Briefly, coal samples were mixed with a mixture of concentrated hydrofluoric (HF, 40%) and hydrochloric acid (HCl, 6 mol/L) in a 1:2.5 volume ratio, heated to 60 °C in a water bath, and kept at a constant temperature for 4 h, after which the solution was washed with deionized water until it was neutral and dried in an oven for recovery. The demineralized anthracite samples were noted as JZSD.

2.2. High Temperature Treatment

In the present study, remineralization of the JZSD samples was performed by individually adding five types of minerals (kaolinite (K), quartz (Q), illite (I), pyrite (P), and dolomite (D)) to the JZSD samples. Some studies have shown that mineral matter has less of an impact on samples with a less than 2% ash yield, but samples with a high ash yield of 17.25% have a higher degree of graphitization. Based on this, we determined the amount of mineral matter to add. The contents of each mineral added into the demineralized samples were 2%, 10%, and 20% (wt%). The graphitization of each demineralized and remineralized sample was carried out using an ultra-high-temperature graphitization furnace. Crucibles containing about 5 g of each powder sample and covered subsequently with lids were fed into the furnace from the top and passed through the high-temperature region, which was inductively heated in an inert atmosphere (Figure 1a,b). The feedstock input and output were continuous operations. These samples were heated to 1700 °C, 2000 °C, 2300 °C, 2600 °C, and 2900 °C at a rising rate of 10 °C/min and kept for 3 h at the set temperature. Afterward, the furnace was naturally cooled to ambient temperature. The high-temperature-treated samples yielded the coal-based graphite products, which were identified by a code that was JZSD plus the mineral content and an abbreviation ending with a heat treatment temperature [17,19,27,28,33,36,44,45]. For example, the products obtained from the demineralized sample and the remineralized sample mixed with 20% kaolinite after heat treatment at 1700 °C were named JZSD-1700 °C and JZSD-20K-1700 °C, respectively. It should be noted that no multiple independent experiments were carried out in this paper because the graphitization equipment is not readily available. A flowchart for this research is shown in Figure 1b.

2.3. X-ray Diffraction Analysis

XRD was carried out using a Rigaku D/MAX-2500PC fully automatic powder diffractometer equipped with a monochromatic Cu K α X-ray source and an internal standard of silicon power [46,47]. Ni-filtered Cu radiation ($\lambda = 1.54056$ Å) produced at 40 kV and 100 mA was used for the analysis. Diffraction measurements were recorded by the continuous sweep method at a scanning rate of 2° /min over the interval from 2.5 to 80° in the 2 θ range. The XRD patterns were analyzed for structural parameters using the MDI Jade5.0 software. This experiment was completed at the China University of Mining and Technology Beijing. The mean interlayer spacing (d₀₀₂), was calculated from the location of the (002) peak by using Bragg's equation. The microcrystalline structural parameters were calculated by using Scherrer's equations: Lc = 0.9 λ / $\beta_{002} \cos(\varphi_{002})$; La = 1.84 λ / β_{100} $\cos(\varphi_{100})$, where φ_{002} and φ_{100} are the peak positions of the (002) and (100) bands, respectively; β_{002} and β_{100} denote the full width at half maximum (FWHM) of the (002) and (100) peaks, respectively. The degree of graphitization (DOG) and the average number of layers <N> were determined by the following equations: DOG = (3.440-d₀₀₂)/(3.440-3.354), <N> = Lc/d₀₀₂ [17,28,34,41,42,48–51].



Figure 1. (a) Experimental procedures and experimental apparatus for thermal treatment; (b) a flowchart of the study.

3. Results

3.1. Characterization of Raw Samples

The samples were crushed to <20-mesh for the petrographic analysis and crushed to <60-mesh for the geochemical analysis [41]. The volatile matter yield of the raw sample was 5.27%, the hydrogen content was 2.19%, and the mean random vitrinite reflectance value was 4.50% (Table 1), indicating the JZS sample was a typical anthracite. According to the textural and morphological features observed under the microscope, the maceral composition of the JZS sample was determined to be 54.5% vitrinite and 45.2% inertinite (Figure 2a,b, Table 1).

Sample –	Proximate Analysis (%)					Ultimate Analysis (%)				Macerals (Vol%)		D /0/
	M _{ad}	A _{ad}	VM _{daf}	FC _{daf}	C _{daf}	H _{daf}	N _{daf}	\mathbf{S}_{daf}	O _{daf}	V	Ι	Kr /%
JZS	2.15	5.00	5.27	94.73	94.57	2.19	1.08	0.42	1.73	54.5	45.2	4.50

Table 1. Geochemical and	petrographic characters	of the raw JZS anthracite.
--------------------------	-------------------------	----------------------------

Note: FC, fixed carbon (dry, ash-free basis, daf); VM, volatile matter; M, moisture (air-dried basis, ad); A, ash yield (dry basis, d); V, vitrinite; I, inertinite; Rr, random vitrinite reflectance (% in oil). Data were partially obtained from Li et al. [41].



Figure 2. Optical micrograph images and high-resolution transmission electron microscopy images of the JZS sample. (**a**) Pyrofusinite (Pf); (**b**) vitrinite (V); (**c**) basic structural unit (BSU).

HRTEM can reveal the nano-scale carbon structure of coal [19,42,52–54]. In Figure 2c, the HRTEM images of the JZS sample are shown, and the corresponding selected-area electron diffraction (SAED) is inserted. It is possible to discern that the carbon layers that formed the basic structural unit (BSU) were relatively few in number, short in length, rather contorted, and randomly oriented. The electron diffraction patterns showed only one or two diffuse rings, which is typical of the amorphous carbon structure of anthracite.

Information on the structural changes in the raw and demineralized samples were characterized by XRD. The ash yield of the JZS raw anthracite was 5.00%, and the inorganic composition of the raw sample consisted mainly of kaolinite, illite, and ankerite (Figure 3a, low-temperature ashing anthracite sample). The X-ray diffractograms of the samples were typical for anthracite, as shown in Figure 3b, and they exhibited broad 20~30° (002) and 40~45° (100) peaks. It was noticed that many of the sharp mineral peaks in the raw coal disappeared after the acid treatment, suggesting that the demineralization process succeeded.



Figure 3. (a) Inorganic mineral types in JZS sample; (b) XRD comparison graph of raw and demineralized coal samples.

3.2. Effect of Thermal Treatment Temperature

The X-ray diffraction patterns of the pristine demineralized anthracite and the materials obtained from the demineralized anthracite treated at temperatures ranging from 1700 to 2900 °C are depicted in Figure 4. All the samples showed a prominent diffraction peak located at approximately 25~26°, and this band exhibited varied characteristics, from broad asymmetry through sharp asymmetry to sharp symmetry, with increasing the temperature (Figure 4a). Four distinct peaks representing the (002), (100), (004), and (110) diffraction planes were easily detected in the XRD spectra. It is generally accepted that a gradually strengthening (002) diffraction peak intensity and a narrowing peak width indicate that the degree of graphitization and crystallinity increases with increasing the treatement temperature. For the demineralized JZSD sample, its (002) band was deconvoluted into two Gaussian peaks (γ 1 and γ 2 peaks) located at 18.3° and 25.0°, respectively (Figure 4b). Similarly, the (002) diffraction peak for the JZSD-2000 °C sample was split into two peaks, namely the γ 2 and (002) peaks, at approximately 25.2° and 25.8°, respectively, as shown in Figure 4c. The broad $\gamma 1$ peak at 2 θ of the 18–21° band was attributed to amorphous carbon, which only contributed to the background intensity. Some researchers believe that a γ^2 peak with a 20 of 24~25° can be ascribed to graphite-like structures (crystalline carbon), reasoning that the γ 2 band represents nano-scaled graphite crystallites, which are attached by other functional groups in the coal structure [55,56]. The peak at $\sim 26^{\circ}$ was due to the (002) band of the graphite reflection [50,57–60]. This finding demonstrated that when the temperature rose, the amount of disordered carbon (γ 1) and graphite-like carbon (γ 2) progressively declined, and the amount of graphite carbon gradually rose. Moreover, starting from a temperature of 2600 °C, the modulated (10) diffraction band in the samples separated into two well-defined (100) and (101) peaks (enlarged image inserted in Figure 4a), which were comparable to the results of natural microcrystalline graphite, as reported previously [41,42,52–54,61,62]. Additionally, two diffraction peaks at 54.5° and 77.43° attributed to (004) and (110), respectively, became clearly visible.



Figure 4. (a) XRD patterns of JZSD after different temperature treatments; curve-fitting of (002) peak of (b) JZSD and (c) JZSD-2000 $^{\circ}$ C, showing deconvoluted peaks representing γ 1, γ 2, and (002).

XRD parameters for the series samples were shown in Table 2. The d_{002} spacing gradually decreases from 0.3498 to 0.3380 nm, and the FWHM (002) of the samples progressively reduces from 4.365 to 0.417 (°2 θ). In comparison to d_{002} , the variation in FWHM (002) is more regular as the temperature changes, with correlation coefficient R² as high as 0.91, while the R² after linear fitting of d_{002} is 0.88 (Figure 5a). Therefore, the FWHM (002) seems to more accurately reflect the graphitization degree, similar results also reported by Li et al. for naturally graphitized coals [41]. Furthermore, we also have noticed that the evolution process of microcrystalline sizes La and Lc over temperature accelerates at temperatures above 2000 °C, both with an overall S-shaped growth (Figure 5b). The above XRD data show that temperature is the most important factor for graphitization, as with similar results obtained by previous reports [6,12,14,16,19,23].

Table 2. Structural parameters for demineralized samples at different temperatures and samples with different mineral additions after treatment at 2900 °C.

Samples	d ₀₀₂ /nm	FWHM(002)/°20	Lc/nm	La/nm	<n></n>	DOG
JZSD	0.3498	4.365	1.85	5.41	5	_
JZSD-1700 °C	0.3446	2.895	2.79	8.06	8	
JZSD-2000 °C	0.3452	1.748	4.62	11.89	13	_
JZSD-2300 °C	0.3402	0.620	13.04	25.61	38	0.437
JZSD-2600 °C	0.3385	0.439	18.43	55.95	54	0.643
JZSD-2900 °C	0.3380	0.417	19.4	65.13	57	0.702
JZSD-20K-2900 °C	0.3390	0.433	18.68	55.41	55	0.585
JZSD-20I-2900 °C	0.3382	0.345	23.45	67.92	69	0.673
JZSD-20P-2900 °C	0.3382	0.353	22.92	68.45	68	0.673
JZSD-20Q-2900 °C	0.3387	0.386	20.95	52.89	62	0.614
JZSD-20D-2900 °C	0.3385	0.407	19.87	58.77	59	0.643
JZSD-2K-1700 °C	0.3481	2.748	2.94	10.63	8	_
JZSD-10K-1700 °C	0.3431	2.400	3.37	9.08	10	0.108
JZSD-20K-1700 °C	0.3405	1.067	7.58	29.54	22	0.407
JZSD-2P-2000 °C	0.3449	1.644	4.92	11.16	14	_
JZSD-10P-2000 °C	0.3441	1.608	5.03	13.77	15	_
JZSD-20P-2000 °C	0.3382	0.693	11.67	33.27	35	0.673
ATOD1-2400 °C	0.3448	_	5.0	12.5	_	_
ATO-2400 °C	0.3430	_	6.4	19.5	_	
ATOD4-2400 °C	0.3398	_	11.0	39.3	—	

Note: FWHM, full width at half maximum of (002) diffraction peak; Lc and La, crystallite size; <N>, the average number of layers; DOG, degree of graphitization. The last three sample data are cited from previous studies [18].



Figure 5. (a) The variations in FWHM (002) and d_{002} with increasing temperature; (b) the changes in the microcrystalline parameter (La and Lc) with increasing temperature.

3.3. Effect of Mineral Matter Type

The XRD analysis of the series of heated samples was carried out to investigate the effect of the different minerals on the graphitization of anthracite. Kaolinite, illite, and quartz had a high purity, and the other two minerals (pyrite and dolomite) contained small amounts of impurities (Figure 6a). The XRD profiles of the thermal simulation products with the addition of different minerals after the heat treatment at 1700 °C are shown in Figure 6b. Although the (002) diffraction peaks of each sample were clear and obvious, the peak shapes showed different characteristics, among which the JZSD sample with added kaolinite showed the sharpest and strongest (002) band and also showed (101) and (110) peaks, indicating a three-dimensional structural order. The samples with dolomite and illite had a relatively broader (002) peak than the JZSD-20K-1700 °C sample, whereas the samples containing quartz and pyrite showed broad, weak (002) diffraction peak intensities, as shown at the bottom of Figure 6b. The above phenomena indicated that the addition of the different minerals affected the orderly arrangement of the organic matter during the graphitization process, in which the minerals (especially kaolinite) showed a prominent promotion of graphitization. In addition, the non-graphite phases (moissanite (SiC), oldhamite (CaS), and iron) were identified by XRD in the samples treated at 1700 °C, as shown in Figure 6b. For the samples treated at 2900 °C, there were no significant differences in the XRD patterns of the samples with the different added minerals, all of which showed characteristic diffraction peaks of graphite and were almost free of impurities peaks (Figure 6c). Table 2 also shows that all the graphitized samples at 2900 °C had d_{002} values that were only slightly greater than the well-crystallized graphite layer spacing (0.3354 nm). However, the samples with different added minerals showed different crystallite sizes (La and Lc) and average number of stacked layers (<N>) after graphitization at 2900 °C. As a result, the degree of graphitization for anthracite was regulated by the final heating temperature, whereas the mineral type affected the final crystallite size.



Figure 6. (a) XRD spectra of original minerals; JZSD sample with 20% content of different minerals after graphitization at different temperatures: (b) 1700 °C; (c) 2900 °C.

In Figure 7, the type of mineral matter is plotted against the d_{002} (nm) and FWHM (002) values of the heat-treated materials at 1700 °C. It was found that the layer spacing of all the samples with minerals added, except for pyrite, showed a decreasing trend (Figure 7a), while the FWHM values of all the samples with different minerals added decreased in all

cases, as shown in Figure 7b. The JZSD-20K sample displayed the sharpest (002) diffraction peak, as shown in Figure 6b, along with noticeable (101) and (110) peaks. The JZSD-20P-1700 °C sample had the largest d_{002} (0.3475nm) value despite having a lower FWHM (002) value than the demineralized coal sample JZSD-1700 °C, indicating that the presence of pyrite had little impact on the graphitization and even increased the interlayer spacing. Dolomite, illite, and, lastly, quartz all had a certain degree of catalysis for graphitization but were much less effective than kaolinite.



Figure 7. The relationship between the type of mineral matter and XRD parameters for the heattreated materials at 1700 °C: (**a**) d_{002} ; (**b**) FWHM (002). The dashed lines with arrows show the extent of catalytic graphitization level compared to the demineralized sample.

The association between the mineral species and the corresponding crystallite parameters (La and Lc) of the samples treated at 1700 °C is depicted in Figure 8. It should be noted that the La and Lc values of the demineralized samples were the lowest values compared to those of the samples with added minerals. This demonstrated that under the influence of temperature, the minerals underwent phase changes and contributed to the growth of graphite microcrystals, although each mineral did so in a unique manner. It was noted that the microcrystal size increased significantly in the presence of kaolinite (Figure 8), which was also evidenced by our HRTEM images of the JZSD-20K-1700 °C sample shown in the Supplementary Material. This may be related to the interaction between kaolinite and organic matter at certain temperatures, the exact reaction mechanism of which is not currently known. Based on the relationship between the crystalline parameters and mineral type (Figure 8), it was found that dolomite promoted development along the c (stacking) direction over the lateral direction, whereas pyrite showed the opposite effect.

3.4. Effect of Mineral Matter Content

Figure 9a displays the XRD patterns of the heat-treated samples with added quantities of minerals. It was observed that the (002) diffraction peaks gradually became sharp and symmetrical with the increase in the content of kaolinite and pyrite under the same heat treatment conditions. In particular, the XRD features of the JZSD-20K-1700 °C sample had an even higher graphitization degree than those of the samples with 2% and 10% added pyrite treated at 2000 °C (Figure 9a). The measured FWHM (002) value (1.067) of the JZSD-20K-1700 °C sample was lower than that of the JZSD-20P-2000 °C (1.644) and JZSD-20P-2000 °C (1.608) samples. Combined with the performance of the pyrite-added samples at 1700 °C, it was demonstrated that the different minerals had different catalytic action temperature points, and a suitably high percentage of mineral content (20%) effectively accelerated the conversion of organic matter to graphite, which was consistent with the conclusions obtained from a previous study [18]. For example, the degree of

graphitization of the ATOD4 sample (ash = 19.07 wt%) was higher than that of the ATOD1 (ash = 2.07 wt%) and ATO (ash = 10.12 wt%) samples after heat treatment at 2400 °C, as shown in Table 2.



Figure 8. The relationship between the type of mineral matter and crystallite size for the heat-treated materials at 1700 °C.



Figure 9. (a) XRD diffraction patterns of products after heat treatment with various kaolinite and pyrite contents at 1700 °C and 2000 °C, respectively; (b) XRD diffraction patterns of products after heat treatment with various kaolinite and pyrite contents at 2900 °C.

Graphite powder could be obtained under the conditions with a temperature of 2900 °C for all the samples with added kaolinite or pyrite contents of 2%, 10%, and 20%. The XRD patterns used to characterize the graphite powder showed that the only phase was graphite after being treated at 2900 °C (Figure 9b). The new phases formed by mineral

decomposition or reaction with disordered carbon were not visible in the final products or were undetectable due to their extremely low content, indicating that under ultrahigh temperature conditions, regardless of the mineral content, they eventually escaped from the reaction system. Based on the aforementioned phenomena, it can be concluded that the mineral content of the raw coal had a significant impact on the final product's microstructure but not on its degree of graphitization. A similar conclusion was also reported by Qiu et al., who found that the crystal structure of the final graphite, either single crystal or polycrystalline, may depend on the content of minerals in the original anthracite [44].

When the mineral content percentages were plotted against the X-ray parameter FWHM (002) in Figure 10, it was observed that the best-ordered materials were obtained from the samples with 20% added kaolinite after heat treatment up to 1700 °C, and the FWHM (002) of all the samples showed a regular variation with increasing the mineral content, except for the samples with pyrite. A linear fit was performed separately for the different minerals, as shown in Figure 10. There appeared to be little or no influence of the content of pyrite on the structural properties of the obtained material ($R^2 = 0.02$). However, the samples marked with boxes in Figure 10 that had a 2% pyrite addition, in contrast to the samples with the same quantity of other minerals added, had the smallest FWHM (002) value after the heat treatment. This was consistent with other studies that claimed that samples with ash contents below 2% did not exhibit a significant catalytic effect of the mineral matter [12,28]. Additionally, it was noted that the structural order of the obtained materials gradually improved as the content of kaolinite, dolomite, or illite increased. There was a strong correlation between the content of these three types of minerals and the degree of graphitization, with correlation coefficients, R^2 , greater than 0.9 $(R^2 = 0.98 \text{ for illite}, R^2 = 0.94 \text{ for kaolinite}, \text{ and } R^2 = 0.92 \text{ for dolomite})$ being obtained. Furthermore, the conversion of organic matter to graphite was made easier by the high quartz content, and the formation and decomposition of silicon carbide were intimately tied to the graphitization process [27,28,36]. Therefore, it was concluded that increasing the concentration of the three minerals (kaolinite, dolomite, and illite) under high-temperature conditions < 1700 °C could significantly speed up the graphitization process and lower the initial graphitization temperature.



Figure 10. The changes in crystallinity parameter FWHM (002) with increasing the content of mineral matter. Linear fitting line and the coefficient R^2 are shown.

4. Discussion

The differences in the structural and graphitization degree of the samples with different minerals added were probably due to the composition and structural features of the minerals. Therefore, it was necessary to investigate how the minerals affected the growth of the microcrystals during the graphitization process. The La/Lc value can be used to depict the priority growth along the basal plane and vertical direction during graphitization under high-temperature treatment. Larger La/Lc values indicate that the layers tend to extend, and smaller La/Lc values indicate that the layers tend to stack. The variations in the La/Lc values of the demineralized samples and samples with 20% different minerals added under high-temperature treatment are shown in Figure 11a. It was found that when the temperature was 1700 $^{\circ}$ C, the La/Lc values of the set of samples were more scattered than those at other temperatures, indicating that the minerals had different catalytic graphitization effects at this temperature (Figure 11a). The relationship between the La/Lc value and the mineral species at 1700 °C is depicted in Figure 11b. A high La/Lc value implies that the layers tend to extend along the basal planes, whereas a low La/Lc value suggests that the layers tend to stack vertically [63]. It was observed that the La/Lc values of all the samples were between 2.5 and 5.5, and the La/Lc values made it possible to group the samples into three types (Figure 11b). The first type of samples grew preferentially along the basal plane during the graphitization, with their La/Lc values distributed in the range from 4.5 to 5.2, including the JZSD-20P-1700 °C, JZSD-20Q-1700 °C, and JZSD-20I-1700 °C samples. The second category contained only one sample, JZSD-20K-1700 °C, with an La/Lc value of 3.9. The third group of samples with La/Lc values below 2.89 contained two samples, JZSD-1700 °C and JZSD-20D-1700 °C, and more preferentially formed the microcrystalline column described by Oberlin et al. [13].



Figure 11. (a) The La/Lc values of demineralized and samples with 20% different minerals added changed with the increase in heat treatment temperature. (b) The relationship between the type of mineral matter and La/Lc value.

The catalytic effect of minerals is significantly influenced by their physical and chemical properties. For instance, the temperature at which a mineral decomposes plays a crucial role in its catalytic activity. Kaolinite decomposes at 600–650 °C, illite at 850 °C, pyrite at 520–950 °C, dolomite at 750 °C, and quartz is chemically stable with a high melting point of about 1600 °C. In some cases, the complete removal of catalysts during low-temperature graphitization at 1700 °C may not be possible due to certain mineral elements interacting with carbon, leading to the formation of carbides that only break down at high temperatures. In the process of graphite formation, the role of quartz has been studied by some scholars [44,55,56]. The research shows that molten quartz reacts with disordered carbon to form silicon carbide with a structure similar to graphite. This generated SiC can decompose into graphite and silicon under sustained high-temperature conditions. Therefore, the formation and decomposition reactions of silicon carbide are the true mechanism for quartz catalyzing the graphitization of anthracite. In addition, adjusting the quartz content can affect the crystal structure of coal-based graphite products. Research on the catalytic graphitization of anthracite with the addition of illite and kaolinite is relatively scarce and will be detailed in the future. Below, the roles of dolomite and pyrite in the graphitization process of anthracite are discussed in detail.

Dolomite is a binary composite carbonate of MgCO₃ and CaCO₃. Qian et al. researched the thermal decomposition of dolomite in an Ar atmosphere and found that the products of the thermal reaction are MgO and Ca(OH)₂, which are deliquesced by CaO [64]. Subsequently, Ca(OH)₂ is decomposed into CaO at a higher temperature.

$$CaMg (CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \tag{1}$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{2}$$

$$Ca(OH)_2 \rightarrow CaO + H_2O$$
 (3)

The literature shows that the presence of calcium oxide during the pyrolysis of coal significantly increases the yield of gas, and magnesium has been used as a catalyst to graphitize anthracite at low temperatures [30,65]. Therefore, it is speculated that the decomposition of dolomite will destroy the C-H bonds of aromatic hydrocarbons and accelerate the dehydrogenation in the graphitization process. Moreover, CaS was identified in the JZSD-20D-1700 °C sample. Guan et al. found that Ca(OH)₂ and CaO were quite effective at capturing sulfur in the gaseous phase as CaS [66]. It can be inferred that the organic S in anthracite is precipitated as H₂S and reacts with CaO at temperatures below 1700 °C.

$$CaO + H_2S \rightarrow CaS + H_2O \tag{4}$$

There are active cleavage sites on the inner and outer surfaces of calcium oxide, and its polarity affects the stability of the condensed aromatic ring's electron cloud, which may be the reason why calcium oxide reacts with sulfur-containing functional groups. Moreover, on the nanometer scale, it was observed that graphite nanocrystals with thick stacking layers and three graphite single crystals with different orientations that underwent vertical merging coexisted, as shown on the right side of Figure 12. In addition, the La/Lc value of the JZSD-20D-1700 °C sample was lower than that of the JZSD-1700 °C sample, as shown in Figure 11a. The above phenomena showed that the JZSD-20D-1700 °C sample tended to be stacked vertically, and the vertical stacking continued until 2000 °C (Figure 11a). In addition, CaS was unable to remain stable in the reaction system as the temperature was increased to 2000 °C, indicating that dolomite had a small catalytic effect at ultra-high temperatures.

The samples with pyrite added showed an opposite structural growth priority (Figure 11). Pyrite is the most abundant and dominant sulfide compound in coal. It is generally agreed that the decomposition of pyrite occurs in steps over the temperature range 520–950 °C, but only 70% of pyrite is reduced to Fe at 950 °C [67]. Chen et al. suggest that the hydrocarbons of coal can promote the reduction of pyrite in pyrolysis [67].

$$FeS_2 (pyrite) \rightarrow FeS_{1.2} (pyrrhotite) \rightarrow FeS$$
 (5)

$$FeS + H_2 \rightarrow Fe + H_2S$$
 (6)

Srinivasan et al. investigated the effect of pyrite on free radical formation in coal by electron spin resonance spectroscopy and concluded that the formation of free radicals in coal is facilitated by the pyrite-to-pyrrhotite conversion mechanism and by the presence of pyrrhotite itself [68]. In addition, this study found the presence of an iron phase in the JZSD-20P-1700 °C and JZSD-20P-2000 °C samples (Figures 9a and 6b), but it also found a continuous increase in the microcrystalline length La in the series of JZSD-20P samples at temperatures of 1700–2600 °C (Figures 11a and 13). It was therefore presumed that the sulfur in the pyrite spilled out as a gas rather than as sulfur incorporated into organic matter under high temperatures and that the formation of iron continued to promote the graphitization of the organic matter. Some related studies have shown that amorphous carbon has a good solubility in iron, and iron can permeate through organic matter in a liquid phase [31,38,45]. Amorphous carbon near liquid iron is consistently dissolved and arranged in an orderly manner, and it precipitates as graphite at higher temperatures, thus accelerating the graphitization of organic matter. Tang et al. argue that Fe promotes the integration of irregular five- and seven-membered rings into two regular aromatic six-membered rings and that these two processes continue in the process of catalytic graphitization [31]. Based on the above phenomena, the authors suggest that the mechanism of the pyrite-catalyzed graphitization of anthracite is that the decomposition of pyrite at lower temperatures (~950 $^{\circ}$ C) allows sulfur to escape as H₂S or SO₂, while the removal of heteroatoms from the edges of graphite microcrystals in organic matter, such as the basic structural units (BSUs) or the molecular orientation domains (MOD), leads to the formation of a large number of free radicals. As the temperature increases, the newly generated iron is locally oriented by dissolving amorphous carbon or reacting with carbon to form metal carbides, thus promoting the growth of graphite microcrystals along the La direction in a selective manner and the lateral coalescence of a large number of carbon radicals. Furthermore, this catalysis occurs throughout the graphitization process until ultra-high-temperature conditions (the boiling point of iron is 2750 °C), at which point the iron escapes from the system as a gas phase and the graphite microcrystals undergo vertical stacking (Figures 11a and 13).



Figure 12. Schematic diagram of the production of synthetic graphite by the action of dolomite. The arrows indicate the direction of movement of the aromatic layer.



Figure 13. The schematic diagram for the production of synthetic graphite by the action of pyrite. The arrows indicate the direction of movement of the aromatic layer.

5. Conclusions

In this study, a series of coal-based graphite samples synthesized from anthracite with minerals as catalysts were mainly examined using X-ray diffractograms (XRD). The following findings were found based on the series of single high-temperature-run samples:

- (1) For the sample series without adding additional minerals (the JZSD series), the crystallite sizes of these samples showed an increasing trend with the treatment temperature. The differences in the structure of the samples treated with different minerals added were observed from the earliest stages of graphitization (1700~2000 °C) and were mainly attributed to the composition and content of the minerals. In addition, an appropriate increase in the mineral content could effectively decrease the initial graphitization temperature of organic matter and accelerate the graphitization process.
- (2) The La/Lc parameters made it possible to group the samples after the heat treatment with the addition of different minerals into three main groups: (i) the JZSD-20P-1700 °C, JZSD-20I-1700 °C and JZSD-20Q-1700 °C group; (ii) the JZSD-20D-1700 °C group; and (iii) the JZSD-20K-1700 °C group. In terms of the minerals selected for this experiment, the dolomite favored the vertical stacking of organic aromatic layers, while three minerals, pyrite, quartz, and illite, favored the lateral extension of aromatic layers. The highest degree of graphitization was observed in the kaolinite, and the kaolinite could promote microcrystal growth both in the lateral and vertical directions simultaneously.
- (3) The dolomite could accelerate the vertical stacking of graphite microcrystals, probably through dehydrogenation and sulfur fixation at temperatures ranging from 1700~2000 °C, but as the temperature increased, the dolomite had a diminishing effect. The decomposition of the pyrite could aid in forming a large number of free radicals by removing heteroatoms at the edge of the basic structural units or molecular orientation domains, while the newly generated iron probably promoted the preferential growth of graphite microcrystals along the La direction.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/min13060749/s1, Figure S1: The HRTEM image of the JZSD-20K-1700 °C sample.

Author Contributions: Data curation, H.C.; software, H.C.; investigation, H.C.; validation, H.Z. and H.C.; formal analysis, H.C.; writing—original draft preparation, H.C.; writing—review and editing, H.C. and K.L.; supervision, Q.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the National Natural Science Foundation of China (Grant No.42002187) and the Fundamental Research Funds for the Central Universities (2022XJDC01).

Data Availability Statement: Not available.

Acknowledgments: The authors acknowledge support for the samples from the Jinzhushan mine. Sincere thanks are given to Hunan Xirui Automation Equipment Co. Ltd. for providing the high-temperature experimental equipment.

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

References

- Li, Y.; Tian, X.D.; Song, Y.; Yang, T.; Wu, S.J.; Liu, Z.J. Preparation and lithium storage of anthracite-based graphite anode materials. *New Carbon Mater.* 2022, *37*, 1163–1169. [CrossRef]
- 2. Deng, R.Y.; Chu, F.L.; Yu, H.Y.; Kwofie, F.; Qian, M.Z.; Zhou, Y.; Wu, F.X. Electrochemical performance of expanded graphite prepared from anthracite via a microwave method. *Fuel Process. Technol.* **2022**, 227, 107100. [CrossRef]
- 3. Shi, M.; Song, C.L.; Tai, Z.G.; Zou, K.Y.; Duan, Y.; Dai, X.; Sun, J.J.; Chen, Y.Z.; Liu, Y.N. Coal-derived synthetic graphite with high specific capacity and excellent cyclic stability as anode material for lithium-ion batteries. *Fuel* **2021**, *292*, 120250. [CrossRef]
- 4. Wang, T.; Wang, Y.B.; Cheng, G.; Ma, C.; Liu, X.J.; Wang, J.T.; Qiao, W.M.; Ling, L.C. Catalytic Graphitization of Anthracite as an Anode for Lithium-Ion Batteries. *Energy Fuels* **2020**, *34*, 8911–8918. [CrossRef]
- 5. Camean, I.; Lavela, P.; Tirado, J.L.; Garcia, A.B. On the electrochemical performance of anthracite-based graphite materials as anodes in lithium-ion batteries. *Fuel* **2010**, *89*, 986–991. [CrossRef]
- 6. Gonzalez, D.; Montes-Moran, M.A.; Garcia, A.B. Graphite materials prepared from an anthracite: A structural characterization. *Energy Fuels* **2003**, *17*, 1324–1329. [CrossRef]
- 7. Gonzalez, D.; Montes-Moran, M.A.; Suarez-Ruiz, I.; Garcia, A.B. Structural characterization of graphite materials prepared from anthracites of different characteristics: A comparative analysis. *Energy Fuels* **2004**, *18*, 365–370. [CrossRef]
- 8. Krebbers, L.T.T.; Lottermoser, B.G.G.; Liu, X. Computed Tomography of Flake Graphite Ore: Data Acquisition and Image Processing. *Minerals* **2023**, *13*, 247. [CrossRef]
- 9. Xing, B.; Zhang, C.; Cao, Y.; Huang, G.; Liu, Q.; Zhang, C.; Chen, Z.; Yi, G.; Chen, L.; Yu, J. Preparation of synthetic graphite from bituminous coal as anode materials for high performance lithium-ion batteries. *Fuel Process. Technol.* **2018**, 172, 162–171. [CrossRef]
- Andresen, J.M.; Burgess, C.E.; Pappano, P.J.; Schobert, H.H. New directions for non-fuel uses of anthracites. *Fuel Process. Technol.* 2004, 85, 1373–1392. [CrossRef]
- 11. Adamczyk, Z.; Komorek, J.; Bialecka, B.; Calus-Moszko, J.; Klupa, A. Possibilities of Graphitization of Unburned Carbon from Coal Fly Ash. *Minerals* **2021**, *11*, 1027. [CrossRef]
- 12. Oberlin, A.; Terriere, G. Graphitization studies of anthracites by high resolution electron microscopy. *Carbon* **1975**, *13*, 367–376. [CrossRef]
- 13. Oberlin, A. Carbonization and graphitization. Carbon 1984, 22, 521–541. [CrossRef]
- 14. Franklin, R.E. Crystallite growth in graphitizing and non-graphitizing carbons. *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.* **1951**, 209, 196–218. [CrossRef]
- 15. Li, R.; Tang, Y.; Che, Q.; Ma, P.; Luo, P.; Lu, X.; Dong, M. Effects of Coal Rank and Macerals on the Structure Characteristics of Coal-Based Graphene Materials from Anthracite in Qinshui Coalfield. *Minerals* **2022**, *12*, 588. [CrossRef]
- 16. Atria, J.V.; Rusinko, F.; Schobert, H.H. Structural ordering of Pennsylvania anthracites on heat treatment to 2000–2900 degrees C. *Energy Fuels* **2002**, *16*, 1343–1347. [CrossRef]
- 17. Huan, X.; Tang, Y.G.; Xu, J.J.; Lan, C.Y.; Wang, S.Q. Structural characterization of graphenic material prepared from anthracites of different characteristics: A comparative analysis. *Fuel Process. Technol.* **2019**, *183*, 8–18. [CrossRef]
- 18. Gonzalez, D.; Montes-Moran, M.A.; Garcia, A.B. Influence of inherent coal mineral matter on the structural characteristics of graphite materials prepared from anthracites. *Energy Fuels* **2005**, *19*, 263–269. [CrossRef]
- 19. Nyathi, M.S.; Clifford, C.B.; Schobert, H.H. Characterization of graphitic materials prepared from different rank Pennsylvania anthracites. *Fuel* **2013**, *114*, 244–250. [CrossRef]
- 20. Wang, L.; Qin, R.; Li, Y.; Zhang, H. On the difference of graphitization behavior between vitrinite- and inertinite-rich anthracites during heat treatment. *Energy Sources Part A-Recovery Util. Environ. Eff.* **2022**, *44*, 4991–5003. [CrossRef]
- 21. Rodrigues, S.; Suarez-Ruiz, I.; Marques, M.; Flores, D.; Camean, I.; Garcia, A.B. Development of graphite-like particles from the high temperature treatment of carbonized anthracites. *Int. J. Coal Geol.* **2011**, *85*, 219–226. [CrossRef]
- 22. Rodrigues, S.; Suarez-Ruiz, I.; Marques, M.; Camean, I.; Flores, D. Microstructural evolution of high temperature treated anthracites of different rank. *Int. J. Coal Geol.* **2011**, *87*, 204–211. [CrossRef]
- 23. Zeng, H.; Xing, B.; Cao, Y.; Xu, B.; Hou, L.; Guo, H.; Cheng, S.; Huang, G.; Zhang, C.; Sun, Q. Insight into the microstructural evolution of anthracite during carbonization-graphitization process from the perspective of materialization. *Int. J. Min. Sci. Technol.* **2022**, *32*, 1397–1406. [CrossRef]

- 24. Pusz, S.; Kwiecinska, B.K.; Duber, S. Textural transformation of thermally treated anthracites. *Int. J. Coal Geol.* 2003, 54, 115–123. [CrossRef]
- Pusz, S.; Duber, S.; Kwiecinska, B.K. The study of textural and structural transformations of carbonized anthracites. *Fuel Process. Technol.* 2002, 77, 173–180. [CrossRef]
- 26. Li, J.; Qin, Y.; Chen, Y.; Shen, J. Microstructural Characteristics of Graphite Microcrystals in Graphitized Coal: Insights from Petrology, Mineralogy and Spectroscopy. *Minerals* **2022**, *12*, 1189. [CrossRef]
- Rodrigues, S.; Marques, M.; Ward, C.R.; Suarez-Ruiz, I.; Flores, D. Mineral transformations during high temperature treatment of anthracite. *Int. J. Coal Geol.* 2012, 94, 191–200. [CrossRef]
- Rodrigues, S.; Suarez-Ruiz, I.; Marques, M.; Flores, D. Catalytic role of mineral matter in structural transformation of anthracites during high temperature treatment. *Int. J. Coal Geol.* 2012, 93, 49–55. [CrossRef]
- 29. Finkelman, R.B.; Dai, S.; French, D. The importance of minerals in coal as the hosts of chemical elements: A review. *Int. J. Coal Geol.* 2019, 212, 103251. [CrossRef]
- 30. Yang, F.; Chen, H.; Guo, J.; Zheng, P. Catalytic graphitization of anthracite-derived carbon as the anode for Li/K-ion batteries. *J. Mater. Sci. -Mater. Electron.* **2022**, *33*, 4862–4868. [CrossRef]
- 31. Tang, L.; Mao, Q.; You, Z.; Yao, Z.; Zhu, X.; Zhong, Q.; Xiao, J. Catalytic graphitization in anthracite by reduced iron particles and investigating the mechanism of catalytic transformation via molecular dynamics. *Carbon* **2022**, *188*, 336–348. [CrossRef]
- 32. Mochida, I.; Ohtsubo, R.; Takeshita, K.; Marsh, H. Catalytic graphitization of graphitizable carbon by chromium, manganese and molybdenum oxides. *Carbon* **1980**, *18*, 25–30. [CrossRef]
- 33. Feng, B.; Bhatia, S.K.; Barry, J.C. Structural ordering of coal char during heat treatment and its impact on reactivity. *Carbon* **2002**, 40, 481–496. [CrossRef]
- 34. Vlahov, A. XRD graphitization degrees: A review of the published data and new calculations, correlations, and applications. *Geol. Balk* **2021**, *50*, 11–35. [CrossRef]
- 35. Wu, Y.; Li, K.; Wang, Z.; Hu, M.; Cao, H.; Liu, Q. Fluctuations in Graphitization of Coal Seam-Derived Natural Graphite upon Approaching the Qitianling Granite Intrusion, Hunan, China. *Minerals* **2021**, *11*, 1147. [CrossRef]
- 36. Pappano, P.J.; Schobert, H.H. Effect of Natural Mineral Inclusions on the Graphitizability of a Pennsylvania Anthracite. *Energy Fuels* **2009**, *23*, 422–428. [CrossRef]
- 37. Ōya, A.; Fukatsu, T.; Ōtani, S.; Marsh, H. Catalytic graphitization of cokes by indigeneous mineral matter. *Fuel* **1983**, *62*, 502–507. [CrossRef]
- Bonijoly, M.; Oberlin, M.; Oberlin, A. A possible mechanism for natural graphite formation. *Int. J. Coal Geol.* 1982, 1, 283–312. [CrossRef]
- 39. Evans, E.L.; Jenkins, J.L.; Thomas, J. Direct electron microscopic studies of graphitic regions in heat-treated coals and coal extracts. *Carbon* **1972**, *10*, 637–642. [CrossRef]
- Badenhorst, C.; Santos, C.; Lazaro-Martinez, J.; Bialecka, B.; Cruceru, M.; Guedes, A.; Guimaraes, R.; Moreira, K.; Predeanu, G.; Suarez-Ruiz, I.; et al. Assessment of Graphitized Coal Ash Char Concentrates as a Potential Synthetic Graphite Source. *Minerals* 2020, 10, 986. [CrossRef]
- 41. Li, K.; Rimmer, S.M.; Liu, Q. Geochemical and petrographic analysis of graphitized coals from Central Hunan, China. *Int. J. Coal Geol.* **2018**, 195, 267–279. [CrossRef]
- Li, K.; Liu, Q.; Cheng, H.; Hu, M.; Zhang, S. Classification and carbon structural transformation from anthracite to natural coaly graphite by XRD, Raman spectroscopy, and HRTEM. Spectrochim. Acta Part A-Mol. Biomol. Spectrosc. 2021, 249, 119286. [CrossRef] [PubMed]
- 43. Quan, Y.; Liu, Q.; Li, K.; Zhang, H.; Yang, Y.; Zhang, J. Simultaneous fluorination and purification of natural block coaly graphite into fluorinated graphene with tunable fluorination degree. *Mater. Today Commun.* **2022**, *32*, 104130. [CrossRef]
- 44. Qiu, T.; Yang, J.-G.; Bai, X.-J. Investigation on microstructural changes of Anthracite during Graphitization and effect of Silica content on product crystal structure. *Energy Sources Part A-Recovery Util. Environ. Eff.* **2021**, *43*, 769–782. [CrossRef]
- 45. Wang, L.; Qiu, T.; Guo, Z.; Shen, X.; Yang, J.; Wang, Y. Changes and Migration of Coal-Derived Minerals on the Graphitization Process of Anthracite. *ACS Omega* **2021**, *6*, 180–187. [CrossRef]
- 46. Yuan, L.; Liu, Q.; Mathews, J.P.; Zhang, H.; Wu, Y. Quantifying the Structural Transitions of Chinese Coal to Coal-Derived Natural Graphite by XRD, Raman Spectroscopy, and HRTEM Image Analyses. *Energy Fuels* **2021**, *35*, 2335–2346. [CrossRef]
- 47. Quan, Y.; Liu, Q.; Zhang, S.; Zhang, S. Comparison of the morphology, chemical composition and microstructure of cryptocrystalline graphite and carbon black. *Appl. Surf. Sci.* **2018**, 445, 335–341. [CrossRef]
- 48. Biscoe, J.; Warren, B. An x-ray study of carbon black. J. Appl. Phys. 1942, 13, 364–371. [CrossRef]
- 49. Laggoun-Défarge, F.; Lallier-Verges, E.; Suárez-Ruiz, I.; Cohaut, N.; Bautista, A.J.; Landais, P.; Prado, J. Evolution of Vitrinite Ultrafine Structures during Artificial Thermal Maturation; ACS Publications: Washington, DC, USA, 1994. [CrossRef]
- 50. Lu, L.; Sahajwalla, V.; Kong, C.; Harris, D. Quantitative X-ray diffraction analysis and its application to various coals. *Carbon* **2001**, 39, 1821–1833. [CrossRef]
- 51. Seehra, M.S.; Pavlovic, A.S. X-Ray diffraction, thermal expansion, electrical conductivity, and optical microscopy studies of coal-based graphites. *Carbon* **1993**, *31*, 557–564. [CrossRef]
- 52. Zhang, H.; Li, K.; Sun, J.; Sun, Z.; Yuan, L.; Liu, Q. The structural evolution and mutation of graphite derived from coal under the influence of natural igneous plutonic intrusion. *Fuel* **2022**, *322*, 124066. [CrossRef]
- 53. Li, K.; Liu, Q.; Hou, D.; Wang, Z.; Zhang, S. Quantitative investigation on the structural characteristics and evolution of high-rank coals from Xinhua, Hunan Province, China. *Fuel* **2021**, *289*, 119945. [CrossRef]
- Li, K.; Liu, Q.; Rimmer, S.M.; Huggett, W.W.; Zhang, S. Investigation of the carbon structure of naturally graphitized coals from Central Hunan, China, by density-gradient centrifugation, X-ray diffraction, and high-resolution transmission electron microscopy. *Int. J. Coal Geol.* 2020, 232, 103628. [CrossRef]
- 55. Shao, Y.; Wang, S.; Li, X. The Effect of Silicon-Containing Minerals on Coal Evolution at High-Temperature Pre-Graphitization Stage. *Minerals* **2023**, *13*, 20. [CrossRef]
- 56. Chen, G.; Cao, D.; Wang, A.; Wei, Y.; Liu, Z.; Zhao, M. A High-Temperature Thermal Simulation Experiment for Coal Graphitization with the Addition of SiO₂. *Minerals* **2022**, *12*, 1239. [CrossRef]
- 57. Burgess-Clifford, C.E.; Narayanan, D.L.; Van Essendelft, D.T.; Jain, P.; Sakti, A.; Lueking, A.D. The effect of calcination on reactive milling of anthracite as potential precursor for graphite production. *Fuel Process. Technol.* **2009**, *90*, 1515–1523. [CrossRef]
- Neupane, B.; Ju, Y.; Silwal, B.R.; Singh, P.K.; Huang, C. Structural investigations of Eocene coals from foreland basin of central Nepal Himalaya. *Energy Explor. Exploit.* 2017, 35, 713–733. [CrossRef]
- 59. Zhang, Y.; Kang, X.; Tan, J.; Frostt, R.L. Influence of Calcination and Acidification on Structural Characterization of Anyang Anthracites. *Energy Fuels* **2013**, *27*, 7191–7197. [CrossRef]
- 60. Wang, L.; Cao, D.; Peng, Y.; Ding, Z.; Li, Y. Strain-Induced Graphitization Mechanism of Coal-Based Graphite from Lutang, Hunan Province, China. *Minerals* **2019**, *9*, 617. [CrossRef]
- Zhang, S.; Liu, Q.; Zhang, H.; Ma, R.; Li, K.; Wu, Y.; Teppen, B.J. Structural order evaluation and structural evolution of coal derived natural graphite during graphitization. *Carbon* 2020, 157, 714–723. [CrossRef]
- Zhang, S.; Song, B.; Cao, C.; Zhang, H.; Liu, Q.; Li, K.; Teppen, B.J. Structural Evolution of High-Rank Coals during Coalification and Graphitization: X-ray Diffraction, Raman Spectroscopy, High-Resolution Transmission Electron Microscopy, and Reactive Force Field Molecular Dynamics Simulation Study. *Energy Fuels* 2021, 35, 2087–2097. [CrossRef]
- 63. Chen, H.; Wang, S.; Zhang, X.; Zhao, Y.; Zhang, H. A study of chemical structural evolution of thermally altered coal and its effect on graphitization. *Fuel* **2021**, *283*, 119295. [CrossRef]
- 64. Huang, Q.; Wei, K.; Xia, H. A novel perspective of dolomite decomposition: Elementary reactions analysis by thermogravimetric mass spectrometry. *Thermochim. Acta* **2019**, 676, 47–51. [CrossRef]
- 65. Zhu, T.Y.; Zhang, S.Y.; Hung, J.J.; Wang, Y. Effect of calcium oxide on pyrolysis of coal in a fluidized bed. *Fuel Process. Technol.* **2000**, *64*, 271–284.
- Guan, R.G.; Li, W.; Li, B.Q. Effects of Ca-based additives on desulfurization during coal pyrolysis. *Fuel* 2003, *82*, 1961–1966. [CrossRef]
- 67. Chen, H.K.; Li, B.Q.; Zhang, B.J. Decomposition of pyrite and the interaction of pyrite with coal organic matrix in pyrolysis and hydropyrolysis. *Fuel* **2000**, *79*, 1627–1631. [CrossRef]
- 68. Srinivasan, G.; Seehra, M.S. Effect of pyrite and pyrrhotite on free radical formation in coal. Fuel 1983, 62, 792–794. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.





Article Computed Tomography of Flake Graphite Ore: Data Acquisition and Image Processing

Leonard T. Krebbers *^(D), Bernd G. Lottermoser ^(D) and Xinmeng Liu

Institute of Mineral Resources Engineering, RWTH Aachen University, Wüllnerstraße 2, 52062 Aachen, Germany

* Correspondence: krebbers@mre.rwth-aachen.de

Abstract: A solid knowledge of the mineralogical properties (e.g., flake size, flake size distribution, purity, shape) of graphite ores is necessary because different graphite classes have different product uses. To date, these properties are commonly examined using well-established optical microscopy (OM), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) and SEM-based automated image analysis. However, these 2D methods may be subject to sampling errors and stereological effects that can adversely affect the quality of the analysis. X-ray microcomputed tomography (CT) is a nondestructive imaging technique allowing for examination of the interior and exterior of solid materials such as rocks and ores in 3D. This study aimed to explore whether CT can provide additional mineralogical information for the characterisation of graphite ores. CT was used in combination with traditional techniques (XRD, SEM-EDS, OM) to examine a flake graphite ore in 3D. A scanning protocol for the examined graphite ore was established to acquire high-quality CT data. Quantitative mineralogical information on key properties of graphite was obtained by developing a deep learning-based image processing strategy. The results demonstrate that CT allows for the 3D visualisation of graphite ores and provides valid and reliable quantitative information on the quality-determining properties that currently cannot be obtained by other analytical tools. CT allows improved assessment of graphite deposits and their beneficiation.

Keywords: computed tomography; natural graphite; segmentation; ore analysis; machine learning; lithium-ion batteries

1. Introduction

Natural graphite is an allotrope of carbon comprising a multitude of layers of graphene, i.e., one-atom thick, hexagonal lattice layer of carbon with carbon atoms connected to each other by covalent bonds [1]. The individual graphene layers are held together by van der Waals forces. These weak interplanar interactions endow the mineral graphite with exceptional properties such as refractoriness, high heat and electrical conductivity, greasiness and high thermal resistance [2]. Graphite is applied in a variety of technological applications including lithium-ion batteries (LIB), fuel cells, two-dimensional graphene electronics and fibre optics [2,3]. Consequently, natural graphite has been recognised as a critical raw material by mega economies such as the United States and the European Union because of its high economic importance and supply risk [4,5]. Today, China accounts for almost 75% of the global natural graphite production, followed by Mozambique and Brazil. Together, the three countries represent around 90% of the world's production [6].

Natural graphite is found in the Earth's crust in a variety of geological settings and results from the conversion of carbonaceous matter through metamorphic processes into graphite (graphitisation) or by deposition from carbon-bearing fluids [7,8]. There are various classification schemes, one of which divides graphite deposits according to their formation conditions into (1) lump (vein), (2) flake and (3) amorphous (microcrystalline) graphite [7]. In market terms, graphite is classified according to the particle (flake) size (Table 1). In contrast to many other mineral resources, the quality of graphite ore is



Citation: Krebbers, L.T.; Lottermoser, B.G.; Liu, X. Computed Tomography of Flake Graphite Ore: Data Acquisition and Image Processing. *Minerals* 2023, *13*, 247. https:// doi.org/10.3390/min13020247

Academic Editors: Qinfu Liu, Kuo Li and Shuai Zhang

Received: 13 January 2023 Revised: 3 February 2023 Accepted: 6 February 2023 Published: 9 February 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/). not solely determined predominantly based on grade, but rather on its mineralogical properties such as grain (flake) size, distribution, shape and purity. These properties are directly related to market applications and product price [9,10]. Graphite deposits that contain a high proportion of large graphite flakes tend to have higher purities and carbon content. The flake size distribution is deposit-specific and decisive for the economic viability of a deposit as well as the ultimate use of the concentrates produced [11]. To date, only graphite with high purity and large flake sizes can be used for LIB [12]. There are recent developments to use smaller flakes for LIB manufacturing. Regardless, rigorous characterisation of the raw material is key to assessing ore quality and achieving the best possible beneficiation product.

Classification	Size in µm	Carbon Content of Concentrates (%)
Amorphous	<75	75–90
Small flake	75-150	90–97
Medium flake	150-180	90–97
Large flake	180-300	90–97
Jumbo	300-500	90–97
Super jumbo	>500	90–97

Table 1. Market terminology of natural graphite and general properties (modified after [10,13]).

Graphite raw materials are conventionally characterised using X-ray powder diffraction (XRD), differential thermal analysis/thermogravimetry (DTA/TG), inductively coupled plasma mass spectrometry (ICP-MS), scanning electron microscopy coupled with an energy dispersive detector (SEM-EDS), Raman spectroscopy and optical microscopy (OM) as well as SEM-based automated mineralogy systems such as QEMSCAN (quantitative evaluation of minerals by scanning electron microscopy) and MLA (mineral liberation analyser), e.g., [14–17]. Results of these techniques provide vital information on the presence and properties of graphite ores. In some cases, the acquired information cannot be related to any dimensional geometries of the analysed samples (e.g., XRD). By contrast, OM, SEM-EDS, QEMSCAN and MLA allow for 2D visualisation of graphite ores. However, these techniques are time-consuming, and their sample preparation is destructive and requires careful sectioning of the original sample (e.g., drill hole) to select representative sample material. Moreover, results of the above-mentioned methods must be translated into the third dimension and are therefore subject to stereological bias [18]. For ores of complex mineralogy and microstructure such as graphite ores, where grain size distribution is an important assessment feature, this can be challenging. In view of the fact that graphite ores and deposits and their products represent 3D arrays of mineral assemblages, there is a need to acquire information on the 3D distribution of the quality-determining properties (i.e., flake size, intergrowth) of graphite in ores to achieve optimal processing and target use of graphite ores.

A novel tool to display the 3D distribution of mineral phases is X-ray microfocus computed tomography (CT). For example, several scientific studies have demonstrated the use of CT to define the in situ location of gold grains and their distribution within gold ores [19–22]. Ghorbani et al. successfully used CT for the 3D characterisation of crack and mineral dissemination in sphalerite ore particles [23]. Godel et al., Godel and Sittner et al. studied the 3D distribution of platin group metals (PGMs) to understand ore-forming processes [24–26]. Le Roux et al. quantified tungsten ore mineral content and ore grade using CT to assess the quality of the tungsten ore [27]. Similarly, Rozendaal et al. demonstrated the ability to quantify the final product quality grain size distribution, perform grain shape definition and identify external and internal mineral textures of a Ti-Zr placer deposit [28].

To date, however, the use of CT has not been comprehensively tested to characterise graphite raw materials. This study explores the application of CT for the characterisation of graphite ores. An image protocol was developed to acquire appropriate CT data. Furthermore, an advanced image processing strategy was established that was based on deep learning algorithms to extract quantitative information on key microstructural features of the flake graphite ore in 3D. This study demonstrates that CT imaging of graphite ores requires careful development of image protocols and processing strategies, which can then produce new insights into graphite ore properties.

2. Materials and Methods

2.1. Conventional Mineralogical and Petrographic Analyses

A flake graphite ore sample was provided by the German-based company NGS Trading & Consulting GmbH (Leinburg, Germany) from the Yanxin graphite mine (Shangdong province, China). XRD was carried out on a ~2.5 g aliquot of the sample, which was ground in 100% ethanol in a McCrone micronizing mill using synthetic agate pellets for 5 min. Micronized aliquots were air-dried and subsequently analysed on a Rigaku Ultima IV powder X-ray diffractometer (Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Canada). The Rigaku Ultima IV XRD is equipped with a Co source that was operated at 38 kV and 38 mA. XRD patterns were collected from 5 to 80° 2g using a step size of 0.02° 2q at a rate of 1.2° 2q/minute. Qualitative phase identification was performed using the JADE (Rigaku, Tokyo, Japan) and EVA (Bruker, Billerica, MA, USA) software packages. Mineral phases were identified with reference to the International Center for Diffraction Data Powder Diffraction File 4+ database (ICDD PDF4+). For petrographic analysis, a thin section and cylindrical-shaped polished block were prepared by MK Factory (Stahnsdorf, Germany). Both samples were examined using a LEICA DM 2700P polarization microscope (Institute of Mineral Resource Engineering, RWTH Aachen University, Aachen, Germany). Microphotographs were taken with a LEICA FLEXCAM C1 camera to establish an image mosaic of the polished section using the LEICA LAS software. Scanning electron microscopy combined with an electron dispersive spectrometer (SEM-EDS) was used to provide further insights on the mineralogy and microstructure of the graphite ore specimen, using a FEI 650F scanning electron microscope equipped with two Bruker XFlash 5030 detectors (Institute of Mineralogy and Economic Geology, RWTH Aachen University, Aachen, Germany) (15 kV, 10 nA).

2.2. Computed Tomography

In this study, a ProCon Alpha micro-CT system was used, which is equipped with a five-axes-manipulation system between an XWT-240-TCHE plus X-ray tube with a maximum voltage of 240 kV and an XRD 1611 AP3 detector system with 4064 \times 4064 pixels (100 mm²) (Institute of Mineral Resources Engineering, RWTH Aachen University, Aachen, Germany). For the scanning procedure, a cylindrically shaped, polished graphite sample (14 mm diameter, 11.5 mm thickness) was investigated. CT measures the attenuation of an X-ray that passes through sample object [18]. The X-ray attenuation depends on the material density and atomic number as well as the X-ray energy applied [29,30]. A CT measurement is the collection of 2D sample projections (radiographs), which are taken as the sample rotates 360° around the vertical axis between the X-ray tube and the detector. The detector collects the number and intensity of transmitted X-rays of each projection and thus provides X-ray attenuation information. Based on this information, an X-ray attenuation coefficient is calculated for each pixel of the acquired sample projection. This coefficient is displayed as a distinct grey-scale value in the projection image [31]. The collection of radiographs is then stacked to create a 3D volume, comprising a cubical matrix of grey-scale voxels (3D pixels). Thus, CT allows for the 3D analysis of multicomponent materials such as ore and rocks, providing nondestructive internal microstructural information on mineral volume, mineral size, mineral distribution, association, orientation and porosity, e.g., [32–35].

2.2.1. Image Acquisition

Scan parameters were determined in the course of several test measurements and iteratively optimised to obtain low-noise, high-contrast images with as few artefacts as

possible in the shortest possible time. Attenuation curves were calculated based on the samples' mineralogy, as determined by XRD, OM and SEM-EDS (Figure 1).



Figure 1. Linear attenuation coefficients as a function of X-ray energy for the major minerals occurring in the scanned sample. The values displayed in the graph calculated based on end member compositions, and densities and were calculated using the XCOM Photon Cross-Sections Database NIST [36].

Attenuation curves were calculated by multiplying the mass coefficient by mass density. The nature of X-ray attenuation is predominantly a function of photoelectric absorption and Compton scattering. Photoelectric absorption occurs when the total energy of an incoming X-ray photon is transferred to an inner electron, causing the electron to be ejected. The probability of this effect is heavily dependent on the atomic number (Z) of the absorbing material and the X-ray energy; photoelectric absorption is proportional to Z^{4-5} [36,37]. In Compton scattering, the probability of X-ray absorption is proportional to only Z, as the incoming X-ray photon interacts with a free or outer electron, ejecting the electron. Hence, the probability of this effect is more dependent on the electron density of the material [38]. The photoelectric effect prevails in low energies (approximately 50-100 keV), whereas Compton scattering dominates in energies >5 MeV [39]. Thus, to increase the attenuation contrast between graphite and similar attenuating gangue phases as well as the epoxy resin, the application of lower voltages is recommended. However, using lower voltages results in decreasing penetration capability and the production of more artefacts, especially when high absorbing phases are present. To achieve a good signal-to-noise ratio, a longer exposure time is required in this case, as this is proportional to the number of photons recorded per projection. Thus, given that the sample contains highly absorbing phases, voltage and exposure time were adjusted accordingly to achieve minimum beam hardening on one hand and maximum contrast on the other. To further reduce noise, the number of averages per projection was adjusted accordingly. Lastly, to maintain optimal focal spot size, which determines the X-ray flux and resolution capability of the XCT system, the applied power of the X-ray beam was set slightly higher than the scan resolution. The final scanning conditions are summarised in Table 2.

Reconstruction of the scanned sample was performed with the VGStudio Max 3.5. software [40] based on filtered back-projection (FBP) and a beam hardening correction to address cupping artefacts and streak artefacts generated due to the polychromatic nature of the beam.

Acquisition	Parameters	
Voltage [keV]	100	
Current [µA]	110	
Exposure time [s]	1.35	
No. of averages	4	
Binning	1 imes 1	
No. of projections	2500	
Scanning time [h:mm]	9:05	

Table 2. Scanning conditions of the scanned flake graphite ore sample.

2.2.2. Pre-Processing

When the attenuation coefficient values are converted into CT numbers, a certain amount of noise is always present in the CT images due to statistical variations. Therefore, digital image filters were applied prior to segmentation to enhance the quality of the scan by reducing noise and increasing grey value contrast, for example. The actual operation is applied on a 2D CT slice image. The software used, ORS Dragonfly (Version 2022.1) [41], offers a broad range of filtering operations, which can be applied iteratively. A three-filter combination produced the best results (Figure 2). First, a median filter was applied to denoise the image. This was followed by the unsharp filter, using an unsharp factor of 3 to increase the edge contrast of grains. Since the unsharp filter produces noise, the median filter was applied again to denoise the image.



Figure 2. CT volume slice before (A) and after image filtering (B).

2.2.3. Image Processing

Image processing was carried out using ORS Dragonfly. The software possesses different machine learning and deep learning algorithms that can be used for segmenting different phases simultaneously. Machine learning (ML) refers to a class of model-based computational techniques for processing data [42]. Deep learning (DL) is a subset of ML, featuring many interconnected processors (neurons) that work in parallel. These processors are predominately built on a convolutional neural network (CNN) architecture, which is particularly efficient for image processing [43]. To achieve accurate segmentation, the network must be trained to identify structures and learn how to make predictions (inference stage) for subsequent calculations [43]. Therefore, single or multiple regions of interest on different 2D image slices are created and used to manually select groups of voxels which belong to different segmentation classes. These slices are considered ground truth data, on which basis the algorithm is trained and validated (supervised classification). Consequently, the network allows for automatic segmentation of the entire data set.

The segmentation procedure was performed on a digitally cut cylindrical subvolume (10.53 mm diameter, 8.21 mm thickness) so that (a) the epoxy mount, in which the section

was embedded, was excluded as well as the cone-beam effect (depth-related greyscale gradients); (b) operation time was accelerated by reducing the data size; (c) each horizontal slice was of equal area; and (d) the topmost slice had the same surface as that of the polished section to enable subsequent comparison with mineralogical and petrographic OM and SEM-EDS data. Regarding the model architecture, Random Forest [44], U-Net [45] and sensor3D [46] models were tested and trained. The mineralogical and petrographic information obtained using XRD, SEM-EDS and OM was essential to interpret the CT radiographs and to identify the phases according to their grey-scale values. Three classes were determined, comprising graphite, high X-ray attenuating phases (i.e., pyrite, pyrrhotite, rutile, zircon) and the remaining gangue minerals. These were labelled manually on a randomly selected area (frame) of a 2D slice to establish a first training data set. The model was then tested on a new slice, and wrongly classified voxels were corrected and attributed to the training data. The accuracy of a model and thus the segmentation result depends on the network parameters, which need to be selected properly in accordance with the properties of the data information to be segmented. After several trial runs with different combinations of parameters and training slices, the sensor3D network was identified to perform best, and therefore, it was used for subsequent segmentation operations until no further improvement could be achieved (Figure 3).



Figure 3. CT volume slice of the scanned specimen before (**A**) and after segmentation (**B**). The colours represent the segmented classes: graphite (dark grey), high X-ray absorbing phases (particularly pyrrhotite, pyrite and accessories of zircon) (yellow) and the silicate matrix (pink).

The final model architecture is summarised in Table 3. In total, 6 frames were created, and the training time was 216 min. A total of 80% of the labelled data were selected by default for training the model and the remaining 20% for validating the model. Furthermore, the sensor3D model was trained for 20 epochs with early stopping enabled to avoid overfitting, whereby the model stopped automatically if the validation loss increased. The model applied reached a dice coefficient of 0.9971, which is an indicator of the model's accuracy.

Table 3. Model architecture of the DL network.
--

Model Parameter	Value	Explanation
Patch size	64	Size of the areas (patches) into which the input image is divided
Batch size	32	Input layer, defines number of patches being evaluated
Epochs per frame	20	One training operation
Stride-to-input ratio	0.1	Defines the position of the neighbouring patches
Dice score	0.9971	Measurement of the precision of a deep learning model based on the similarity of prediction and ground truth data

3. Results

3.1. Mineralogy and 2D Petrography

The flake graphite ore samples consist of a quartz-dominated matrix with plagioclase (anorthite and albite), microcline, biotite, pyrite and pyrrhotite as well as small quantities of rutile, clinochlore and clay minerals. Zircon is present as an accessory. Foliation structure is present primarily due to graphite and biotite \pm clinochlore arrangement. Graphite occurs as deformed euhedral–subhedral, platy-shaped crystals, varying in grain size from ~15 to 1900 µm, with most of the flakes >100 µm. The graphite particles are mostly disseminated in the matrix with some large particles attached to each other. Some flakes are deformed and broken apart along the cleavage plains. The grain boundaries of the flakes are of straight or polygonal structure. Quantities of rutile as well as pyrrhotite and pyrite are present as subhedral to euhedral crystals in the matrix. Both pyrite and pyrrhotite are occasionally attached to graphite flakes, where they may occur as elongated crystals along basal cleavage planes of graphite (Figure 4). Biotite is occasionally moderately replaced by clinochlore and mostly associated with graphite. Clay minerals are present along cracks, cleavages of feldspar and grain boundaries. Given the high quartz content, secondary minerals and foliation texture, the ore can be considered an altered graphite gneiss.

3.2. Computed Tomography

Figure 5 shows a CT volume slice from the scanned flake graphite ore sample. The assignment of grey values to their corresponding phases was based on the XRD, SEM-EDS and OM examinations. Graphite appears dark grey and can be recognised by its typical flaky shape. The phases with the brightest grey values are pyrites and pyrrhotites. In addition, two grey value ranges can be identified: (1) combined quartz, plagioclase and clay minerals, as well as (2) combined biotite, clinochlore and microcline feldspar. The differentiation between the individual minerals within the respective grey value ranges is not possible, as their grey values are too similar.

For the quantitative analysis of the CT data, the volume, aspect ratio and voxel count were calculated from the segmented classes. Based on these parameters, the graphite volume was refined so that particles wrongly labelled as graphite could be removed from the segmented data. To ensure that realistic grain shapes could be imaged, only particles <4.64 \times 4.64 \times 4.64 μ m (100 voxels) were considered for the analysis. A total of 1877 graphite particles were identified. The segmented volume comprises 533.99 mm³ and the graphite volume 19.77 mm³. This corresponds to a volumetric proportion of 3.7% graphite (Table 4).

Figure 6 shows the individual graphite particles (Figure 6A), comprising the sample as well as their volumetric distribution (Figure 6B) in 3D. Graphite flakes are aligned and occur mostly disseminated in the ore matrix. The flakes exhibit a subhedral to euhedral shape and vary in grain size. A few, and particularly larger, flakes are subparallel to parallel attached together.



Figure 4. OM (**A**,**B**), SEM images (**C**,**D**) and (**E**) XRD patterns of the flake graphite ore sample. (**A**) Parallel aligned graphite flakes intergrown with biotite. Graphite flakes are embedded in a silicate matrix comprising quartz, plagioclase (anorthite and albite), biotite and alkali feldspar (microcline). Secondary clay minerals occasionally replace plagioclase and appear along grain boundaries (transmitted light, PPL). (**B**) Disseminated super jumbo flake with intergrowth of pyrite and pyrrhotite along basal cleavage planes embedded in silicate matrix. Pyrite, pyrrhotite and rutile are also present as subhedral crystals (reflected light, PPL). (**C**) Disseminated parallel to subparallel oriented graphite flakes, partly deformed and broken apart along basal cleavage planes. (**D**) Graphite flake intergrown with a subhedral crystal of pyrrhotite. Note the colloform nodule of pyrite in the pyrrhotite grain. Abbreviations: Po = pyrrhotite, Py = pyrite, Qtz = quartz, Bt = biotite, Kfs = alkali feldspar, Plg = plagioclase, Rt = rutile, Cm = clay minerals, PPL = plane-polarised light.







Figure 6. Three-dimensional CT images of the cylindrical subvolume after segmentation: (**A**) colourcoded graphite particles and (**B**) volumetric distribution of the graphite flakes. The gangue minerals comprising the ore matrix are semitransparent. The cylinder has a diameter of 10.53 mm and a thickness of 8.21 mm.

Properties of the	e Subvolume
Length	8 mm
Diameter	10.53 mm
Volume cylinder	533.99 mm ³
Volume graphite	19.77 mm ³
Volume % graphite	3.7%
Number of graphite particles	1877

Table 4. Segmentation and analysis results of the sample.

To assess the quality of the sample based on the grain size distribution, the equivalent spherical diameter was calculated using the volume of each particle (Equation (1)).

$$ESD = \sqrt[3]{\frac{6 \times volume}{\pi}} \tag{1}$$

Figure 7A shows the cumulative in situ particle size distribution of graphite as determined by CT. In terms of particle numbers, small flakes represent the largest proportion of all particles, followed by amorphous and large flake particles (Figure 7B). In relation to the volume of all graphite particles, super jumbo flakes account for the highest proportion of all classes (Figure 7C). Properties of each class are summarised in Table 5.

The volumetric distribution of the classes is also illustrated in Figure 8. By highlighting the individual graphite classes (Figure 8B–E), it becomes apparent that especially the super jumbo and jumbo fractions are occasionally parallel to subparallel attached to each other. The other classes are predominantly disseminated throughout the matrix.



Figure 7. Distribution of graphite types according to CT measurements. (**A**) Cumulative particle analysis, (**B**) number of particles corresponding to each class and (**C**) volumetric proportion of each class in the sample.



Figure 8. Three-dimensional CT images of the segmented subvolume. (**A**) Volumetric distribution of the graphite flakes in terms of market-related classes comprising super jumbo size (red), jumbo (orange), large flake (yellow), medium flake (green), small flake (blue) and amorphous (violet). The gangue matrix is set fully transparent. A corresponding video is provided in Supplementary Materials. Figure 8B–E individual classes highlighted: (**B**) super jumbo size flakes, (**C**) jumbo flake graphite, (**D**) large flake graphite and (**E**) combined medium flake (green), small flake (blue) and amorphous graphite (violet).

	Amorphous	Small Flake	Medium Flake	Large Flake	Jumbo	Super Jumbo
Particles (n)	387	770	180	333	146	61
Particles (%)	20.62	41.02	9.59	17.74	7.78	3.25
Volume (mm ²)	0.05	0.55	0.42	2.23	4.4	12.13
Volume (%)	0.23	2.78	2.11	11.28	22.23	61.36

Table 5. Properties of the graphite classes determined.

Since graphite deposits can be very heterogeneous in terms of flake size and graphite content distribution, it is important to measure a large and representative sample volume. Figure 9 illustrates the distribution of graphite concentration from top to bottom in the cylindrical subvolume. For this purpose, the graphite concentration for each slice was measured by subtracting the segmented graphite area per slice from the area of the cylinder. In total, 1550 slices were measured, with a thickness of 0.0053 mm per slice. The graphite concentration varies significantly throughout the volume, from 2.46 to 6.97%. Particularly in the upper range of the subsample (slice 0 to 60), the graphite concentration is higher than in the rest of the sample, where the concentration varies from 2.46 to 4.66%.



Figure 9. Graphite content per slice of the cylindrical subvolume. The dashed horizontal line represents the average graphite concentration of 3.7%.

In addition to particle size distribution and graphite content, textural properties such as flake thickness or impurities also play an important role in the evaluation of a graphite ore. Figure 10 shows the analytical result of a single particle, exemplified by grain thickness. A jumbo flake with an ESD of 421 μ m and a volume of 0.04 mm³ was extracted from the segmented graphite volume, and for the thickness measurement, the particle volume was extracted to a surface mesh. The differences in the colour markings indicate the differences in thickness along the flake. The average thickness is 56 μ m. Further textural properties are listed in Table 6.



Figure 10. Jumbo flake after thickness measurement. The ESD of the flake is 421 μ m.

Table 6. Selected textural properties of an individual graphite flake.

Flake Pro	perties
Volume	0.04 mm ³
ESD	421 μm
Thickness (mean)	56 μm
Feret diameter (max)	1196 µm
Feret diameter (min)	497 μm
Surface area	2.3 mm^2

Figure 11 features a subhedral graphite flake associated with an iron sulfide grain. In contrast to the 2D image, the 3D image exhibits that the flake is not only attached to the iron sulfide but also intergrown with it.



Figure 11. Jumbo-sized flake associated with an iron sulfide mineral in 2D (**A**) and 3D (**B**). The CT volume slice (**A**) shows that the graphite flake is attached to the sulfide mineral. By contrast, the rendered 3D image (**B**) reveals that the sulfide mineral is intergrown with the graphite flake. The longest axis of the flake is 1690 μ m.

3.3. Comparison of 2D Petrographic Data with 3D CT Data

To evaluate the validity of the CT results, a modal mineralogy analysis obtained from optical microscopy analyses was compared with the topmost slice of the CT sample volume (Figure 12). This slice was not part of the segmented cylinder due to abundant imaging artefacts. The topmost slice was trained using the same DL strategies as described above. A set of microphotographs was stitched together to reveal the total surface of the polished section. The stitched image was processed using ORS Dragonfly, applying a global threshold operation. Thereby, the graphite content was measured by subtracting the area of segmented flakes from the total area (86.92 mm²). According to the OM analysis, the graphite content is 3.3%. The graphite content of the topmost CT volume slice is 2.99%, which is a difference of 9.39% compared to the OM measurement.



Figure 12. Segmentation result of the CT volume topmost slice and the stitched OM image. The rainbow-coloured scale shows the distribution of the longest axis of the individual flakes.

Details of graphite analyses as performed by OM and CT are given in Tables 7 and 8. A total amount of 169 graphite flakes were identified using OM (Table 7), whereas 156 flakes were identified in the topmost slice using CT imaging (Table 8). In particular, more amorphous and small flake grains were found with OM compared to CT. On the other hand, more jumbo flakes were identified in the topmost slice by CT. Overall, the relative proportion of graphite in each class is similar for both OM and CT, with the exception of the jumbo and amorphous classes (Figure 13).

Table 7. Physical	properties of	f graphite as	determined by	y OM in a	polished section.
-------------------	---------------	---------------	---------------	-----------	-------------------

	Amorphous	Small Flake	Medium Flake	Large Flake	Jumbo	Super Jumbo	Total
Particles (n)	26	20	11	31	25	56	169
Particles (%)	15.38	11.83	6.51	18.34	14.79	33.14	100
Area (mm ²)	0.02	0.04	0.04	0.09	0.24	2.44	2.87
Area (%)	0.63	1.44	1.27	3.07	8.50	85.09	100

Table 8. Physical properties of graphite as determined by CT in the topmost slice after segmentation.

	Amorphous	Small Flake	Medium Flake	Large Flake	Jumbo	Super Jumbo	Total
Particles (n)	22	20	10	20	35	49	156
Particles (%)	14.10	12.82	6.41	12.82	22.44	31.41	100
Area (mm ²)	0.02	0.06	0.05	0.15	0.44	1.87	2.60
Area (%)	0.77	2.43	1.78	5.96	16.90	72.16	100





4. Discussion

4.1. Graphite Characterisation

In recent years, an increasing number of scientific studies have recognised the utility of CT for ore characterisation [19–27]. Despite this, the application of CT to characterise graphite raw materials is limited, with prior studies having only provided rudimentary descriptions of graphite through the use of CT. Ren et al. examined drill cores of graphite ore using CT to distinguish minerals with high and low X-ray attenuation [47], while Fatima et al. analysed the spatial distribution of various ore minerals, including graphite, with CT [48].

Traditionally, information on graphite ore mineral properties is obtained by XRD, sieve analysis, SEM-EDS or OM examination, e.g., [16,49,50]. These methods provide liberation sizes with accuracies of $<120-150 \ \mu m$ [51]. SEM-based automated mineralogy has been recently introduced to establish more precise liberation information [16]. Furthermore, the method provides quantitative information on impurities, grain size distribution and modal mineralogy. MLA thereby extracts information on modal mineralogy on 2D surfaces and mineral associations, which are based on linear contacts and phases exposed at the samples' section surface. For ores with a heterogeneous grain size distribution, this may lead to erroneous information (Figure 9). Moreover, graphite is a very soft mineral and may be affected by mechanical abrasion during sample preparation [16]. This can result in misinterpretations of key textural features. CT, in contrast, as demonstrated in this study, can assess a more representative volume and modal mineralogy nondestructively without stereological bias.

Information on graphite impurities is vital. During graphite ore genesis, other minerals may be deposited between graphite layers, stacks or clusters. Such impurities are attached to flake surfaces or are trapped between flakes (intercalated) [52]. Impurities adhering to the surface can be detached from the flake surface by attrition, without significantly influencing flake size. Those impurities between the layers can only be removed by additional thermal or chemical processes, and such ore treatment methods are costintensive. Characterising impurities appropriately is therefore crucial to effectively remove this material. Such information on impurities (Figure 11), as provided by 3D CT imaging, allows the appropriate design of flow sheets for the beneficiation of graphite ores.

The results demonstrate that CT is an excellent addition to conventional methods such as XRD, OM and SEM to extract key microstructural information for assessing the quality of a graphite ore. While established techniques exhibit better resolutions and information on the gangue mineralogy, they do not present information about the real spatial distribution and volume fraction of graphite within ore samples. CT provides exceptional 3D microstructural data of graphite ore and a more representative characterisation of the quality demanding properties of graphite particles such as in situ grain size, grain size distribution, shape and impurities. In addition, the CT method enables precise measurement of individual flake thickness (as shown in Figure 10 and Table 6), which is important for predicting flake breakage during liberation. Thin flakes are more prone to breaking during comminution, making it more difficult to maximize their size. Knowledge on particle thickness therefore aids in selecting the appropriate comminution technique. Lastly, it is also possible to generate 3D information on individual grains and their impurities (Figure 11).

4.2. CT Data Acquisition

In order to acquire valid CT images and data on geological materials, the mineralogy of the samples needs to be known. Thus, CT cannot be used as a stand-alone technique. Mineralogical methods such as XRD and OM are required to acquire and interpret CT data. Moreover, CT operation requires an experienced operator to achieve appropriate results, particularly for the resolution of minerals with similar attenuation coefficients. The contrast of the grey-scale image in the CT depends on different factors such as X-ray energy applied, as well as the atomic number and density of the phases comprising the sample measured [31]. The choice of the optimal beam intensity to resolve all minerals is infinite. As the investigated ore is rich in heavy minerals such as pyrite and pyrrhotite, it would have required high beam intensities for adequate X-ray penetration to prevent artefacts. This, however, decreases the X-ray absorption capacity of the lower absorbing minerals such as graphite, and silicates, because the attenuation using X-ray energies >100 kV is more sensitive to the mineral's density [38]. Choosing lower X-ray energies would have increased the attenuation differences between lower absorbing fraction (Figure 1) as it is more sensitive to the atomic number [39], but it would have also increased beam hardening, particularly due to the presence of the iron sulfides. A possible solution to achieve high contrasts of the low X-ray attenuating minerals and to minimise beam hardening would be to combine multiple scans with different X-ray intensities. However, as the primary goal was to differentiate graphite from the gangue material, the acquisition parameter selected to image the graphite ore showed a good balance between contrast and beam hardening prior to the high absorbing phases. Thus, it was possible to differentiate between graphite, pyrite, pyrrhotite, rutile and silicate matrix based on the grey-scale contrast of the CT image.

Even though good scan quality was achieved, minerals may exhibit a large range of grey-scale values due to the polychromatic nature of X-rays and the co-occurrence of minerals with different X-ray attenuation. Reliable mineral segmentation of CT data, particularly of complex rock samples such as the specimen used for this study, is therefore challenging. However, using the deep learning algorithms for segmentation as featured by ORS Dragonfly, segmentation of minerals does not solely rely on grey value contrast, as it also considers textural features such as grain shape. By providing the DL model sufficient training data, it was possible to differentiate between areas exhibiting the same grey values. Such areas also contained imaging artefacts, produced by high-absorbing sulfide minerals (Figure 5) as well as gangue material.

The accuracy of the segmentation method, however, may be limited due to certain factors. The first factor is the partial volume effect (PVE) [31]. If a single voxel consists of more than one phase, the CT number represents the average of the X-ray attenuation of all phases present. Consequently, all particles below voxel size are affected by the PVE and cannot be imaged. Directly related to the PVE is the blurring of the CT data, particularly in samples with phases of large attenuation differences, as in the investigated specimen [53]. Blurring complicates the quantitative interpretation of CT data, particularly at grain boundaries and for small particles, as it causes each voxel to contain portions of the surrounding voxels. Consequently, phases approaching the spatial resolution of the CT

data also contain voxels that reflect the surrounding material. Segmentation will therefore lead to an over- or underestimation of the labelled volume [54]. One way to minimise the effect is to increase the image resolution, but this comes at the cost of sample size. Another method is to refine the segmentation result by eroding or dilating the segmented volume. However, it is not possible to fully eliminate these artefacts as they originated from the voxelised data themselves. In addition to imaging artefacts, another source of error is derived from the manual segmentation process that must be conducted to provide the training data and at the inference stage. These are the most exhausting steps, and there will inevitably be some inadvertent errors in labelling among the large number of pixels (4096 × 4096) comprising each slice. Consequently, there will be some judgement errors for pixels located at grain boundaries and those reflecting small particles, due to the above mentioned PVE and blur artefacts but also regardless of them. Therefore, to minimise this bias, only graphite flakes comprising >100 voxels (ca. 25 μ m ESD) were considered for the analysis.

A comparison of the topmost CT sample slice with the stacked OM image shows good agreement in terms of graphite content, number of particles and grain size distribution. However, several factors must be considered that hinder a direct comparison. Due to blurring, a complete overlap of the two cut surfaces was not possible. Further, the slight difference in the size of individual flakes (Figure 12) and number of jumbo flakes, large flakes and super jumbo flakes (Tables 6 and 7) may be explained by the fact that some flakes were not yet connected to the 2D radiograph and/or were incorrectly identified as two separate or one entire grain, respectively, because of the PVE. The PVE also affects the calculation of the total graphite content, as it results in an under- or overestimation of the segmented surface, as mentioned above. The lower number of identified amorphous flakes in the CT image can be attributed to both the scanning resolution and the PVE. Lastly, the slice was not part of the segmented volume as it represents the topmost slice of the cylinder. As mentioned above, the topmost slice is more affected by artefacts than inner slices. Surfaces that are parallel to the X-ray beam at the top and bottom of the sample will not penetrate properly, which will lead to image artefacts and thus a lack of detail in the data. Consequently, to be able to include the topmost slice in the volume, the scanning geometry should be mounted at a slight angle to avoid parallel alignment of the circular base and top surfaces of the cylinder to the X-ray beam. This reduces artefacts and thus enables a better comparison.

5. Conclusions

This study explored the use of CT for establishing the physical properties of graphite in geological ores. The results reveal that CT is a valid and innovative technique that can be effectively used to characterise graphite. It enables nondestructive, in situ 3D visualisation and provides quantitative information on critical mineralogical aspects such as flake size, flake size distribution, shape and impurities that cannot be determined with other currently available analytical tools.

Given that graphite raw materials should be assessed by their mineralogical properties [9–11,13], the additional information provided by CT should allow improved resource recovery and beneficiation processes. By obtaining in situ information on flake size, flake size distribution and flake thickness before and after comminution, the yield of the process may be quantified. Thus, CT can provide information on ore characteristics and impurities in 3D, which may help to further improve the process design.

Prior knowledge on the samples' mineralogy is required to appropriately acquire quantitative CT data and allow the possibility of differentiating between similar attenuating phases. Furthermore, the resolution of CT is not as high as, for example, OM or SEM-EDS. Against this background, CT cannot be used as a stand-alone technology. Hence, in combination with traditional methods, CT analyses allow for an improved understanding of graphite ores and products.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min13020247/s1, Video S1: Graphite classes.

Author Contributions: Conceptualisation, L.T.K.; methodology, L.T.K.; formal analysis, L.T.K.; investigation, L.T.K. and X.L.; data curation, L.T.K.; writing—original draft preparation, L.T.K.; writing—review and editing, L.T.K. and B.G.L.; visualisation, L.T.K.; project administration, L.T.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Exploratory Research Space of the RWTH Aachen University, grant number SFUoA001.

Data Availability Statement: Data supporting the findings of this study will be made available from the corresponding author, upon reasonable request.

Acknowledgments: The authors thank NGS Trading & Consulting GmbH for providing the sample used in this study. The authors are also grateful to four anonymous reviewers for their helpful and constructive feedback.

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

References

- 1. Chung, D.D.L. Review Graphite. J. Mater. Sci. 2002, 37, 1475–1489. [CrossRef]
- 2. Pierson, H.O. Handbook of Carbon, Graphite, Diamonds and Fullerenes: Processing, Properties and Applications; William Andrew: Norwich, NY, USA, 2012; ISBN 9780815517399.
- 3. Bessel, C.A.; Laubernds, K.; Rodriguez, N.M.; Baker, T.K. Graphite Nanofibers as an Electrode for Fuel Cell Applications. *J. Phys. Chem. B* 2001, *105*, 1115–1118. [CrossRef]
- 4. European Commission. Study on the EU's list of Critical Raw Materials; European Commission: Luxembourg, 2020.
- U.S. Geological Survey. List of Critical Minerals. Available online: https://www.usgs.gov/news/national-news-release/usgeological-survey-releases-2022-list-critical-minerals (accessed on 19 December 2022).
- 6. U.S. Geological Survey. Mineral Commodity Summaries—Graphite; USGS: Reston, VA, USA, 2022.
- 7. Simandl, G.J.; Paradis, S. Graphite deposit types, their origin, and economic significance. *Br. Columbia Minist. Energy Mines Br. Colomb. Geol. Surv.* 2015, *3*, 163–171.
- 8. Luque, F.J.; Huizenga, J.-M.; Crespo-Feo, E.; Wada, H.; Ortega, L.; Barrenechea, J.F. Vein graphite deposits: Geological settings, origin, and economic significance. *Min. Depos.* 2014, 49, 261–277. [CrossRef]
- Chehreh Chelgani, S.; Rudolph, M.; Kratzsch, R.; Sandmann, D.; Gutzmer, J. A Review of Graphite Beneficiation Techniques. *Miner. Process. Extr. Metall. Rev.* 2016, 37, 58–68. [CrossRef]
- 10. Jara, A.D.; Betemariam, A.; Woldetinsae, G.; Kim, J.Y. Purification, application and current market trend of natural graphite: A review. *Int. J. Min. Sci. Technol.* 2019, 29, 671–689. [CrossRef]
- 11. Damm, S. *Rohstoffrisikobewertung—Graphit*; Deutsche Rohstoffagentur (DERA) in der Bundesanstalt für Geowissenschaften und Rohstoffe (BGR): Berlin, Germany, 2021; ISBN 3948532486.
- 12. Moradi, B.; Botte, G.G. Recycling of graphite anodes for the next generation of lithium ion batteries. *J. Appl. Electrochem.* **2016**, *46*, 123–148. [CrossRef]
- 13. Scogings, A. Graphite: Where size matters. Aust. Paydirt 2015, 1, 78–79.
- 14. Dill, H.G.; Kus, J.; Goldmann, S.; Suárez-Ruiz, I.; Neumann, T.; Kaufhold, S. The physical-chemical regime of a sulfide-bearing semi-graphite mineral assemblage in metabasic rocks (SE Germany)—A multidisciplinary study of the missing link between impsonite and graphite. *Int. J. Coal Geol.* **2019**, *214*, 103262. [CrossRef]
- 15. Crespo, E.; Luque, F.J.; Barrenechea, J.F.; Rodas, M. Influence of grinding on graphite crystallinity from experimental and natural data: Implications for graphite thermometry and sample preparation. *Mineral. Mag.* **2006**, *70*, 697–707. [CrossRef]
- 16. Sandmann, D.; Haser, S.; Gutzmer, J. Characterisation of graphite by automated mineral liberation analysis. *Miner. Process. Extr. Metall.* **2014**, *123*, 184–189. [CrossRef]
- 17. Al-Ani, T.; Leinonen, S.; Ahtola, T.; Salvador, D. High-Grade Flake Graphite Deposits in Metamorphic Schist Belt, Central Finland—Mineralogy and Beneficiation of Graphite for Lithium-Ion Battery Applications. *Minerals* **2020**, *10*, 680. [CrossRef]
- 18. Spencer, S.; Sutherland, D. Stereological correction of mineral liberation grade distributions estimated by single sectioning of particles. *Image Anal. Stereol.* 2000, *19*, 175–182. [CrossRef]
- 19. Kyle, J.R.; Ketcham, R.A. In situ distribution of gold in oes using high resolution X-ray computed tomography. *Econ. Geol.* 2003, 98, 1697–1701. [CrossRef]
- 20. Kyle, J.R.; Mote, A.S.; Ketcham, R.A. High resolution X-ray computed tomography studies of Grasberg porphyry Cu-Au ores, Papua, Indonesia. *Min. Depos.* **2008**, *43*, 519–532. [CrossRef]
- 21. Chisambi, J.; von der Heyden, B.P.; Tshibalanganda, M.; Le Roux, S.G. Gold Exploration in Two and Three Dimensions: Improved and Correlative Insights from Microscopy and X-Ray Computed Tomography. *Minerals* **2020**, *10*, 476. [CrossRef]

- Dominy, S.C.; Platten, I.M.; Howard, I.E.; Elangovan, P.; Armstrong, R.; Minnitt, R.C.A.; Abel, R.L. Characterisation of gold ores by X-ray computed tomography—Part 2: Applications to the determination of gold particle size and distribution. In Proceedings of the 1st AusIMM International Geometallurgy Conference, Brisbane, Australia, 5–7 September 2011; pp. 293–309.
- 23. Ghorbani, Y.; Becker, M.; Petersen, J.; Morar, S.H.; Mainza, A.; Mainza, J.-P. Use of X-ray computed tomography to investigate crack distribution and mineral dissemination in sphalerite ore particles. *Miner. Eng.* **2011**, *24*, 1249–1257. [CrossRef]
- 24. Godel, B.; Barnes, S.J.; Barnes, S.-J.; Maier, W.D. Platinum ore in three dimensions: Insights from high-resolution X-ray computed tomography. *Geology* **2010**, *38*, 1127–1130. [CrossRef]
- Godel, B. High-Resolution X-Ray Computed Tomography and Its Application to Ore Deposits: From Data Acquisition to Quantitative Three-Dimensional Measurements with Case Studies from Ni-Cu-PGE Deposits. *Econ. Geol.* 2013, 108, 2005–2019. [CrossRef]
- 26. Sittner, J.; Brovchenko, V.; Siddique, A.; Buyse, F.; Boone, M.; Renno, A.D.; Cnudde, V. Three-Dimensional Distribution of Platinum Group Minerals in Natural MSS-ISS Ores From the Norilsk One Deposit, Russia. *Front. Earth Sci.* 2022, 10. [CrossRef]
- 27. Le Roux, S.G.; Du Plessis, A.; Rozendaal, A. The quantitative analysis of tungsten ore using X-ray microCT: Case study. *Comput. Geosci.* 2015, *85*, 75–80. [CrossRef]
- Rozendaal, A.; Le Roux, S.G.; Du Plessis, A.; Philander, C. Grade and product quality control by microCT scanning of the world class Namakwa Sands Ti-Zr placer deposit West Coast, South Africa: An orientation study. *Miner. Eng.* 2017, 116, 152–162. [CrossRef]
- 29. Mees, F.; Swennen, R.; van Geet, M.; Jacobs, P. *Applications of X-Ray Computed Tomography in the Geosciences*; Geological Society: London, UK, 2003; ISBN 1862391394.
- Jerram, D.A.; Mock, A.; Davis, G.R.; Field, M.; Brown, R.J. 3D crystal size distributions: A case study on quantifying olivine populations in kimberlites. *Lithos* 2009, 112, 223–235. [CrossRef]
- 31. Kyle, J.R.; Ketcham, R.A. Application of high resolution X-ray computed tomography to mineral deposit origin, evaluation, and processing. *Ore Geol. Rev.* 2015, *65*, 821–839. [CrossRef]
- Jerram, D.A.; Higgins, M.D. 3D Analysis of Rock Textures: Quantifying Igneous Microstructures. *Elements* 2007, 3, 239–245. [CrossRef]
- 33. Gualda, G.A.R.; Rivers, M. Quantitative 3D petrography using x-ray tomography: Application to Bishop Tuff pumice clasts. J. *Volcanol. Geotherm. Res.* **2006**, 154, 48–62. [CrossRef]
- Vásrhelyi, L.; Kónya, Z.; Kukovecz, Á.; Vajtai, R. Microcomputed tomography-based characterization of advanced materials: A review. *Mater. Today Adv.* 2020, 8, 100084. [CrossRef]
- 35. Cnudde, V.; Boone, M.N. High-resolution X-ray computed tomography in geosciences: A review of the current technology and applications. *Earth-Sci. Rev.* 2013, 123, 1–17. [CrossRef]
- 36. Berger, M.J.; Hubbell, J.H.; Seltzer, S.M.; Chang, J.; Coursey, J.S.; Sukumar, R.; Zucker, D.S.; Olsen, K. X-COM: Photon Cross Sections Database. Available online: http://physics.nist.gov/PhysRefData/Xcom/Text/XCOM (accessed on 5 December 2022).
- 37. van Grieken, R.; Markowicz, A. Handbook of X-Ray Spectrometry; CRC Press: Boca Raton, FL, USA, 2001; ISBN 9780203908709.
- Hsieh, J. Computed Tomography: Principles, Design, Artifacts, and Recent Advances; SPIE Press: Bellingham, WA, USA, 2003; ISBN 9780819444257.
- Ketcham, R.A.; Carlson, W.D. Acquisition, optimization and interpretation of X-ray computed tomographic imagery: Applications to the geosciences. *Comput. Geosci.* 2001, 27, 381–400. [CrossRef]
- 40. Volume Graphics GmbH. VGSTUDIO MAX 3.5; Volume Graphics GmbH: Heidelberg, Germany, 2021.
- 41. Object Research Systems. Dragonfly; Object Research Systems: Montreal, QC, Canada, 2021.
- 42. Zhou, Z.-H. *Machine Learning*; Springer Nature: Berlin/Heidelberg, Germany, 2021; ISBN 9789811519673.
- Li, X.; Zhang, G.; Li, K.; Zheng, W. Deep Learning and Its Parallelization. In *Big Data: Principles and Paradigms*; Buyya, R., Calheiros, R.N., Dastjerdi, A.V., Eds.; Elsevier: Cambridge, MA, USA; Morgan Kaufmann: Burlington, MA, USA, 2016; pp. 95–118. ISBN 978-0-12-805394-2.
- 44. Breiman, L. Random Forests. Mach. Learn. 2001, 45, 5–32. [CrossRef]
- Ronneberger, O.; Fischer, P.; Brox, T. U-Net: Convolutional Networks for Biomedical Image Segmentation. In Proceedings of the International Conference on Medical image computing and computer-assisted intervention, Munich, Germany, 5–9 October 2015; pp. 234–241.
- 46. Novikov, A.; Major, D.; Wimmer, M.; Lenis, D.; Bühler, K. Deep Sequential Segmentation of Organs in Volumetric Medical Scans. *IEEE Trans. Med. Imaging* **2019**, *38*, 1207–1215. [CrossRef]
- 47. Ren, Y.; Li, J.; Sun, X.; Li, Z.; Sun, Z. Genesis of Metal Sulfides and Its Significance on Graphite Mineralization in the Huangyangshan Graphite Deposit, East Junggar, Xinjiang Province, China. *Minerals* **2022**, *12*, 1450. [CrossRef]
- Fatima, A.; Venkatesh, A.S.; Mukherjee, R.; Agrawal, A.K.; Singh, B.; Sarkar, P.S.; Kashyap, Y.; Shripathi, T. 3D spatial distribution of ore mineral phases using high resolution synchrotron micro-computed tomography (μCT) combined with optical microscopy. *Appl. Radiat. Isot.* 2019, 148, 49–59. [CrossRef]
- 49. Jara, A.D.; Woldetinsae, G.; Betemariam, A.; Kim, J.Y. Mineralogical and petrographic analysis on the flake graphite ore from Saba Boru area in Ethiopia. *Int. J. Min. Sci. Technol.* **2020**, *30*, 715–721. [CrossRef]
- 50. Zhang, X.; Zhang, L.Y.; Qiu, Y.S.; Qu, X. Beneficiation of a Low-Grade Flaky Graphite Ore from Australia by Flotation. *AMR* **2015**, 1090, 188–192. [CrossRef]

- 51. Mitchell, C.J. *Industrial Minerals Laboratory Manual: Flake Graphite;* Technical Report WG/92/30; British Geological Survey: Nottingham, UK, 1993; p. 31.
- 52. Kim, B.G.; Choi, S.K.; Park, C.L.; Chung, H.S.U.N.; Jeon, H.S.O. Inclusion of Gangue Mineral and Its Mechanical Separation from Expanded Graphite. *Part. Sci. Technol.* **2003**, *21*, 341–351. [CrossRef]
- 53. Hanna, R.D.; Ketcham, R.A. X-ray computed tomography of planetary materials: A primer and review of recent studies. *Geochemistry* 2017, 77, 547–572. [CrossRef]
- 54. Ketcham, R.A. Accurate three-dimensional measurements of features in geological materials from X-ray computed tomography data. In *Advances in X-ray Tomography for Geomaterials;* Desrues, J., Viggiani, G., Bésuelle, P., Eds.; ISTE: London, UK, 2006; pp. 143–148.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.



Article The Effect of Silicon-Containing Minerals on Coal Evolution at High-Temperature Pre-Graphitization Stage

Yan Shao¹, Shaoqing Wang^{1,*} and Xueqi Li^{1,2}

- ¹ School of Geosciences and Surveying Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China
- ² Wulanmulun Coal Mine, CHN Energy Shendong Coal Group, Ordos 017205, China
- * Correspondence: wangzq@cumtb.edu.cn

Abstract: Coal is a carrier of carbon enrichment, so it has the potential for the preparation of coalbased carbon materials. In this paper, LT anthracite and TSG bituminous coal were selected, and the corresponding graphitized samples were prepared from high-temperature treatment. The effects of silicon-containing minerals on coal evolution during the high-temperature pre-graphitization stage were investigated by XRD, Raman spectroscopy, and SEM. The results showed that with increasing temperature, the silicon-containing samples showed smaller d_{002} and ID_1/IG , and higher L_c , while L_a presented a slight increase. It was found by SEM that the micromorphology of all samples was mainly massive structures. Meanwhile, irregular polyhedral structures also were observed in silicon-containing samples at 1300 °C, which were related to the formation and deposition of SiC. The carbothermal reactions of silicon-containing minerals continued to generate SiC and precipitate with increasing temperature, resulting in the gradual transformation of the needle-like structures into polyhedral structures. However, SiC was completely decomposed at 2800 °C. These changes indicated that during the pre-graphitization stage, silicon-containing minerals form SiC to advance the reduction of the interlayer spacing and the increase of longitudinal layer stacking height, thereby enhancing structural ordering and graphitization degree, while it had less effect on the lateral size. This will help to further understand the role of silicon-containing minerals in the coal pregraphitization stage and also provide useful information about synthetic coal-based graphite.

Keywords: coal; silicon-containing minerals; pre-graphitization stage; structural evolution; micromorphology

1. Introduction

Graphite has been applied in the electrode, chemical, biomedical, refractory, and other traditional industries because of its special structures and excellent properties [1–4]. With further research on graphite, it will be used for new energy, precision electronic components, nuclear and aerospace, and has become an important strategic resource to support the development of high technology fields [3–7]. Graphite can be divided into natural graphite and artificial graphite. Natural graphite has more intergrowth minerals, and the disseminated grain size is very small [8]; therefore, it is difficult for natural graphite to be sorted and purified, which greatly limits the utilization of natural graphite. Furthermore, with the increase in the price of natural graphite, the utilization of large-scale graphite resources is affected by the cost [3]. Thus, it is necessary to make reasonable use of natural graphite and explore suitable materials to develop artificial graphite. Compared with natural graphite, artificial graphite is usually made of organic carbon materials through high-temperature carbonization and graphitization, which has better performance and adjustability due to the influence of raw materials and temperature [2,4,7].

Coal is a carbon-rich material, and the heteroatoms and small molecular compounds are continuously removed, and the final product of evolution is graphite under the combined effect of stratigraphic temperature and pressure [9–11]. Thus, it is a good precursor for



Citation: Shao, Y.; Wang, S.; Li, X. The Effect of Silicon-Containing Minerals on Coal Evolution at High-Temperature Pre-Graphitization Stage. *Minerals* 2023, *13*, 20. https://doi.org/ 10.3390/min13010020

Academic Editor: John A. Jaszczak

Received: 8 November 2022 Revised: 17 December 2022 Accepted: 19 December 2022 Published: 23 December 2022



Copyright: © 2022 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/). preparing artificial graphite and has great potential in the future. A number of researchers have paid more attention to the graphitization of coal and obtained great results [12–20]. Franklin experimentally confirmed that anthracite was graphitizable above 2500 °C [21]. Atria et al. [13] studied the structural ordering of three Pennsylvania anthracites at different heat-treated temperatures and reported that the temperature of 2700 °C may be a "graphitization jump", indicating that temperature played an important role during coal graphitization. By studying anthracite heated at high ambient pressure at temperatures up to 2800 °C, Bustin et al. [22] reported that graphite began to appear at temperatures as low as 600 °C, suggesting that the pressure compensated for the partial strain energy of coal graphitization. Cao et al. [23] concluded that temperature was the fundamental driving force for coal graphitization and the tectonic stress shortened the time of graphitization. Zhang et al. [24] proposed the formation of graphite-like structures was a successive process during high-temperature graphitization of coal, followed by carbonization (<1000 °C), secondary carbonization and pre-graphitization (1000~2000 °C), and graphitization (>2000 °C). The reflectance of vitrinite (R_0) is one of the important parameters to characterize the degree of coalification. The extension of basic structural units in coal sharply increases, which marks the end of coalification and the beginning of graphitization [9,25]. The turbostratic structures begin to evolve into ordered structures when $d_{002} = 0.334$ nm, which is also regarded as the starting point of graphitization [26]. In addition, d₀₀₂ is usually used to divide graphite (<0.338 nm), semi-graphite (0.338~0.340 nm), semi-anthracite (0.340~0.348 nm), and anthracite (>0.344 nm) [9,24].

Besides the treatment temperature and pressure, some characteristics of anthracite have been explored to influence its graphitization process. Among them, minerals have been considered graphitization catalysts [2,6,7,27–31]. Baraniecki et al. [32] found that the addition of iron or ferrosilicon particles considerably reduced the temperature at which coal graphitization occurs. Pappano et al. [28,33] found that the minerals that played a key role during coal graphitization were similar to those contained in high-quality graphite deposits. Lin et al. [34] systematically studied the graphitization process of a graphite block doped with Si and Ti by HRTEM at the atomic scale and proposed the related catalytic mechanisms. Liu et al. [35] reported that the transformation of creating silicon carbide above 1300 °C in carbothermal reduction played a significant catalytic role in the graphite structure of the coal. Li et al. [36] discussed the catalytic graphitization process of coke carbon with iron and pointed out that the carbon dissolution–graphite precipitation mechanism could explain this process very well.

Although many studies have been conducted on coal graphitization, there is still a lack of systematic research on the influence of silica-containing minerals at the coal pregraphitization stage. In this paper, quartz has been added into demineralized coal as a typical silicon-containing mineral for preparing silicon-containing samples. Longtan No. 6 (LT) anthracite and Tangshangou No. 12 (TSG) bituminous coal were selected, and the related raw coal, demineralized coal, and quartz-added demineralized coal were prepared for high-temperature treatment. XRD, Raman spectroscopy, and SEM were applied to analyze the structural evolution of samples. Based on the above analysis, we also tried to further understand the role of silicon-containing minerals on coal pre-graphitization. The findings of this work provide new ideas for the research of coal-based graphite and the clean efficient utilization of coal. It will also be of great practical significance to improve the added value and resource utilization of coal resources.

2. Samples and Methods

2.1. Sample Selection and Preparation

The experimental coal samples were anthracite collected from the Longtan No. 6 coal seam (LT) and bituminous coal from the Tangshangou No. 12 coal seam (TSG) according to the Chinese National Standard GB/T 482-2008. The samples were crushed into 18 meshes to make polished grain mounts for the mean maximum vitrinite reflectance (R_o) measurement, 80 meshes for proximate and ultimate analysis, and 200 meshes for demineralization and

high-temperature experiments. Table 1 lists the results of R_o proximate and ultimate analyses of the samples. For LT raw coal, the minerals were mainly quartz, chlorite-serpentine, kaolinite, calcite, and a small amount of granular pyrite, while the minerals in TSG raw coal were dominated by kaolinite, quartz, and pyrite. The raw coal samples were called TL6 and TSG12, respectively. The demineralization of raw coal was treated via a series of acid treatments (HF and HCl solutions) and was marked as LT6T and TSG12T, respectively. The detailed procedure for demineralization was described in previous work [5]. After demineralized treatment, the silicon-containing minerals were almost removed from raw coal.

Table 1. Basic parameters of coal sa	mple
--------------------------------------	------

$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Sample R _o		Prox	imate Analys	is (%)	Ultimate Analysis (wt.%, daf)				
LT 5.67 3.64 19.76 4.96 94.90 1.18 2.79 0.56 TSG 1.02 2.37 18.23 32.08 83.65 3.91 10.93 0.90	ownpre	10	M _{ad}	A _d	V _{daf}	С	Н	0 *	Ν	S
TSG 1.02 2.37 18.23 32.08 83.65 3.91 10.93 0.90	LT	5.67	3.64	19.76	4.96	94.90	1.18	2.79	0.56	0.56
	TSG	1.02	2.37	18.23	32.08	83.65	3.91	10.93	0.90	0.60

M: moisture; A: ash; V: volatile; ad: air dry; d: dry; daf: dry ash free; C: carbon; H: hydrogen; O: oxygen; N: nitrogen; St: total sulfur. * By difference.

Quartz, a typical silicon-containing mineral, was selected to explore the effect of the silicon-containing minerals on the coal pre-graphitization stage. To better observe its role, the quartz was ground into 200 mesh and then thoroughly mixed with the demineralized coal at the mineral mixing ratio of 10%, which were individually called LT6T-Q and TSG12T-Q.

2.2. High-Temperature Treatment

The final temperature of the high-temperature treatment was set as 1300 °C, 1450 °C, 1600 °C, 1900 °C, and 2800 °C, respectively. Every 5 g of the sample within a graphite crucible was placed in a medium-frequency induction graphitization furnace and heated to the final temperature. The heating rate was controlled at 10 °C/min and the temperature was maintained for 3 h after reaching the final temperature. To avoid interference with atmospheric factors such as air, argon was used to preserve the sample during the whole heating process. Then, treated samples were sealed and stored for further analysis and testing.

2.3. X-ray Diffraction

The XRD data collection was recorded by a D8 ADVANCE diffractometer with CuK α radiation. The operating conditions of the X-ray tube: I = 10 mA, U = 30 kV. Powdered samples were scanned from 10° to 80° in the 2 θ range with a 0.02° step interval and a 0.012 θ step width. The average lateral size (L_a), stacking height (L_c), and interlayer spacing (d₀₀₂) of the average crystallite structures have been established as XRD structural parameters. The d₀₀₂ was determined by Bragg's Equation (1), and L_a and L_c were calculated by Scherrer Equations (2) and (3), respectively. The relevant equations are as follows:

$$d_{002} = \lambda / 2\sin\theta_{002} \tag{1}$$

$$L_c = 0.89\lambda/\beta_{002}\cos\theta_{002} \tag{2}$$

$$L_a = 1.84\lambda/\beta_{100}\cos\theta_{100} \tag{3}$$

The λ is the wavelength of the radiation used, which is 0.154056 nm in this experiment. θ_{002} and θ_{100} are the positions of the peaks of 002 and 100, respectively, and β_{002} and β_{100} are the peak width at half height of the peaks of 002 and 100, respectively.

2.4. Raman Spectroscopy

Raman spectra were measured using a Renishaw Invia Raman spectrometer with microscopy, equipped with $10 \times$ and $50 \times$ objectives. Raman spectra were excited by an

argon ion laser (532 nm) with the experiment power of 50 mW. The sample was scanned in the range of $100\sim3500$ cm⁻¹. Each measurement was accumulated 10 times to reduce noise in average spectra, and the data acquisition time for each spectrum was 20 s. To obtain further data, peak separation Raman spectroscopy analysis was carried out using the Origin software.

2.5. SEM/EDS

SEM examination was used to observe the microstructure characteristics of samples under different heating temperatures by using a SU8220 field emission scanning electron microscope with a magnification of up to 800,000 times and an acceleration voltage of 3~5 kV. Then, the samples treated with 1300 °C, 1900 °C, and 2800 °C were observed by SEM.

3. Results and Discussion

3.1. Mineral Features at the Pre-Graphitization Stage

The XRD profiles of the selected samples are illustrated in Figure 1. Similar to the results reported by other authors [37-39], each XRD profile has two obvious peaks in the range of $10/15 \sim 30^{\circ}$ and $40 \sim 50^{\circ}$ (2 θ), corresponding to the 002 and 100 peaks, respectively. The 002 and 100 peaks individually correlated to the stacking of aromatic layers and the extension of the aromatic molecules in the plane of the layers [40]. The 002 peak of the graphite is symmetrical and sharp [41], but for coal, the shape of the 002 peak was broad and asymmetric, and the intensity of the 002 peak was higher than that of the 100 peak, which was attributed to the γ peak on its left-hand side. The γ peak was associated with the aliphatic side chains or also assigned to the irregular packing of buckled aromatic layers [38,42]. As seen in Figure 1, all samples showed broad 002 and 001 peaks at 1300 °C. From 1300 °C to 1900 °C, the position of the 002 peak shifted to higher angles, the shape became sharper and the intensity increased with increasing temperature. When the temperature reached 2800 °C, only the characteristic graphite peaks—such as the 002, 100, 101, and 004 peaks—were observed in the XRD profile. The clear appearance of the (004) peak, a nearly three-dimensional crystalline order structure in coal-based graphite samples is supposed to exist [41]; however, the difference between the samples was the mineral peaks formed.

For LT6 (Figure 1a), the β -SiC and Fe₃Si peaks were found in the XRD profile at 1300 °C and existed almost in the range of 1300~1900 °C, while they disappeared at 2800 °C. However, there was only Fe₃Si in TL6T at 1300 °C and presented at 1300~1900 °C (Figure 1c). Up to 2800 °C, the XRD spectrum of LT6T also exclusively observed the characteristic peaks of graphite, which was similar to LT6. The XRD patterns of TSG12 showed significantly similar features to LT6 as the temperature increased (Figure 1b), whereas Fe was observed in TSG12T at 1300 °C and decomposed higher than 1900 °C (Figure 1d). For two quartzadded demineralized samples, their XRD patterns presented similar evolution trends with increasing temperature, shown in Figure 1e,f. It can be seen that β -SiC and Fe₂Si were characterized in both quartz-added samples at 1300 °C and were continuously observed at the pre-graphitization stage. Similarly, only graphite characteristic peaks were found at 2800 °C. Therefore, it can be inferred that the original minerals were transformed to form new silicon-containing minerals (such as SiC and Fe₃Si) during the pre-graphitization process, promoting the development of graphitization [11,32]. After demineralization treatment, the silicon was removed, and some Fe reacted with carbon to produce austeniticlike structures in TSG12T. As the temperature gradually increased, austenitic-like structures were removed and only the coal-based graphite was left in the reaction system. However, the Fe₃Si observed in LT6T may be attributed to incomplete demineralization. For quartzadded demineralized coal, SiC was generated by the reduction of quartz, and Fe₃Si was converted into Fe₂Si due to the excess of silicon at 1300 °C. This process also kept occurring within the pre-graphitization stage. When the temperature reached 2800 °C, the SiC peaks disappeared and the graphite peaks were clearly observed.



Figure 1. XRD patterns of samples at different temperatures. (**a**) LT6; (**b**) TSG12; (**c**) LT6T; (**d**) TSG12T; (**e**) LT6T-Q; (**f**) TSG12T-Q.

3.2. *Chemical Structural Evolution during the Pre-Graphitization Stage* 3.2.1. XRD Analysis

XRD is a non-destructive technique to determine the stacking structure in carbon materials for reflecting the graphitization degree of carbonaceous materials [39,43]. To obtain accurate structural parameters, the 002 and 100 peaks were peak-fitted and the calculated structural parameters (d_{002} , L_c , L_a) of different samples are shown in Figure 2.



Figure 2. Comparison of XRD structure parameters at different temperatures. d₀₀₂: (**a**) LT6, LT6T, TSG12, and TSG12T; (**b**) LT6T, LT6T-Q, TSG12T, and TSG12T-Q; L_c: (**c**) LT6, LT6T, TSG12, and TSG12T; (**d**) LT6T, LT6T-Q, TSG12T, and TSG12T-Q; L_a: (**e**) LT6, LT6T, TSG12, and TSG12T; (**f**) LT6T, LT6T-Q, TSG12T and TSG12T-Q.

The parameter d_{002} is a measure of the perfection in the stacking structure periodicity [38]. The d_{002} values of all samples showed a decreasing trend with the increase in temperature (Figure 2a,b). Compared with raw coal and demineralized coal, the d_{002} of LT6 and TSG12 at the pre-graphitization stage was always correspondingly smaller than that of LT6T and TSG12T, respectively (Figure 2a). At 1900 °C, the d_{002} of LT6 was closer to 0.3440 nm, making the beginning of the graphitization of coal [44]. Up to 2800 °C, the d_{002} of LT6 and LT6 reached almost the same value, while the d_{002} of TSG12T was slightly larger than that of TSG12. In Figure 3b, the d_{002} of demineralized coals was also larger than that of the corresponding quartz-added coals at the pre-graphitization stage and then tended to be the same at 2800 °C. This indicated that silicon-containing minerals showed a positive effect on the reduction of interlayer spacing of the coal crystallite structure at the pre-graphitization stage. In addition, the d_{002} of LT6 coal was relatively smaller at the same preparation conditions, suggesting that anthracite had a better promotion effect.



Figure 3. Raman spectra of samples at different temperatures. (a) LT6; (b) LT6T; (c) TSG12; (d) TSG12T; (e) LT6T-Q; (f) TSG12T-Q.

Figure 2c,d showed the change in L_c for different samples with increasing temperature. All coal samples had similar trends, in which the L_c increased slightly below 1900 °C, and then significantly increased above 1900 °C. For LT coal, the L_c of both LT6 and LT6T-Q was larger than that of LT6T at 1300~1900 °C, while their L_c was closed at 2800 °C. Similarly, the evolution of L_c for three TSG samples also showed the same trend. Therefore, the changes of L_c suggested that silicon-containing minerals were beneficial to the growth of stacking height at the pre-graphitization stage.

As seen in Figure 2e,f, at the pre-graphitization stage, the L_a of LT6T was larger than that of LT6T and closer to LT6T-Q, while the L_a of TSG12T was slightly higher than that of TSG12 and TSG12T-Q. This change indicated that silicon-containing minerals presented less effect on the lateral size of coal crystallites or slightly inhibited its extension at the pre-graphitization process.

3.2.2. Raman Spectroscopy Analysis

Raman spectroscopy has been widely used to provide important information for the degree of structural order of carbonaceous materials, and its characteristic spectra generally exist in the first-order region and second-order region, which corresponded to $800 \sim 2000 \text{ cm}^{-1}$ and $2400 \sim 3400 \text{ cm}^{-1}$, respectively [45–51]. The Raman spectra of all samples exhibited a similar evolution trend, as shown in Figure 3. In the first-order Raman spectrum, just one band at about 1580 cm^{-1} (G band) for the single crystals of graphite was found and defined as the E_{2g2} mode of graphite [52,53]. On the other hand, the spectrum of the graphite bar exhibits additional bands (D or "defect" bands), which are known to be characteristic of disordered graphite [54]. Compared with the G peak, the D band becomes more intense with an increasing degree of disorder in the graphitic structure [54]. As seen in Figure 3, the D_1 peak was clear, the shape of the D_1 and G peaks of samples were wider, and the intensity of the D_1 peak was also greater than that of the G peak at the pre-graphitization stage, indicating that the coal structure was disordered in this stage. Up to 2800 $^{\circ}$ C, the D₁ and G peaks of samples became sharp and the intensity of the D₁ peak significantly decreased, which was much lower than that of the previous stage, indicating that the coal-based graphite crystals with smaller particles possibly begin to form in the sample and the defects structures still existed [36]. The graphite mainly has three non-overlapping bands located at about 2480, 2670, and 3240 $\rm cm^{-1}$ in the second-order Raman spectrum, indicating the second-order Raman spectrum of graphite is simple [50]. However, for the samples, it can be seen in Figure 3 that the second-order Raman spectra were complex and significantly different from that of the graphite, which separately were the 2D₁ peak (the overtone of the D₁ peak), the D₁+G peak (the combination of the D₁ peak and G peak), and the $2D_2$ peak (the overtone of the D_2 peak). As the temperature increased, the $2D_1$ peak shape gradually became narrower and more intense, which also indicated that the coal structure tended to be ordered with the increase in temperature. A similar result was reported by Xu et al. that the intensity of 2D1 increased with the enhancement of coalification because the high-temperature treatment of coal was equivalent to the process of coalification [50]. At the same time, a new peak around 2450 cm^{-1} was observed that is hard to interpret because its origin is still controversial. Li et al. [55,56] considered this a sign of the formation of graphitized structure in the structural evolution of carbon materials, while it was not present during the process of carbonization. As shown in Figure 2, it can be inferred that the existence of silicon-containing minerals in coal strongly promoted the degree of structural order. Raman spectra were peak-fitted to more accurately describe the differences in crystallite structure, and detailed assignments for various functional groups of coals are listed in Table 2 [47–50]. The ID_1/IG (the peak area or integrated intensities) has been extensively used to evaluate crystalline or graphite-like carbon structures, and the ID_1/IG ratio normally decreases with an increasing extent of graphitization [57,58]. The band peak is a function of the peak intensity and the FWHM and is virtually a combined parameter of those two parameters [52,57]. Therefore, ID₁/IG characterized the peak area ratio between the D_1 peak and G peak in this paper, and the variation of ID_1/IG for different samples was calculated and shown in Figure 4.

Table 2. Chemical shifts and assignment of Raman spectrum of coal [45,46,48,49,57].

Туре	Shift/cm ⁻¹	Assignment
D_1	1350	The ring breathing vibration in the graphite subunit or polycyclic aromatic hydrocarbon compounds (PAHs) or to aromatics with 6 or more rings
D_2	1620	Disordered graphite lattice
D ₃	1500	C _{aromatic} -C _{alkyl} aromatic (aliphatic) ethers, C-C on hydro-aromatic rings, C-C on aliphatic structures or olefin-like structures
D_4	1200	C _{aromatic} -C _{alkyl} ; aromatic (aliphatic) ethers; C-C on hydro-aromatic rings; hexagonal diamond carbon sp ³ ; C-H on aromatic rings
G	1580	The aromatic ring breathing in the graphene sheets, aromatic ring quadrant breathing, alkene C=C
$2D_1$	2560	Overtone of the D_1 band, C-C between aromatic rings, large aromatic rings system
D_1+G	2860	Combination of D ₁ band and G band, large aromatic rings system
2G	3180	Overtone of the G band, the ring breathing vibration



Figure 4. Comparison of Raman structure parameters at different temperatures. (**a**) LT6 and LT6T; (**b**) TSG12 and TSG12T; (**c**) LT6t and LT6T-Q; (**d**) TSG12T and TSG12T-Q.

For LT coal (Figure 4a,c), the ID_1/IG of LT6 significantly increased at the pre-graphitization stage and then rapidly decreased above 1900°C, whilst ID₁/IG of LT6T and LT6T-Q showed a decreasing trend at the pre-graphitization stage and also sharply decreased above 1900 °C. It was obvious that the ID_1/IG of LT6T-Q was always relatively smaller than that of LT6T. These changes indicated that the mixed minerals in raw coal would hinder the ordered arrangement of structures at pre-graphitization, but the existence of only silicon-containing minerals in coal would promote structural alignment and become more gradually ordered in this stage. In TSG coal (Figure 4b,d), the turning point of ID₁/IG with temperature occurred at 1600 °C for three samples, which showed that the ID₁/IG increased at 1300~1600 °C and then significantly decreased above 1600 °C. This indicated that the structural evolution of bituminous coal must first be spliced with disordered microcrystalline layers, which reduced the degree of order, and then the layers gradually became parallel and ordered again as the temperature increased [59]. Similarly, the ID₁/IG of TSG12T-Q was always relatively smaller than that of TSG12T. Therefore, the evolution of ID_1/IG could prove that silicon-containing minerals promoted structural rearrangement and improved the order of coal at the pre-graphitization stage.

3.3. Characteristics of Minerals and Morphology

The SEM images of raw coal and demineralized coal at different heating temperatures are presented in Figure 5. At 1300 °C (Figure 5a–h), the micromorphology of the sample was clear, mostly angular and dense massive structures. In addition, some irregular polyhedron structures with a few tiny particles were also found, whose EDS showed that C was the main element. In addition, there were more pore structures on the surface of demineralized coal, which may be caused by the minerals being dissolved during the demineralization. At 1900 °C (Figure 5i–p), the micromorphology of the sample was similar to that at 1300 °C, it was still dominated by clearly distinguishable massive structures. However, the difference was that the surface of the massive structures clearly showed layers at this stage. Up to 2800 °C (Figure 5q–x), similar to the SEM characteristics at other temperatures, it was still dominated by massive structures with porous or layered surfaces, and a small amount of polyhedral structure. Combined with XRD, d₀₀₂ at this temperature was extremely close to 0.3354 nm, which was the interlayer spacing of the ideal single-

crystal graphite. It was inferred that most of the substances in the sample, except graphite, had evaporated at this stage, so it was not conducted for EDS analysis. Therefore, with or without demineralization, the whole micromorphology of the samples was dominated by massive structures, indicating that they did not change with temperature. Based on EDS results, it can be inferred that the formation of the few polyhedral structures observed may be related to the minerals. Meanwhile, based on the samples and test results, pyrite was present in both raw coals, and iron-containing minerals were detected in XRD and SEM of raw coal and demineralized coal, as well as in XRD of quartz-added demineralized coal. Therefore, it was inferred that the polyhedron structures may also be associated with the unremoved pyrite due to the insufficient dissolution of pyrite by the acid used for demineralization [11].



Figure 5. SEM and EDS analysis of raw coal and demineralized coal. LT6: (**a**,**b**) 1300 °C, (**i**,**j**) 1900 °C, and (**q**,**r**) 2800 °C; LT6T: (**c**,**d**) 1300 °C, (**k**,**l**) 1900 °C, and (**s**,**t**) 2800 °C; TSG12: (**e**,**f**) 1300 °C, (**m**,**n**) 1900 °C, and (**u**,**v**) 2800 °C; TSG12T: (**g**,**h**) 1300 °C, (**o**,**p**) 1900 °C, and (**w**,**x**) 2800 °C.

Figure 6 illustrates the SEM images of quartz-added samples. At 1300 °C (Figure 6a-d), the micromorphology of the samples was mainly massive structures, with sizes ranging from 10 to 40µm. In addition, some fine needle-like structures with different lengths were also observed in Figure 6b,d, in which the main element was C with less O and Si. With the increase in temperature, the massive structures were still the main micromorphology in coal with smooth or layered surfaces (Figure 6e–l). Some long columnar structures were also found at 1900 °C, and the constituent elements were unchanged, but the content of Si had a slight increase, as shown in Figure 6f,h. Up to 2800 °C, the long columnar structures were transformed into polyhedral structures (Figure 6i-l). Combined with XRD analysis, the needle-like structures can be attributed to the formation of the needle-like multilayer structures of quartz-SiC-carbon, in which the recrystallized quartz reacted with excess carbon to produce SiC growth based on quartz crystals and the surface of carbonaceous elements [19]. As the temperature increased, the reaction continued to produce SiC attached to the needle-like structures, increasing its length and diameter, and eventually producing the long columnar structure. At 2800 °C, SiC in samples had completely decomposed and the C elements in it were redeposited on the columnar structures to form the polyhedral structure.



Figure 6. SEM and EDS analysis of coal samples with quartz added. LT6T-Q: (**a**,**b**) 1300 °C, (**e**,**f**) 1900 °C, and (**i**,**j**) 2800 °C; TSG12T-Q: (**c**,**d**) 1300 °C, (**g**,**h**) 1900 °C, and (**k**,**l**) 2800 °C.

3.4. Effect of Silicon-Containing Minerals on the Pre-Graphitization Stage

The comparison of raw and demineralized coals showed that the raw coals exhibited smaller d_{002} and larger L_c values than the corresponding demineralized coal (Figure 2). Combining Raman and SEM analysis, it can be inferred that the existence of mixed mineral matter in raw coal gave rise to a decrease in interlayer spacing and an increase in stacking

height and made it easier for the structure to rearrange into a more ordered structure. In order to further explore the influence of silicon-containing minerals, demineralized samples containing 10wt% quartz were conducted, and significant changes in its chemical structural characteristics and micromorphology were observed. It showed smaller d_{002} and ID_1/IG , and higher L_c , while L_a presented a slight increase. The reduction of the quartz occurred at 1300 °C, forming needle-like SiC. With increasing temperature, the needle-like structures gradually grew in length and diameter, eventually producing the quartz-SiC-carbon multilayer long columnar structure. Above 1900 °C, SiC was decomposed by heat and the carbon-rich polyhedral structures became the main microstructure. These changes indicated that the formation and dissolution of SiC at the pre-graphitization stage was conducive to the movement and rearrangement of the coal molecular structure, resulting in the reduction of interlayer spacing, the development of longitudinal layer stacking height, and the enhancement of structural ordering. Therefore, the height of the aromatic planes grew during the pre-graphitization stage, and the width increased slightly [34,60].

4. Conclusions

In order to further explain the effect of silica-containing minerals on coal during the pre-graphitization stage, LT anthracite and TSG bituminous coal were selected as the subjects in this paper. Graphitized samples of raw coal, demineralized coal, and quartz-added demineralized coal were prepared via high-temperature treatments. XRD and Raman spectroscopy were applied to reveal structural change, and the micro-morphological features were observed by SEM. The effect of silicon-containing minerals on coal at the pre-graphitization stage was discussed by comparing the characteristics of different samples. The results showed that silicon-containing minerals played a positive role in structural evolution at this stage, as evidenced by the relatively smaller d_{002} and ID_1/IG , and the relatively larger L_c and L_a of the samples with silicon-containing minerals. Meanwhile, SEM observation found that the main micromorphology of the samples at different temperatures were massive structures, and the increase in temperature did not change the basic morphology but only decreased its mineral content. A small amount of irregular polyhedral structures was also found at the pre-graphitization stage, which was formed by the reaction of silicon-containing minerals with carbon in samples and the continuous accumulation of quartz-SiC-carbon multilayer polyhedral structures. At higher temperatures, SiC was completely decomposed and the carbon element was redeposited to produce graphite. Therefore, it could be inferred that silica-containing minerals promoted structural rearrangement by forming SiC during the pre-graphitization stage, which was beneficial to improve the structural order, reducing the interlayer spacing and promoting the development of longitudinal layer stacking height, thereby accelerating the graphitization process. In addition, it was found that LT anthracite showed a relatively better graphitization effect.

Author Contributions: Conceptualization, S.W., Y.S. and X.L.; investigation, X.L.; validation, Y.S.; experimental analysis, Y.S. and X.L.; writing—original draft preparation, S.W. and Y.S.; writing—review and editing, S.W.; funding acquisition, S.W. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (grants 42030807 and 42072196), and the Key R & D Program of Ningxia Hui Autonomous Region (grant 2021BEG02015).

Data Availability Statement: The data is available upon reasonable request from the corresponding tauthor.

Acknowledgments: All authors gratefully appreciate Xiaoxia Song for providing Tangshangou coal samples. The authors thank Yixiu Zhang, Jinsong Deng for sample preparation.

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

References

- 1. Klemens, P.G.; Pedraza, D.F. Thermal conductivity of graphite in the basal plane. Carbon 1994, 32, 735–741. [CrossRef]
- 2. Ōya, A.; Marsh, H. Phenomena of catalytic graphitization. J. Mater. Sci. 1982, 17, 309–322. [CrossRef]
- 3. Gao, T.M.; Chen, Q.S.; Yu, W.J.; Shen, L. Projection of China's graphite demand and development prospects. *Resour. Sci.* 2015, 37, 1059–1067.
- 4. Kwiecińska, B.; Petersen, H.I. Graphite, semi-graphite, natural coke, and natural char classification—ICCP system. *Int. J. Coal Geol.* **2004**, *57*, 99–116. [CrossRef]
- 5. Zhang, X.M.; Wang, S.Q.; Chen, H.; Li, X.Q.; Zhang, Y.X. An investigation on the graphitization of low-rank coal: Evolutional characteristics of aromatic structure. *J. China Coal Soc.* **2022**, *47*, 2768–2778.
- 6. Liu, X.Y.; Tao, H.C.; Tang, C.Y.; Yang, X.L. Anthracite-derived carbon as superior anode for lithium/potassium-ion batteries. *Chem. Eng. Sci.* 2022, 248, 117200. [CrossRef]
- 7. Wang, Q.L.; Yu, M.Q.; Gong, J.N.; Zhang, F.T. Study on the properties of coal-based high-purity graphite. *Mater. Express* 2019, 9, 668–674. [CrossRef]
- 8. Guo, R.N.; Li, W.B.; Han, Y.X. Progress on the separation, purification and application of natural graphite. *Chem. Ind. Eng. Prog.* **2021**, 40, 6155–6172.
- 9. Li, H.T.; Cao, D.Y.; Zhang, W.G.; Wang, L. XRD and Raman spectroscopy characterization of graphitization trajectories of high-rank coal. *Spectrosc. Spectr. Anal.* **2021**, *41*, 2491–2498.
- 10. Tang, Y.G.; Xu, J.J.; Huan, X.; Wang, S.Q.; Chen, P.X. Preparation and spectroscopic characterization of coal-based graphene from anthracite in Xiaofalu, Yunan, China. *J. China Coal Soc.* **2020**, *45*, 740–748.
- 11. Gong, L.B. *Research on the Influence of Mineralizers on Coal Graphitization and Its Control Mechanism;* Hebei University of Engineering: Handan, China, 2021.
- 12. Oberlin, A.; Terriere, G. Graphitization studies of anthracites by high resolution electron microscopy. *Carbon* **1975**, *13*, 367–376. [CrossRef]
- 13. Atria, J.V.; Rusinko, F.; Schobert, H.H. Structural ordering of Pennsylvania anthracites on heat treatment to 2000~2900 °C. *Energy Fuels* **2002**, *16*, 1343–1347. [CrossRef]
- 14. Rodrigues, S.; Suárez-Ruiz, I.; Marques, M.; Flores, D.; Camean, I.; García, A.B. Development of graphite-like particles from the high temperature treatment of carbonized anthracites. *Int. J. Coal Geol.* **2011**, *85*, 219–226. [CrossRef]
- 15. Rodrigues, S.; Suárez-Ruiz, I.; Marques, M.; Camean, I.; Flores, D. Microstructural evolution of high temperature treated anthracites of different rank. *Int. J. Coal Geol.* **2011**, *87*, 204–211. [CrossRef]
- 16. Borunova, A.B.; Streletskii, A.N.; Permenov, D.G.; Leonov, A.V. The effect of the mechanical activation dose on the defective structure of artificial graphite. *Colloid J.* **2015**, *77*, 125–134. [CrossRef]
- 17. Qiu, T. Research on the Graphitization Process of Coal and the Migration Rule of Coal-Derived Minerals; China University of Mining and Technology: Xuzhou, China, 2019.
- 18. Tian, Y. The Influence of Mineralizer on Coal Graphitization and Its Mechanism; Hebei University of Engineering: Handan, China, 2021.
- 19. Nyathi, M.S.; Clifford, C.B.; Schobert, H.H. Characterization of graphitic materials prepared from different rank Pennsylvania anthracites. *Fuel* **2013**, *114*, 244–250. [CrossRef]
- 20. Zhou, Q.; Zhao, Z.B.; Zhang, Y.T.; Meng, B.; Zhou, A.N.; Qiu, J.S. Graphene sheets from graphitized anthracite coal: Preparation, decoration, and application. *Energy Fuels* **2012**, *26*, 5186–5192. [CrossRef]
- 21. Franklin, R.E. Crystallite growth in graphitizing and non-graphitizing carbons. *Proc. R. Soc. Lond. Ser. A Math. Phys. Sci.* **1951**, 209, 196–218.
- 22. Bustin, R.M.; Ross, J.V.; Rouzaud, J.-N. Mechanisms of graphite formation from kerogen: Experimental evidence. *Int. J. Coal Geol.* **1995**, *28*, 1–36. [CrossRef]
- 23. Cao, D.Y.; Li, X.M.; Zhang, S.R. Influence of tectonic stress on coalification-stress degradation mechanism and stress polycondensation mechanism. *Sci. China (Ser. D Earth Sci.)* 2006, 1, 59–68. [CrossRef]
- 24. Zhang, X.M.; Wang, S.Q.; Chen, H.; Wang, X.X.; Deng, J.S.; Li, X.Q.; Zhang, Y.X. Observation of carbon nanostructure and evolution of chemical structure from coal to graphite by high temperature treatment, using componential determination, X-ray diffraction and high-resolution transmission electron microscope. *Fuel* **2023**, *332*, 126145. [CrossRef]
- 25. Li, J.Q.; Qin, Y.; Chen, Y.L. Occurrence and origin of graphite microcrystal in meta-anthracite. Coal Geol. Explor. 2020, 48, 27–33.
- 26. Franklin, R.E. The structure of graphitic carbons. Acta Crystallogr. 1951, 4, 253. [CrossRef]
- 27. González, D.; Montes-Morán, M.A.; Garcia, A.B. Influence of inherent coal mineral matter on the structural characteristics of graphite materials prepared from Anthracites. *Energy Fuels* **2005**, *19*, 263–269. [CrossRef]
- 28. Pappano, P.J.; Schobert, H.H. Effect of natural mineral inclusions on the graphitizability of a Pennsylvania anthracite. *Energy Fuels* **2009**, *23*, 422–428. [CrossRef]
- 29. Rodrigues, S.; Suárez-Ruiz, I.; Marques, M.; Flores, D. Catalytic role of mineral matter in structural transformation of anthracites during high temperature treatment. *Int. J. Coal Geol.* **2012**, *93*, 49–55. [CrossRef]
- 30. Liu, B.; He, Q.H.; Jiang, Z.H.; Xu, R.F.; Hu, B.X. Relationship between coal ash composition and ash fusion temperatures. *Fuel* **2013**, *105*, 293–300. [CrossRef]
- 31. Wang, L.P.; Yao, Z.X.; Guo, Z.M.; Shen, X.F.; Li, Z.A.; Zhou, Z.Q.; Wang, Y.L.; Yang, J.G. Effects of solvent extraction on the microstructure of bituminous coal-based graphite. *Carbon Lett.* **2022**, *32*, 741–749. [CrossRef]

- 32. Baraniecki, C.; Pinchbeck, P.H.; Pickering, F.B. Some aspects of graphitization induced by iron and ferro-silicon additions. *Carbon* **1969**, *7*, 213–224. [CrossRef]
- Pappano, P.J. A Mechanism of Pennsylvania Anthracite Graphitization Involoving Carbide Formation and Decomposition; The Pennsylvania State University: State College, PA, USA, 2003.
- 34. Lin, Q.Y.; Feng, Z.H.; Liu, Z.J.; Guo, Q.G.; Hu, Z.J.; He, L.L.; Ye, H.Q. Atomic scale investigations of catalyst and catalytic graphitization in a silicon and titanium doped graphite. *Carbon* **2015**, *88*, 252–261. [CrossRef]
- 35. Liu, H.Y.; Xu, L.; Jin, Y.; Fan, B.G.; Qiao, X.L.; Yang, Y.X. Effect of mineral matter on structure and dielectric properties of chars. *Fuel* **2018**, 222, 370–374. [CrossRef]
- Li, H.T.; Zhang, H.; Li, K.J.; Zhang, J.J.; Sun, M.M.; Su, B.X. Catalytic graphitization of coke carbon by iron: Understanding the evolution of carbon Structure, morphology and lattice fringes. *Fuel* 2020, 279, 118531. [CrossRef]
- Lu, L.; Sahajwalla, V.; Kong, C.; Harris, D. Quantitative X-ray diffraction analysis and its application to various coals. *Carbon* 2001, 39, 1821–1833. [CrossRef]
- Li, M.F.; Zeng, F.G.; Chang, H.Z.; Xu, B.S.; Wang, W. Aggregate structure evolution of low-rank coals during pyrolysis by in-situ X-ray diffraction. *Int. J. Coal Geol.* 2013, 116–117, 262–269. [CrossRef]
- 39. Jiang, J.Y.; Yang, W.H.; Cheng, Y.P.; Liu, Z.D.; Zhang, Q. Molecular structure characterization of middle-high rank coal via XRD, Raman and FTIR spectroscopy: Implications for coalification. *Fuel* **2019**, *239*, 559–572. [CrossRef]
- 40. Takagi, H.; Maruyama, K.; Yoshizawa, N.; Yamada, Y.; Sato, Y. XRD analysis of carbon stacking structure in coal during heat treatment. *Fuel* **2004**, *83*, 2427–2433. [CrossRef]
- Li, J.Q.; Oin, Y.; Chen, Y.L.; Shen, J.; Song, Y.; Wang, Z.W. Structural characteristics and evolution of meta-anthracite to coaly graphite: A quantitative investigation using X-ray diffraction, Raman spectroscopy, and high-resolution transmission electron microscopy. *Fuel* 2023, 333, 126334. [CrossRef]
- 42. Lin, Q.; Guet, J.M. Characterization of coals and macerals by X-ray diffraction. Fuel 1990, 69, 821–825. [CrossRef]
- 43. Wang, S.Q.; Sun, Y.B.; Shu, K.K.; Jiang, D.; Ma, W. Structural characterization of coal components of Late Permian coals from Southern China by X-ray diffraction and Raman spectroscopy. *J. Biochem. Anal. Stud.* **2017**, *2*, 1–5.
- 44. Seehra, M.S.; Pavlovic, A.S. X-ray diffraction, thermal expansion, electrical conductivity, and optical microscopy studies of coal-based graphites. *Carbon* **1993**, *31*, 557–564. [CrossRef]
- 45. Keown, D.M.; Li, X.J.; Hayashi, J.; Li, C.Z. Evolution of biomass char structure during oxidation in O₂ as revealed with FT-Raman spectroscopy. *Fuel Process. Technol.* **2008**, *89*, 1429–1435. [CrossRef]
- 46. Morga, R. Micro-Raman spectroscopy of carbonized semifusinite and fusinite. Int. J. Coal Geol. 2011, 87, 253–267. [CrossRef]
- Baysal, M.; Yürüm, A.; Yıldız, B.; Yürüm, Y. Structure of some western Anatolia coals investigated by FTIR, Raman, ¹³C solid state NMR spectroscopy and X-ray diffraction. *Int. J. Coal Geol.* 2016, 163, 166–176. [CrossRef]
- 48. Zhang, Y.L.; Li, Z.S. Raman spectroscopic study of chemical structure and thermal maturity of vitrinite from a suite of Australia coals. *Fuel* **2019**, *241*, 188–198. [CrossRef]
- Vranjes-Wessely, S.; Misch, D.; Issa, I.; Kiener, D.; Fink, R.; Seemann, T.; Liu, B.; Rantitsch, G.; Sachsenhofer, R.F. Nanoscale pore structure of Carboniferous coals from the Ukrainian Donets Basin: A combined HRTEM and gas sorption study. *Int. J. Coal Geol.* 2020, 224, 103484. [CrossRef]
- Xu, J.; Tang, H.; Su, S.; Liu, J.W.; Han, H.D.; Zhang, L.P.; Xu, K.; Wang, Y.; Hu, S.; Zhou, Y.B.; et al. Micro-Raman spectroscopy study of 32 kinds of Chinese coals: Second-order Raman spectrum and its correlations with coal properties. *Energy Fuels* 2017, 31, 7884–7893. [CrossRef]
- Xu, J.; Xiang, X.R.; Xu, K.; He, L.M.; Han, H.D.; Su, S.; Wang, Y.; Hu, S.; Xiang, J. Developing micro-Raman spectroscopy for char structure characterization in the scale of micro- and bulk: A case study of Zhundong coal pyrolysis. *Fuel* 2021, 291, 120168. [CrossRef]
- 52. Sheng, C.D. Char structure characterised by Raman spectroscopy and its correlations with combustion reactivity. *Fuel* **2007**, *86*, 2316–2324. [CrossRef]
- 53. Hinrichs, R.; Brown, M.T.; Vasconcellos, M.A.Z.; Abrashev, M.V.; Kalkreuth, W. Simple procedure for an estimation of the coal rank using micro-Raman spectroscopy. *Int. J. Coal Geol.* **2014**, *136*, 52–58. [CrossRef]
- 54. Sadezky, A.; Muckenhuber, H.; Grothe, H.; Niessner, R.; Pöschl, U. Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information. *Carbon* **2005**, *43*, 1731–1742. [CrossRef]
- 55. Li, K.; Rimmer, S.M.; Liu, Q.; Zhang, Y.M. Micro-Raman spectroscopy of microscopically distinguishable components of naturally graphitized coals from Central Hunan province, China. *Energy Fuels* **2019**, *33*, 1037–1048. [CrossRef]
- 56. Li, K.; Rimmer, S.M.; Liu, Q. Geochemical and petrographic analysis of graphitized coals from Central Hunan, China. *Int. J. Coal Geol.* **2018**, 195, 267–279. [CrossRef]
- 57. Li, X.J.; Hayashi, J.I.; Li, C.Z. FT-Raman spectroscopic study of the evolution of char structure during the pyrolysis of a Victorian brown coal. *Fuel* **2006**, *85*, 1700–1707. [CrossRef]
- 58. Tai, F.C.; Lee, S.C.; Wei, C.H.; Tyan, S.L. Correlation between ID/IG ratio from visible Raman spectra and sp²/sp³ ratio from XPS spectra of annealed hydrogenated DLC film. *Mater. Trans.* **2006**, *47*, 1847–1852. [CrossRef]

- 59. Wang, X.L.; Wang, S.Q.; Hao, C.; Zhao, Y.G.; Song, X.X. Quantifying orientation and curvature in HRTEM lattice fringe micrographs of naturally thermally altered coals: New insights from a structural evolution perspective. *Fuel* **2022**, *309*, 122180. [CrossRef]
- 60. Wang, J.; Morishita, K.; Takarada, T. High-temperature interactions between coal char and mixtures of calcium oxide, quartz, and kaolinite. *Energy Fuels* **2001**, *15*, 1145–1152. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.




Article A High-Temperature Thermal Simulation Experiment for Coal Graphitization with the Addition of SiO₂

Gaojian Chen, Daiyong Cao * 🔍, Anmin Wang, Yingchun Wei 🔍, Zhifei Liu and Meng Zhao

College of Geoscience & Surveying Engineering, China University of Mining & Technology, Beijing 100083, China

* Correspondence: cdy@cumtb.edu.cn

Abstract: The effect of SiO₂ on coal graphitization was investigated by adding SiO₂ as an additive to vitrinite in coal from the Gemudi mining area in Guizhou province (SW China) via a high-temperature heating treatment. The graphitization products of the samples were analyzed by X-ray diffraction (XRD), Raman spectroscopy, and high-resolution transmission electron microscopy (HRTEM), and the influence of the SiO₂ additive on the process of coal graphitization was investigated. The results showed that, with the temperature increases, the graphitization degree of all samples was promoted, and the orderliness of the microcrystalline structure in the vitrinite increased. Compared with the samples without additives, the graphitization degree, graphite lamellae ductility, and stacking degree of the samples with SiO₂ additives were higher, and the carbon layer spacing reached 0.3379 nm at 3000 °C, entering the graphite stage. The Raman spectra showed that the peak intensities of the defect structures (D1 and D2) in the samples with SiO₂ were lower than those of the samples without additives, exhibiting fewer in-plane and interlayer defects in the same temperature, the carbon layer stacking degree of the samples with the SiO₂ additives was higher than that of the samples without SiO₂, and large graphite lamellae with smoother and clearer edges were observed.

Keywords: coal; high temperature; SiO2 additive; coal-based graphite

1. Introduction

Coal-based graphite is the main component of cryptocrystalline graphite and a type of coal-based nonmetallic mineral. Compared with crystalline graphite, coal-based graphite has enriched ore, a high grade, and easy exploitation, accounting for more than half of Chinese graphite production [1].

To explore the formation process and influencing factors of coal-based graphite, many scholars have studied coal-based graphite using laboratory simulation experiments [2,3], but the complexity of the structure and composition of coal and the diversity of controlling factors in the graphitization process make the study of the mechanism and evolution process of coal-based graphite mineralization problematic [4]. The main reason is the lack of understanding of the controlling factors in graphitization, such as the macerals, minerals, temperature, and pressure. The main controlling factors affecting the formation of coal-based graphite can be divided into two categories: internal factors (material composition) and external factors (temperature and pressure) [5]. Due to the complexity of the conditions of graphite formation and the graphitization process, the evolution rate, structural changes, and degree of graphitization vary among the different macerals; that is, there is the "differential graphitization phenomenon" [6,7].

With the gradual progress of coal graphitization research, the influence of inorganic minerals on the evolution of coal-based graphite has been emphasized. Previous studies have found that coal containing compounds of sulfur [8], manganese, iron [9], and calcium [10] was more likely to be graphitized. From the perspective of a structural analysis, some scholars believed that "shell-like carbon layers" were formed around the



Citation: Chen, G.; Cao, D.; Wang, A.; Wei, Y.; Liu, Z.; Zhao, M. A High-Temperature Thermal Simulation Experiment for Coal Graphitization with the Addition of SiO₂. *Minerals* **2022**, *12*, 1239. https://doi.org/10.3390/ min12101239

Academic Editor: Alexandra Guedes

Received: 14 September 2022 Accepted: 26 September 2022 Published: 28 September 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 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/). mineral particles, which were broken down under stress to form flat graphitic carbon layers [11,12]. Bustin [13] believed that mineral particles can transmit tectonic shear stress to the reaction site. It is very difficult to accurately study the graphitization process and influencing factors through the formed natural coal-based graphite. Therefore, some scholars have used simulation experiments to produce coal graphite to investigate the influence of minerals on coal graphitization. Noda [14,15] conducted a simulation experiment at temperatures of 600–850 °C and pressure of 0.32 GPa from the perspective of chemical reactions and proposed that calcium-containing mineral particles could directly participate in the graphitization process as reaction catalysts. Nyathi [16] found that the presence of aluminum-containing clay minerals retarded coal graphitization by simulating Pennsylvania anthracite at 3000 °C. The significant influence of minerals on graphitization has been well-demonstrated by previous simulations, but the research is not sufficiently comprehensive, and the effects of many minerals on graphitization have not yet been studied.

The common minerals in coal are quartz, clay, carbonate, and sulfide, among which SiO₂ widely exists in quartz and kaolinite. SiO₂ is chemically stable, with a melting point of about 1600 °C and a boiling point of about 2230 °C. It has a large specific surface area and high thermal stability, and is commonly used in the preparation of catalyst carriers; additionally, it can directly affect the activity, selectivity, and stability of catalytic reactions under certain conditions [17]. Gonzalez [18] and Pappan [19] conducted simulations on anthracite coal with a continuous temperature increase and discovered the promoter action of graphitization by quartz as well as an explanation of its catalytic mechanism: at temperatures up to 1800 °C, liquid quartz reacts with carbon to produce silicon carbide. Above 2600 °C, silicon carbide decomposes to produce silicon monomers and carbon monomers. The cubic crystalline silicon carbide is similar in structure to graphite and has the effect of promoting the formation of graphite.

Previous studies on the mechanism of the influence of minerals on graphitization mainly have two deficiencies. First, the effect of the differences between the different macerals in coal on the experimental results was neglected [20,21]. Each maceral should be individually tested and analyzed [22]. Second, by directly conducting simulation experiments on raw coal, there may be reactions among minerals in coal ash [23,24], which affects the coal graphitization products and obscures the real influence on the graphitization mechanism [25]. Instead, each mineral should be separately analyzed to exclude the influence of other minerals on graphitization to the greatest extent possible.

The purpose of this study was to research the effect of coal minerals on graphitization by conducting high-temperature simulation experiments. The lean coal collected from the Gemudi mining area in Guizhou province (SW China) was selected as the research object, and vitrinite-rich samples were obtained after hand selection to avoid the influence of the inertinite in the coal [5,26]. SiO₂ powder was selected as an additive to be mixed for the high-temperature simulation experiments, and the post-experimental samples were analyzed using various modern instruments to investigate the effect of SiO₂ in the coal graphitization process.

2. Experimental Samples and Methods

2.1. Selection and Processing of Experimental Materials

2.1.1. Experimental Sample

The coal samples were collected from the Gemudi mining area in Guizhou province (SW China) and had a high vitrinite content. SiO₂ powder with a particle size of 200 mesh was selected as the additive. In order to exclude the influence of the inertinite in the coal on the experiment, the coal samples were hand-selected to obtain vitrinite-enriched samples. According to the Chinese standard GB/T 15588-2013 [27] and GB/T 8899-2013 [28], the obtained samples were observed under a microscope, and the samples with 90% or higher vitrinite purity were used as raw materials for the simulation experiment. The results of the proximate analysis (GB/T 212-2008 [29]) and ultimate analysis (GB/T 476-2001 [30]) are shown in Table 1.

Sample Collection Site	Vitrinite R _{max} /%	C	Component			Proxima	te Analysis			Ultin	nate Anal	lysis	
		Vitrinite	Inertinite	Exinite	M_{ad} /%	A_d /%	V_{daf} /%	FC _d /%	S_t /%	O_{daf} /%	C_{daf} /%	H_{daf} /%	N_{daf} /%
Gemudi	1.7	92.4	7.6	0	0.72	5.72	17.03	78.22	0.74	2.38	90.88	3.98	1.88

 Table 1. Proximate analysis and ultimate analysis of vitrinite in Gemudi.

2.1.2. Demineralization

The purpose of this experiment was to explore the influence of SiO_2 on the graphitization of coal; however, the mineral components in raw coal are very complex, so the influence of the original minerals in the coal on the experiment should be excluded to the greatest extent possible. As a result, the raw coal required for the experiment should be acid-washed and demineralized to remove the other minerals contained in the coal so that interference factors in the experiment can be avoided [31].

The raw coal was crushed to 200 mesh (75 μ m), and 15 g of coal powder was weighed into a plastic beaker and mixed with 80 mL of HCl solution (36% by mass); then, the mixture was stirred in a water bath at 60 °C for 4 h. After this, the HCl solution was filtered out, and 80 mL of the HF solution (40%) was added to the remaining coal. The water bath and acid-washing operations were repeated until the filtrate, after washing with the AgNO₃ solution test, had no precipitates. Then, the acid-washed coal was filtered out with a filter paper and put into an oven at 60 °C for 24 h to obtain demineralized coal.

2.2. High-Temperature Simulation Experiment

2.2.1. Experimental Equipment

An integrated laboratory graphitization furnace (NTG-SML-60W, NTG-SML-60W, Nuotian electric heating technology, Zhuzhou City, China) was used in this experiment. The specific experimental steps were as follows: Every dish was placed in the graphitization furnace after being loaded with 5 g of vitrinite, and the gas was replaced once with a vacuum degree of 5 Pa before heating; then, the whole process was protected by argon with a flow rate of 10 L/min. This experiment used the sectional heating method: the temperature was first raised to 1000 °C at a heating rate of 5 °C/min and kept for 60 min. Then, the temperature was raised to the target temperature point at a rate of 10 °C/min and kept for 90 min. The four experimental temperature points were set at 2100 °C, 2400 °C, 2700 °C, and 3000 °C.

2.2.2. Experimental Scheme

A group of additive-free vitrinite samples (G) and a group of SiO_2 -added samples (GS) were set up for comparative analysis. The four samples in each group correspond to the four temperature points, and the mass of each sample was 5 g.

In GS sample proportioning, too much additive can affect the subsequent analysis and tests and can make it difficult to reveal regular patterns, whereas a smaller amount of additive does not have a catalytic and inhibitory effect. Therefore, the ratio of vitrinite to SiO_2 was selected as 7:3 in this experiment [32] in order to investigate the effect of SiO_2 on graphitization during the high-temperature simulation experiment. The experimental scheme adopted is shown in Table 2.

 Table 2. High-temperature simulation experimental scheme.

	Number									
Temperature	Additive-Free Vitrinite Samples	SiO ₂ -Added Samples								
2100 °C	G-1	GS-1								
2400 °C	G-2	GS-2								
2700 °C	G-3	GS-3								
3000 °C	G-4	GS-4								

2.3. X-ray Diffraction Analysis (XRD)

SmartLab-9kW (Rigaku Corporation, Tokyo, Japan) was used as the XRD test instrument. Copper targets with a 45 kV accelerating voltage and a 200 mA current were chosen. The scan range was set as 20 from 5° to 70°, with a scan rate of 2°/min and an X-ray wavelength of 0.15418 nm. Two diffraction peaks (20 range 20°–30° and 40°–50°, respectively) on the XRD pattern matched the positions of the 002 and 100 peaks in the standard graphite XRD diffraction pattern. The lattice parameters (carbon layer spacing d₀₀₂, diameter La, and stack height Lc) were calculated based on Bragg's equation and Scherre's formula using Jade software (Materials Data, Livermore, CA, USA) [33,34].

XRD is a common method used to study microcrystalline structures in coal. d_{002} , Lc, and La can be obtained by the following method from the spectrum.

(1) d_{002} is the average interlayer spacing of crystallites, which can be obtained according to the Bragg formula; the formula is shown as follows:

$$d_{002} = \lambda / 2 \sin \theta_{002} \tag{1}$$

In the formula, λ is the wavelength of the X-ray, $\lambda = 0.154056$ nm; θ_{002} is the diffraction angle corresponding to the 002 peak, in units of degrees.

(2) Lc is the average height of crystallites in the c-axis direction; the calculation formula is shown as follows:

$$Lc = 1.05\lambda / \beta_{002} cos\theta_{002}$$
 (2)

In the formula, β_{002} is the half-width of the 002 peak.

(3) La is the average diameter of the crystallites, which can be obtained according to the Scherrer crystallite size calculation formula:

$$La = 1.84\lambda/\beta_{100}\cos\theta_{100} \tag{3}$$

In the formula, β_{100} is the half-width of the 100 peak, and θ_{100} is the diffraction angle corresponding to the 100 peak position, in units of degrees.

2.4. Laser Raman Spectroscopy (Raman)

Raman spectroscopy is often used to analyze organic matter [35]. A Horiba LabRAM HR Evolution model high-resolution micro-Raman spectrometer (Horiba, Kyoto, Japan) was used in the Raman spectroscopic experiment. A Nd:YAG (532 nm) laser was used as the excitation light source in the experiment, with a laser power of 100 mW, scanning range of 800 cm⁻¹–3500 cm⁻¹, and exposure time of 10 s. The fitting and processing analyses were conducted with the obtained Raman spectra using the Lorentz function in Origin8.0 software (OriginLab, Northampton, US).

The measured Raman spectra were found in two regions, which were the first-order Raman (700 cm^{-1} – 2000 cm^{-1}) and the second-order Raman (2000 cm^{-1} – 3000 cm^{-1}). The primary Raman could be divided into four types of defect peaks (D1–D4 peaks) and one ordered graphite peak (G peak). The secondary Raman spectrum contained only two peaks (S1 and S2) at the low evolutionary stage, and as the evolution increased, the S1 peak gradually split into two peaks and the S2 peak disappeared [36].

Defect peaks caused by lattice defects and disordered carbon structures (active structures) within the graphite layers are called D peaks [37]. According to different causes and positions, it can be divided into 1350 cm⁻¹ (D1), 1620 cm⁻¹ (D2), 1500 cm⁻¹ (D3), and 1200 cm⁻¹ (D4), whereas the D3 and D4 peaks only appear in samples with high disorder [38]. The secondary Raman spectrum at 2700 cm⁻¹ (S1 peak) is related to the structural order of its three-dimensional lattice. The higher the order, the higher the splitting of its secondary peaks [39].

The quantitative evaluation parameters of Raman spectroscopy for the evaluation of carbon ordering have been studied in detail in previous research. The peak position difference between the D1 and G peaks (P) can be expressed as P(G)-P(D1); the full width

at half maximum of the G peak can be expressed as FWHM (G); the intensity ratio of the D1 and G peaks can be expressed as R1 = ID1/IG; the area ratio of the D1 peak can be expressed as $R_2 = AD1/A(G + D1 + D2)$ [40]; and the ratio of all the types of defect peaks to the total area in the first-order Raman can be expressed as $R_3 = A(D1 + D2 + D3 + D4)/A(D1 + D2 + D3 + D4 + G)$. These parameters have been used to characterize the degree of defects in the structure or the degree of order of carbon materials [41].

These parameters showed a good positive correlation in the samples with a high degree of graphitization, but the correlation of some parameters was not obvious in the samples with a lower degree of graphitization. Therefore, the parameters R₂ and R₃ were used in this study to characterize the degree of structural defects in the samples; R₂ was called the "in-plane defect parameter" to characterize the proportion of in-plane defects (D1), which has high evaluation significance for high-graphitization-degree samples with fewer defects and mainly D1-type defects; R₃ was called the "full defect parameter" to characterize the percentage of all types of defects, which had high physical significance for low-graphitization-degree samples with more defects [42].

2.5. High-Resolution Transmission Electron Microscopy (HRTEM)

A Tecnai G2 F30 field emission transmission electron microscope host (FEI, Portland, OSU, USA) was used in the high-resolution transmission electron microscope (HRTEM) experiment with an accelerating voltage of 300 kV, point resolution of 0.20 nm, line resolution of 0.10 nm, and 0.14 nm information resolution, with a $3000 \times to 500,000 \times$ fold magnification. The specific method was conducted as follows: the samples were ground to 300 mesh, ultrasonically dispersed in ethanol, and then dropped on the microgrid copper mesh. Afterward, the sample was searched for overheads on the holes of the microgrid copper mesh; the particles that had the most particle characteristics were selected in the sample for multiscale observation, and high-resolution images were taken.

3. Results

3.1. X-ray Diffraction Results (XRD)

The GS and G samples after the experiment were analyzed by XRD (Figure 1). The interlayer spacing (d_{002}), average height of the crystallites (Lc), and average diameter of the crystallites (La) were calculated (Table 3).



Figure 1. XRD pattern of experimental samples.

Temperature/°C	Number	$2\theta_{002}/^{\circ}$	FWHM ₀₀₂ /°	$2\theta_{100}/^{\circ}$	FWHM₁₀₀ /°	Lc/nm	La/nm	d ₀₀₂ /nm
2100	G-1	25.85	2.10	42.96	1.86	3.89	9.39	0.3443
2100	GS-1	26.18	1.33	42.38	1.69	6.155	10.27	0.3401
2400	G-2	25.97	1.43	42.94	1.45	5.70	12.09	0.3428
2400	GS-2	26.27	0.74	42.39	0.66	11.04	13.31	0.3392
2700	G-3	26.10	1.02	42.93	1.28	7.98	13.68	0.3411
2700	GS-3	26.3	0.71	42.37	1.15	11.49	15.17	0.3386
3000	G-4	26.23	0.69	42.75	0.99	11.85	17.60	0.3395
3000	GS-4	26.35	0.66	42.17	0.87	12.32	20.03	0.3379

Table 3. XRD parameters of experimental samples.

By observing the XRD pattern and analyzing the lattice parameters, the following conclusions were initially obtained:

(1) For the same precursor, the peaks located near $2\theta = 26^{\circ}$ moved closer to the position of the standard graphite peak ($2\theta = 26.6^{\circ}$) as the experimental temperature increased, and the peak shape became sharp and symmetrical.

(2) The G samples showed a strong nonhomogeneous graphitization phenomenon at 2100 °C–2700 °C; the peak near $2\theta = 26^{\circ}$ exhibited asymmetry, with an ordered carbon-graphite peak (002 peak) and a disordered carbon peak inside [43], reflecting the coexistence of ordered and disordered structures in the samples. This indicated that the graphitization was nonhomogeneous inside and that a large amount of disordered carbon existed. In contrast, the GS samples exhibited nonhomogeneous graphitization only at 2100 °C, and the peaks around $2\theta = 26^{\circ}$ tended to be symmetrical from 2400 °C, with a significantly decreased internal disordered carbon content.

③ Using d₀₀₂ as a measure of the graphitization degree for evaluation, the GS samples had lower d₀₀₂ values than the G samples at the same temperature. The participation of SiO₂ obviously had a positive catalytic effect on graphitization.

(4) Compared with the G samples without additives, the structure of the GS samples appeared significantly ordered at 2100 °C; after 2400 °C, the full width at half maximum (FWHM) of the peak near $2\theta = 26^{\circ}$ was significantly reduced, and an obvious sharp, symmetric graphite peak appeared. The corresponding d_{002} values were all decreased to below 0.340 nm, approaching 0.338 nm; when the temperature reached 3000 °C, the d_{002} of GS-4 was below 0.338 nm, indicating that the sample had entered the graphite stage [44].

(5) At the same temperature, the GS samples had sharper 002 peaks relative to the G samples, with a smaller FWHM and lower asymmetry. At 2700 °C, the 002 peak of GS-3 was sharp and symmetrical, indicating the formation of perfect graphite crystals. In contrast, the 002 peaks of G samples were still less symmetrical at 2700 °C and only tended to be symmetrical at 3000 °C.

G A sharp peak was found in the XRD pattern at 2100 °C for the GS samples at about 20 = 35.5°, which was presumed to be the SiC diffraction peak after consulting the XRD card. The intensity of this peak significantly decreased with an increasing temperature and disappeared at 2700 °C.

3.2. Raman Results

The Raman spectra of the samples at different temperatures were fitted to the split peaks (Figure 2), and the relevant structural characterization parameters were calculated (Table 4). Through the Raman spectrograms and a comparative analysis of the data, the following conclusions were initially drawn:



Figure 2. Raman spectra of experimental samples. (red line: fitted curve; green line: original curve).

(1) With the increasing experimental temperature, the G peak, which characterizes the ordered graphite structure, gradually increased in intensity and approached 1580 cm⁻¹, whereas the intensity of the D peak, which characterizes the disordered structure, decreased. The defect peaks of the G samples were mainly D1 peaks; the defect peaks of the GS samples were dominated by D1 peaks below 2700 °C and by D2 peaks after 2700 °C. The D2 peaks did not completely disappear even in the samples with a high graphitization degree. There were no D3 or D4 peaks representing other heterocyclic defects found in the samples.

(2) As the temperature increased, in the second-order Raman, the S1 peak gradually separated into two peaks, S1' and S1", and the S2 peak gradually decreased. The S2 peak disappeared at 3000 °C for the G samples and at 2700 °C for the GS samples, indicating that the three-dimensional structure gradually formed and became perfected.

③ The Raman parameters $(R_1/R_2/R_3)$ showed a decreasing trend with an increasing temperature. Compared with the G samples at same temperatures, the GS samples had lower $R_1/R_2/R_3$ values, which proved that the GS samples had a higher degree of graphitization and better healing of layer and interlayer defects.

(4) At 3000 °C, the D1 peak disappeared, and the R_1/R_2 value decreased to 0 for GS-4, reflecting the complete healing and disappearance of defects within its graphite layers and the formation of a highly ordered structure.

Temperature/°C	Number	FWHM(G)	R ₁	R ₂	R ₃
2100	G-1	23.33	0.35	0.324	0.391
2100 -	GS-1	21.68	0.19	0.148	0.234
2400	G-2	23.17	0.27	0.296	0.332
2400 -	GS-2	20.89	0.14	0.116	0.169
2700	G-3	23.11	0.23	0.262	0.292
2700 -	GS-3	19.76	0.06	0.047	0.119
3000	G-4	20.50	0.11	0.182	0.203
	GS-4	17.60	0.00	0.000	0.040

Table 4. Raman parameter values of experimental samples.

3.3. High-Resolution Transmission Electron Microscopy (HRTEM)

The formation of carbon layers and the state of defects can be observed by HRTEM [45,46]. Through the HRTEM test of the experimental samples, it was observed that, with the increase in the temperature, the graphite sheets were gradually formed and perfected, whereas the length of the carbon layers and stack thickness were gradually increased.

At 2100 °C, the carbon layers in the G and GS samples started to stack with high curvature and different development directions. Compared with G-1, the carbon layer length and stack thickness were larger in GS-1. Both of them were still dominated by disordered structures (Figure 3a,b).

At 2400 °C, large-sized graphite sheets started to form in GS-2, but there were many defects overall, with a low stacking thickness at the edges and many disordered carbon layers still existing inside. The length of the carbon layers in G-2 developed with an increasing temperature, but the overall structure was still disordered (Figure 3c,d).

At 2700 °C, large graphite sheets formed in GS-3 (Figure 4a), with clear and straight graphite sheet edges, and it was observed that multiple graphite sheets were stacked together in a step-like manner (Figure 4b), reflecting good orientation, but the carbon layers in some graphite sheets were still rough. In G-3, the formation of graphite sheets was also observed, with curved and blurred edges, and there were a large number of disordered carbon layers inside. At the same time, carbon layers similar to those in G-2 were observed at some locations in G-3, indicating the existence of inhomogeneous evolution inside.



Figure 3. HRTEM characteristics of G/GS at 2100 °C–2400 °C. (**a**) 2100 °C GS-1; (**b**) 2100 °C G-1; (**c**) 2400 °C GS-2; (**d**) 2400 °C G-2.



Figure 4. HRTEM characteristics of G/GS at 2700 °C. (**a**) 2700 °C GS-3; (**b**) 2700 °C GS-3; (**c**) 2700 °C G-3; (**d**) 2700 °C G-3.

At 3000 °C, graphite sheets in GS-4 were further developed, and the stack thickness of the internal carbon layers increased (Figure 5a). Additionally, graphite sheet outcrops were observed, with straight edges and clear angles at the corners (Figure 5b). The graphitization in G-4 was also improved, which showed more homogeneous evolution and a large number of graphite sheets were produced. However, the graphite sheets in the G-4 sample still had

a high defect degree; most of the graphite sheets showed curved edges and blurred corners, the internal carbon layers were poorly oriented, and the stack thickness was lower than that of GS-4 (Figure 5c,d).



Figure 5. HRTEM characteristics of G/GS at 3000 °C. (**a**) 3000 °C GS-4; (**b**) 3000 °C GS-4; (**c**) 3000 °C G-4; (**d**) 3000 °C G-4.

Oberlin [12] found that the stages of graphitization include stacking, alignment, dewrinkling, and extension. Qin [47] studied the evolution of macromolecular structural units in coal and found that in the later stage of coalification, carbon layers will occur: splicing, stacking, and collocation of both (splicing–stacking). In the graphitization stage, stacking and splicing–stacking are the main processes. In this experiment, the stacking of carbon layers can be observed at 2100 °C in the G samples, and the number of stacked layers kept rising with the increase in the temperature, whereas simple splicing–stacking between carbon layers occurred and made the carbon layers extend; after 2700 °C, graphite sheets formed by complex splicing–stacking can be found in the G samples.

The graphitization degree of the GS samples was higher than that of the G samples, and graphite sheets had been formed at 2100 °C. During the heating process, the interior was mainly based on the process of eliminating defects. As the temperature increases, the edges of the graphite flakes became straighter and more orderly overall.

In the G samples, the change of carbon layers reflected the occurrence of splicing– stacking, which was consistent with Qin's study. In the GS samples, the carbon layers mainly underwent the defect elimination and dewrinkling found in Oberlin's study.

4. Discussion

The structural evolution during coal graphitization is embodied in two aspects: one is the construction of a three-dimensional graphitic structure, characterized by the decrease in carbon interlayer spacing (d_{002}) and the increase in crystallite sizes (La and Lc), and the other is the elimination of lattice defects, measured by Raman parameters (R_2 and R_3). The evolution process of the structural parameters (d_{002} , La, Lc, R_2 , and R_3) of the G and GS samples with the temperature was drawn as curve diagrams, which revealed the transformation process of the three-dimensional disordered coal structure to an ordered graphite structure with the increase in the temperature, and, in this way, the role of SiO_2 in the coal graphitization process can be explained.

4.1. Carbon Interlayer Spacing Evolved with Temperature

The following rules were found using d_{002} as a standard to evaluate the graphitization degree of the high-temperature experimental samples.

During the whole evolution process, at the same temperature, the d_{002} values of the G samples were higher than those of the GS samples, showing a lower graphitization degree.

Although the graphitization degree of the G samples was lower than that of the GS samples, the evolution rate of the G samples was faster. The d_{002} gap between the G and GS samples gradually decreased with the increase in the temperature.

During the experiment, the d_{002} of the G samples uniformly decreased with the increase in the temperature, whereas the GS samples had the fastest evolution rate between 2100 °C and 2400 °C, and the evolution rate gradually decreased with the increase in the temperature; at 2400 °C–2700 °C, the decrease rate of d_{002} was the lowest, and the GS samples evolved the slowest; at 2700 °C–3000 °C, the decrease rate of d_{002} gradually increased, and the d_{002} of the GS samples gradually advanced to 0.3380 nm, which represents the boundary between graphite and semi-graphite, and reached 0.3379 nm at 3000 °C, implying the formation of standard graphite (Figure 6).



Figure 6. d_{002} of samples with changes in temperature.

By plotting the curve of the d_{002} difference between the G and GS samples as a function of the temperature (Figure 7), it was found that d_{002} gradually decreased and the reduction rate of the d_{002} difference gradually increased with the increase in the temperature, which reflected that the catalytic effect of SiO₂ was gradually weakening with the increase in the temperature. It is presumed to be related to the following two points: (1) When the temperature reaches above 2200 °C, part of SiO₂ may escape out in gaseous form with argon, making the content of SiO₂ decreasing and its influence on graphitization weakening. (2) Using d_{002} as a measure of the graphitization degree for evaluation, the GS samples had a higher graphitization degree than the G samples at 2100 °C, and the energy requirement to continue the graphitization process was also higher than that of the G samples; but the energy provided to G and GS in this experiment was the same, so the graphitization rate of the GS samples was lower than that of the G samples.



Figure 7. d₀₀₂ differences of G and GS sample evolution characteristics with temperature.

By comparing the XRD diffraction curves of the G and GS samples, it was observed that the 002 peak of the G samples had stronger asymmetry, reflecting the nonhomogeneous graphitization phenomenon of the G samples (the state of coexistence of graphite and nongraphitic carbon). With the increase in the temperature, the 002 peak tended to be sharp and symmetrical, and the asymmetry gradually decreased. Okabe [43] also found this phenomenon in high-temperature heat treatment of charcoal and thermosetting resin, which was explained as a result of uneven internal stress release due to the internal expansion of carbon crystals at high temperatures, thus exhibiting a nonhomogeneous spatial location of graphitization (Figure 8).



Figure 8. Non-uniform graphitization phenomenon in XRD spectrum ((**left**): thermoset resin carbon [43]; (**right**): 2100 °C, G-1).

The G samples had stronger nonhomogeneous graphitization phenomena as compared with the GS samples, showing a nonhomogeneous evolutionary nature in the spatial perspective (at different positions) and a homogeneous evolutionary nature in the temporal perspective (at different temperatures); this was mainly due to the relatively consistent bridge bonds and low bond energy of vitrinite, whereas the GS samples were affected by SiO₂, resulting in a non-uniform evolution rate.

4.2. Lattice Defects Evolved with Temperature

The R₃ values for the G and GS samples showed similar evolutionary trends. The defect degree of the graphite lattice rapidly decreased with the increase in the temperature,



but the reduction rate and evolutionary trajectory were not identical for the G and GS samples (Figure 9).

Figure 9. Raman parameter (R₂ and R₃) evolution characteristics with temperature.

(1) Due to the high graphitization degree of the experimental samples, no D3 or D4 defect peaks existed; therefore, the R_2 values representing the in-plane defect degree and the R_3 values representing the overall defect degree showed a tendency to decrease, reflecting the disappearance of lattice defects.

(2) With the temperature increases, at 2100 °C–2700 °C, the reduction rate of inplane defects (R₂) of the GS samples was always higher than that of the G samples; at 2700 °C–3000 °C, the R₂ values of the G samples decreased faster than those of the GS samples, but the D1 peak of GS-4 disappeared at 3000 °C and the R₂ value reduced to 0, reflecting the complete disappearance of in-plane defects. Throughout the experiment, the R₂ values of the GS samples were substantially lower than those of the G samples, which reflected the stronger defect healing ability of the GS samples.

③ The decreasing trend and rate of R₃ values were essentially the same for the GS and G samples, but the GS samples had a lower overall defect degree.

(4) The increase in the temperature would obviously promote the reduction of R_3 values. However, there was a bottleneck in the defect reduction process. Below 2700 °C, the R_3 reduction rate gradually decreased with the increase in the temperature, but when the temperature exceeded 2700 °C, the R_3 values rapidly decreased, and the defects in the graphite lattice gradually disappeared with the increase in the temperature.

The R_3 parameter can reflect the overall defect percentage inside the sample lattice. By plotting the curve of the R_3 difference between the G and GS samples as a function of the temperature (Figure 10), it was found that the overall trend of the curve was flat, and the response of the R_3 difference was not sensitive to the temperature change, which only improved from 0.157 to 0.199. SiO₂ showed the ability to significantly promote the healing of lattice defects during the warming process, but this catalytic ability was slightly improved with the changes in the temperature.



Figure 10. Differences in R₃ of G and GS sample evolution characteristics with temperature.

4.3. Graphite Crystallite Structure Parameters Evolved with Temperature

By establishing regular graphs of La and Lc with the temperature (Figure 11), the influence of SiO_2 on the graphite structure evolution process of vitrinite under high temperatures was revealed, and, thus, the mechanism was also revealed:



Figure 11. XRD parameter (La and Lc) evolution characteristics with temperature.

(1) The evolution trends and rates of La values of GS and G samples were basically the same. The La values of the GS samples were always higher than those of G, which reflected that SiO_2 had a significant effect on increasing the diameter of graphite crystallites, and the difference between the La values of the G and GS samples was basically unchanged, indicating that the ability of SiO_2 to increase the stack height of graphite crystallites did not change with the temperature.

(2) At 2100 °C–2400 °C, the Lc values of the GS samples rapidly increased, and the Lc gap with the G samples reached the maximum at 2400 °C; but after 2400 °C, the Lc growth rate significantly decreased and slowly grew. The Lc gap with the G samples at 3000 °C was no longer obvious, presumably related to SiO₂.

(3) Similar to the Raman parameters (R₃), there was also a bottleneck in the evolution of the graphite crystallite structure parameters (La and Lc) with the temperature located at 2700 °C. Above this temperature, the graphite crystallite structures of the G and GS samples rapidly developed, and La and Lc quickly increased.

The regular curve was drawn for the difference in the La/Lc of the G and GS samples as a function of the temperature (Figure 12). In the process of promoting graphite structure formation, SiO_2 mainly promoted the ductility of the crystallites and increased the crystal size. The higher the temperature, the better the catalytic performance.



Figure 12. Difference in La/Lc of G and GS sample evolution characteristics with temperature.

While SiO₂ showed different effects on the stacking degree, the Lc difference gradually increased before 2400 °C and rapidly decreased after 2400 °C. After the temperature reached 3000 °C, the Lc difference decreased to 0.47, with SiO₂ basically showing no catalytic effect on carbon layer stacking.

4.4. The Mechanism by Which SiO₂ Affects Graphitization

SiO₂ has a melting point of about 1600 °C and a boiling point of about 2230 °C, so it existed in a molten–gaseous state during this experiment. The mechanism of its influence on graphitization should also be discussed in stages.

4.4.1. Catalysis of Graphitization by Molten SiO₂

Powdered SiO₂ changed into a molten state under high temperatures and mixed with the vitrinite. Pappano [19] proposed that the attachment of quartz to the surface could facilitate the growth of graphite crystals. Therefore, it is speculated that, after the vitrinite and SiO₂ were mixed in molten form, the carbon attached to the surface of SiO₂, which enlarged the specific surface area and caused the heated area to increase. At the same temperature, the GS samples obtained more energy than the G samples. According to XRD, the internal graphitization of the GS samples was more homogeneous, reflecting more uniform internal heating and more efficient energy transfer.

The XRD data also confirmed this view: the graphitization degree of the GS-1 sample (2100 °C) was even higher than that of the G-4 sample (3000 °C). The participation of molten SiO₂ enhanced the energy-harvesting ability of the GS samples, allowing a higher graphitization degree achieved under the condition of a lower energy supply. Additionally, the 002 peaks of the GS group samples were highly symmetrical, and the spatial uniformity of their graphitization was significantly higher than that of the G group samples, reflecting the fact that the internal heating was more uniform, and the overall graphitization degree was higher.

4.4.2. Catalysis of Graphitization by Gaseous SiO₂

Gonzalez [18] concluded that coal-based minerals could improve the graphitization properties of anthracite. Pappano [19] suggested that when the temperature reaches 1800 °C, molten quartz would react with carbon to form SiC, and SiC will be decomposed to form elemental silicon and elemental carbon above 2600 °C. Qiu [48] noted that the quartz contained in raw coal reacts with carbon above 2000 °C to produce the intermediate product SiC, and SiC will be decomposed to form graphite at 2600 °C.

Combined with previous research results and these experimental data, the following evolutionary mechanism is proposed (Figure 13):



Figure 13. SiO₂ mechanism diagram.

(1) Below 2100 °C, molten SiO₂ reacted with amorphous carbon to form SiC (SiO₂ + $2C \rightarrow SiC + CO_2$), and a distinct SiC peak was observed at 35.5° in the XRD diffraction pattern. This was one of the reasons for the high symmetry of the 002 peak shape: part of the amorphous carbon was consumed in the reaction, causing a significant decrease in the disordered carbon peak intensity.

②Above 2230 °C, SiO₂ reached its boiling point and vaporized, and most of it escaped out of the furnace with the inert gas. A small amount of quartz remained in the furnace and continued to react with amorphous carbon in the form of a gas phase. At this time, the amount of SiC formation was greatly reduced, and the previously generated SiC started to decompose into graphite and silicon when subjected to continuous high temperatures (SiC \rightarrow Si + C). As a result, the intensity of the graphite peak in the XRD pattern of GS-2 was enhanced, whereas the intensity of the SiC peak was significantly reduced. In addition, with the escape of SiO₂, its catalytic effect on graphitization gradually decreased, and the gap between the graphitization of the G and GS samples gradually decreased.

③ In the XRD pattern at 2700 °C, the SiC peak in GS-3 completely disappeared. The previously formed SiC was completely decomposed to form graphite and silicon, then the generated silicon continued to react with amorphous carbon to form SiC; the cycle continued until the amorphous carbon was exhausted or the elemental silicon was completely carried out with the inert gas.

5. Conclusions

In this study, vitrinite in coal from the Gemudi mining area in Guizhou province was used as the raw material, and, after demineralization treatment, the coal-based graphite was prepared by a high-temperature simulation experiment at 2100–3000 °C with the addition of SiO₂ additives as a variable. The experimental results showed that the SiO₂ in the high-temperature experiment had a great influence on the microstructure of coal-based graphite and played a catalytic role. After analyzing the XRD, Raman, and HRTEM results, the following conclusions can be drawn:

(1) Temperature played a crucial role in the formation and growth of graphite structures and dominated the process of high-temperature graphitization. High temperatures were conducive to the stacking of graphite sheets and the development of carbon layers, and promoted the healing of defects in the graphite lattice; thus, graphite with relatively perfect crystal structures was obtained. (2) At the same temperature, the graphitization degree of the samples containing the SiO₂ additive (GS) was always higher than that of the samples without additives (G). The G samples contained a large amount of amorphous carbon inside, as shown by the high asymmetry of the 002 peaks, whereas the GS samples had a sharper and symmetrical 002 peak shape, exhibiting smaller carbon layer spacing (d₀₀₂), better crystallite structure (La/Lc), and a smaller lattice defect ratio (R_2/R_3).

(3) The catalytic performance of SiO_2 was evaluated according to the change in the microstructure: (1) SiO_2 showed an obvious and stable catalytic effect on the healing of lattice defects, and its catalytic ability slightly increased with temperature change. (2) During the crystallite structure formation, SiO_2 significantly promoted the development and growth of the crystallite plane, and its catalytic ability improved with the temperature increase.

(4) At 1600 °C–2230 °C, this stage was dominated by physical catalysis: SiO₂ created adhesion conditions for carbon in the form of a molten state, expanding the heat area of carbon and improving the energy transfer efficiency. Thus, vitrinite reached the high-temperature graphitization stage under the condition of a lower energy supply.

(5) After 2230 °C, this stage was dominated by chemical catalysis as shown in the following reaction: SiO₂ reacted with amorphous carbon and formed SiC (SiO₂ + 2C \rightarrow SiC + CO₂); SiC was thermally decomposed to form elemental silicon and graphite (SiC \rightarrow Si + C), and then the formed elemental silicon continually combined with amorphous carbon (Si + C \rightarrow SiC). The reaction was repeated until the complete depletion of amorphous carbon or silicon, thereby improving the graphitization degree.

Author Contributions: Data curation, G.C. and M.Z.; formal analysis, G.C. and Z.L.; methodology, A.W.; resources, A.W. and Y.W.; supervision, D.C.; writing—original draft, G.C. All authors have read and agreed to the published version of the manuscript.

Funding: This study was financially supported by the National Natural Science Foundation of China (grant nos. 42072197, 41902170, and 41972174).

Data Availability Statement: Data available on request due to restrictions.

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

References

- Cao, D.Y.; Zhang, H.; Dong, Y.J. Research status and key orientation of coal-based graphite mineral geology. *Earth Sci. Front.* 2017, 24, 317–327. (In Chinese with English abstract)
- 2. Wilks, K.R.; Mastalerz, M.; Ross, J.V. The effect of experimental deformation on the graphitization of Pennsylvania anthracite. *Int. J. Coal Geol.* **1993**, *24*, 347–369. [CrossRef]
- 3. Franklin, R.E. Crystallite Growth in Graphitizing and Non-Graphitizing Carbons. Proc. R. Soc. Lond. Ser. A 1951, 209, 196–218.
- Wang, A.M.; Cao, D.Y.; Wei, Y.C.; Liu, Z.F. Macromolecular structure controlling micro mechanical properties of vitrinite and inertinite in tectonically deformed coals—A case study in Fengfeng coal mine of Taihangshan fault zone (North China). *Energies* 2020, 13, 6618. [CrossRef]
- 5. Buseck, P.R.; Beyssac, O. From Organic Matter to Graphite: Graphitization. *Elements* 2014, 10, 421–426. [CrossRef]
- 6. Wang, L.; Cao, D.Y.; Peng, Y.W. Strain-Induced Graphitization Mechanism of Coal-Based Graphite from Lutang, Hunan Province, China. *Minerals* **2019**, *9*, 617. [CrossRef]
- Wang, A.M.; Wei, Y.C.; Cao, D.Y.; Ding, L.Q.; Zhao, M. Effect of different functional groups on CH₄ adsorption heat and surface free energy of vitrinite during coalification. *Appl. Surf. Sci.* 2022, 597, 153748. [CrossRef]
- 8. Fitzer, E.; Weisenburger, S. Evidence of catalytic effect of sulphur on graphitization between 1400 and 2000 °C. *Carbon* **1976**, *14*, 195–198. [CrossRef]
- 9. González, D.; Montes-Morán, M.A.; Garcia, A.B. Influence of inherent coal mineral matter on the structural characteristics of graphite materials prepared from anthracites. *Energy Fuels* **2005**, *19*, 263–269. [CrossRef]
- 10. Inagaki, M.; Hirano, S.; Saito, H. Accelerating effect of coexisting calcium compounds on graphitization under pressure. *Carbon* **1969**, *7*, 722. [CrossRef]
- 11. Bonijoly, M.; Oberlin, M.; Oberlin, A. A possible mechanism for natural graphite formation. *Int. J. Coal Geol.* **1982**, *1*, 283–312. [CrossRef]
- 12. Oberlin, A. High resolution TEM studies of carbonization and graphitization. Chem. Phys. Carbon 1989, 22, 1–143.
- Bustin, R.M.; Ross, J.V.; Rouzaud, J.N. Mechanisms of graphite formation from kerogen: Experimental evidence. *Int. J. Coal Geol.* 1995, 28, 1–36. [CrossRef]

- 14. Noda, T.; Inagaki, M.; Hirano, S. Effect of coexisting minerals on graphitization of carbon under pressure. III. Accelerating effect of calcium hydroxide. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1738–1740. [CrossRef]
- 15. Noda, T.; Kato, H. Heat treatment of carbon under high pressure. Carbon 1965, 3, 289–297. [CrossRef]
- 16. Nyathi, M.S.; Clifford, C.B.; Schobert, H.H. Characterization of graphitic materials prepared from different rank Pennsylvania anthracites. *Fuel* **2013**, *114*, 244–250. [CrossRef]
- 17. Zhang, D.; Cai, H.; Su, Y. Silica samurai: Aristocrat of energy and environmental catalysis. *Chem Catal.* **2022**, *2*, 1893–1918. [CrossRef]
- 18. González, D.; Montes-Morán, M.A.; Suárez-Ruiz, I.; Garcia, A.B. Structural characterization of graphite materials prepared from anthracites of different characteristics: A comparative analysis. *Energy Fuels* **2004**, *18*, 365–370. [CrossRef]
- 19. Pappano, P.J.; Schobert, H.H. Effect of Natural Mineral Inclusions on the Graphitizability of a Pennsylvania Anthracite. *Energy Fuels* **2009**, *23*, 422–428. [CrossRef]
- 20. Wang, A.M.; Cao, D.Y.; Wei, Y.C. Comparison of nanopore evolution in vitrinite and inertinite in coalbed methane reservoirs during coalification. *J. Nat. Gas Sci. Eng.* **2020**, *78*, 103289. [CrossRef]
- Wang, A.M.; Li, J.; Cao, D.Y.; Wei, Y.C.; Ding, L.Q.; Zhao, M. Comparison of nanopore structure evolution in vitrinite and inertinite of tectonically deformed coals: A case study in the Wutongzhuang coal mine of Hebei province, North China. *Front. Earth Sci.* 2022, 10, 822338. [CrossRef]
- 22. Guedes, A.; Valentim, B.; Prieto, A.C.; Noronha, F. Raman spectroscopy of coal macerals and fluidized bed char morphotypes. *Fuel* **2012**, *97*, 443–449. [CrossRef]
- 23. Mahajan, O.P.; Walker, P.L., Jr. Effect of inorganic matter removal from coals and chars on their surface areas. *Fuel* **1979**, *58*, 333–337. [CrossRef]
- 24. Bai, J.; Li, W.; Li, C.Z.; Bai, Z.; Li, B. Influences of minerals transformation on the reactivity of high temperature char gasification. *Fuel Process. Technol.* **2010**, *91*, 404–409. [CrossRef]
- 25. Qiu, T.; Yang, J.G.; Bai, X.J. Investigation on microstructural changes of Anthracite during Graphitization and effect of Silica content on product crystal structure. *Energy Sources Part A Recovery Util. Environ. Eff.* **2021**, *43*, 769–782. [CrossRef]
- 26. Zou, L.; Huang, B.; Huang, Y.; Huang, Q.; Wang, C.A. An investigation of heterogeneity of the degree of graphitization in carbon–carbon composites. *Mater. Chem. Phys.* **2003**, *82*, 654–662. [CrossRef]
- 27. *GB/T 15588-2013;* Chinese Standard: Classification of Macerals for Bituminous Coal. Standardization Administration of the P.R.C.: Beijing, China, 2013.
- 28. *GB/T 8899-2013*; Determination of Maceral Group Composition and Minerals in Coal. Standardization Administration of the P.R.C.: Beijing, China, 2013.
- 29. *GB/T 212-2008*; Proximate Analysis of Coal. Standardization Administration of the P.R.C.: Beijing, China, 2008.
- 30. *GB/T* 476-2001; Ultimate Analysis of Coal. Standardization Administration of the P.R.C.: Beijing, China, 2001.
- 31. Jorjani, E.; Chapi, H.G.; Khorami, M.T. Ultra clean coal production by microwave irradiation pretreatment and sequential leaching with HF followed by HNO3. *Fuel Process. Technol.* **2011**, *92*, 1898–1904. [CrossRef]
- 32. Yu, Z.Y.; Xie, W.N.; Qiu, T.; Lu, Q.C.; Jiang, H.D.; He, Y.Q. Effect of additives on the microstructure of Coal-based Graphite. *Coal Sci. Technol.* **2021**, *32*, 741–749, (In Chinese with English abstract).
- Lu, L.; Sahajwalla, V.; Kong, C.; Harris, D. Quantitative X-ray diffraction analysis and its application to various coals. *Carbon* 2001, 39, 1821–1833. [CrossRef]
- 34. Li, K.; Rimmer, S.M.; Liu, Q.F. Geochemical and petrographic analysis of graphitized coals from Central Hunan, China. *Int. J. Coal Geol.* **2018**, 195, 267–279. [CrossRef]
- 35. Wang, A.M.; Li, J.; Wei, Y.C.; Yang, C.W.; Nie, J.; Cao, D.Y. Gas migration for terrestrial gas hydrates in the Juhugeng mining area of Muli basin, Qilian Mountains, Northwest China. *Energy Explor. Exploit.* **2020**, *38*, 989–1013. [CrossRef]
- 36. Baysal, M.; Yürüm, A.; Yıldız, B.; Yürüm, Y. Structure of some western Anatolia coals investigated by FTIR, Raman, 13C solid state NMR spectroscopy and X-ray diffraction. *Int. J. Coal Geol.* **2016**, *163*, 166–176. [CrossRef]
- 37. Wang, Y.; Serrano, S.; Santiago-Aviles, J.J. Raman characterization of carbon nanofibers prepared using electrospinning. *Synth. Met.* **2003**, *138*, 423–427. [CrossRef]
- 38. Tuinstra, F. Raman Spectrum of Graphite. J. Chem. Phys. 1970, 53, 1126–1130. [CrossRef]
- 39. Rodrigues, S.; Marques, M.; Suárez-Ruiz, I.; Camean, I.; Flores, D.; Kwiecinska, B. Microstructural investigations of natural and synthetic graphites and semi-graphites. *Int. J. Coal Geol.* **2013**, *111*, 67–79. [CrossRef]
- Beyssac, O.; Goffé, B.; Petitet, J.P.; Froigneux, E.; Moreau, M.; Rouzaud, J.N. On the characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 2003, 59, 2267–2276. [CrossRef]
- 41. Kwiecińska, B.; Petersen, H.I. Graphite, semi-graphite, natural coke and natural char classification-ICCP system. *Int. J. Coal Geol.* **2004**, *57*, 99–116. [CrossRef]
- 42. Rantitsch, G.; Lämmerer, W.; Fisslthaler, E.; Mitsche, S.; Kaltenböck, H. On the discrimination of semi-graphite and graphite by Raman spectroscopy. *Int. J. Coal Geol.* **2016**, *159*, 48–56. [CrossRef]
- 43. Okabe, K.; Shiraishi, S.; Oya, A. Mechanism of heterogeneous graphitization observed in phenolic resin-derived thin carbon fibers heated at 3000 °C. *Carbon* **2004**, *42*, 667–669. [CrossRef]

- 44. Cao, D.Y.; Wei, Y.C.; Li, Y. Determination of identification index and construction of classification and classification system of coal measures graphite. *J. China Coal Soc.* **2021**, *46*, 1833–1846. (In Chinese with English abstract)
- 45. Sharma, S.; Shyam Kumar, C.N.; Korvink, J.G.; Kübel, C. Evolution of glassy carbon microstructure: In situ transmission electron microscopy of the pyrolysis process. *Sci. Rep.* **2018**, *8*, 16282. [CrossRef] [PubMed]
- Li, K.; Liu, Q.; Cheng, H.; Hu, M.; Zhang, S. Classification and carbon structural transformation from anthracite to natural coaly graphite by XRD, Raman spectroscopy, and HRTEM. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 2020, 249, 119286. [CrossRef] [PubMed]
- 47. Qin, Y. The study of furthermore discussion on the making-up of macro-molecular basic structural units in coals. *Earth Sci. Front.* **1999**, *6*, 29–34. (In Chinese)
- 48. Qiu, T. Research on the Graphitization Process of Coal and the Migration Rule of Coal-Derived Minerals. Ph.D. Thesis, China University of Mining and Technology, Beijing, China, 2019. (In Chinese with English abstract)





Article Microstructural Characteristics of Graphite Microcrystals in Graphitized Coal: Insights from Petrology, Mineralogy and Spectroscopy

Jiuqing Li^{1,2}, Yong Qin^{1,2,*}, Yilin Chen^{1,2} and Jian Shen^{1,2}

- School of Resources and Geoscience, China University of Mining and Technology, Xuzhou 221008, China
 Kay Laboratory of Coalbed Methana Resources and Resources Termation Process, Ministry of Education
- ² Key Laboratory of Coalbed Methane Resources and Reservoir Formation Process, Ministry of Education, China University of Mining and Technology, Xuzhou 221008, China
- Correspondence: yongqin@cumt.edu.cn; Tel.: +86-13951353093

Abstract: Graphite microcrystals are the product of coal graphitization and widely exist in the graphitized coal of Yongan Coalfield, Fujian Province, China, which is direct mineralogical evidence for the transformation of coal to graphite. Optical microscopy, scanning electron microscopy (SEM) and micro-Raman spectroscopy were used to detect the morphology and microstructure of the in situ graphite microcrystals. The results show that the volume proportion of graphite microcrystals in graphitized coal samples is between 2.39% and 7.32%, and the optical anisotropy of graphite microcrystals is stronger than that of coal macerals. Graphite microcrystals show the occurrence of attached microcrack inner walls or infilling the cell cavity, with several forms of flakes, needles or aggregates. Under optical microscopy of polarized light and with a retarder plate of 1λ , graphite microcrystals show the color of primary yellow and secondary blue, and the two kinds of colors appear alternately when the microscope is rotating. Additionally, flake-like graphite microcrystals with an isochromatic zone diameter of $10-50 \mu m$ are the most widely distributed in graphitized coal. Under SEM, graphite microcrystals show a rough and irregular edge and are characterized by flow or bubble film structures along with several pores, which is the product of cooling crystallization after the softening and melting of carbon-containing substances. Moreover, flake-like graphite microcrystals developed interlayer pores with a clear outline of loose stacking and were almost entirely composed of pure carbon; a small amount of oxygen is related to oxygen-containing functional groups or structural defects. The micro-Raman spectra of graphite microcrystals in the first-order region are characterized by low-intensity D1 and D2 bands and a high-intensity G band, and the parameters R1 and R2 vary from 0.21-0.39 and 0.60-0.74, respectively. The second-order micro-Raman spectra of graphite microcrystals are characterized by a higher intensity of the 2D1 band and a lower intensity of the other three bands. The parameter R3, derived from the area ratio of the 2D1 band to all the bands in the second-order region, was proposed. The value of R3 ranges between 0.78 and 0.86, and both of them indicate a higher percentage of graphene plane with a highly internal crystallographic structure. Similar to the parameters R1 and R2 in the first-order micro-Raman spectrum, the parameter R3 is an effective parameter to characterize the ordering degree of the microstructure, which may be used to evaluate the graphitization degree of graphitization coal.

Keywords: graphite microcrystals; microstructure; graphitized coal; Raman spectroscopy

1. Introduction

Irreversible changes in coal microstructure and chemical structure caused by magma intrusion into coal measure strata have been widely reported [1–4]. The metamorphism of coal increased under magmatic intrusion and tectonic compression, forming anthracite, meta-anthracite, semi-graphite and coaly graphite [5]. Graphitized coal formed in the natural graphitization process of coal with certain amounts of graphite microcrystals with a clear



Citation: Li, J.; Qin, Y.; Chen, Y.; Shen, J. Microstructural Characteristics of Graphite Microcrystals in Graphitized Coal: Insights from Petrology, Mineralogy and Spectroscopy. *Minerals* **2022**, *12*, 1189. https://doi.org/10.3390/min12101189

Academic Editor: Alexandra Guedes

Received: 31 August 2022 Accepted: 19 September 2022 Published: 22 September 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 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/). outline, strong optical anisotropy, diverse occurrences and different morphologies [6,7], which is also named coaly graphite [8], coal-based graphite [9] or thermally altered coals [10]. The metamorphic degree of graphitized coal is between anthracite and graphite, which is the product of late coalification or graphitization from the precursor of coal. Limited by understanding its structure and properties, approximately half of graphitized coal is erroneously assumed to be normal coal burned as fuel, resulting in a significant waste of resources [8]. The higher carbon content and ordered structure of graphitized coal make it an obvious advantage in the preparation of new carbon materials, such as ideal raw materials for preparing graphene as an anode and isotropic graphite filler-particles for lithium-ion batteries [11,12]. The rational development of graphitized coal resources is an effective way to realize high value-added utilization from coal to carbon and fuel to raw materials.

According to their reactivity, the macerals in coal are divided into active macerals, which include liptinite and vitrinite and one-third of semi-inert macerals, and inert content, which includes inertinite macerals and two-thirds of semi-inert macerals as well as mineral matter [13]. Due to the complexity of coal composition and the reactivity of different macerals to temperature and pressure, the graphitization degree of different macerals varies under the same temperature and pressure [3]. The natural graphitization process of coal is accompanied by the differential evolution of macerals; compared with vitrinite, the evolution of liptinite occurs earlier, while the evolution of inertinite has an obvious hysteresis effect, with an overall trend of the transition from organic macerals to inorganic mineral graphite [7,14]. The microstructure is characterized by the formation of a series of newly formed macerals, and the account varies with the degree of coal metamorphism [15]. Under the observation of optical microscopy, Stach et al. summarized the newly formed constituents after magma intrusion into coal seams into four categories: tar, bituminous solid, small spheres and pyrolytic carbon [16]. Qin and Jiang systematically studied the evolution characteristics of the micropetrology of high-rank coals in China and identified several newly generated macerals with inheritance relationships with the original macerals, classifying them into liptinite according to the optical characteristics [17,18]. Li et al. performed a detailed petrographic analysis of graphitized coals from central Hunan, China, and reported newly formed microscopic components, including pyrolytic carbon, needle graphite and flake graphite, in graphitized samples [15]. Needle and flake graphite microcrystals in graphitized coal were also observed in Fujian coal [7]. Recently, flake graphite, crystalline aggregates and matrix graphite in coal-derived natural graphite were described in detail to reveal the transitions from anthracite to natural graphite [5].

Several scholars have focused on bulk graphitized coal samples and have conducted a series of investigations to assess the transition process from anthracite to graphite, such as proximate analysis and ultimate analysis, X-ray diffraction, high-resolution transmission electron microscopy, Fourier transform infrared spectrometry and thermogravimetric analysis [19–25], which have enhanced the understanding of the macromolecular structure of graphitized coal. Generally, coal is an organic matter dominated by an amorphous carbon structure, graphite belongs to inorganic minerals, σ -bonds and π -bonds make carbon atoms in a hexagonal two-dimensional network and the carbon layers are bound by van der Waals forces [26]. The composition of graphitized coal coexists with organic macerals and inorganic mineral graphite microcrystals, and the optical properties and physicochemical properties of organic macerals have been investigated in a previous study [7,15]; however, few studies can be found in the literature describing the microstructural characteristics of in situ graphite microcrystals in natural graphitized coal, which may provide supplemental information for understanding coal graphitization.

Micro-Raman spectroscopy with a high-efficiency, high-precision and nondestructive nature allows for the analysis of carbonaceous matter, which provides information on the degree of structural ordering and lattice vibrations and is an important and suitable method for studying subtle structural characterization of carbonaceous materials [27], such as graphene, carbon nanotubes (CNTs), carbon black and amorphous carbons such as coal, char and kerogen [27–29]. Scanning electron microscopy (SEM) can directly observe the microstructure of materials from the micron to submicron level, and the elemental composition can be detected with energy dispersive X-ray spectrometry (EDS). In the current study, the microplot analysis methods of optical microscopy, SEM and micro-Raman spectroscopy were used to investigate the microstructure of in situ graphite microcrystals in graphitized coal. The purpose is to understand the transformation process of organic carbon (coal) to an inorganic graphite structure from the perspective of petrology, mineralogy and spectroscopy and deepen the knowledge of graphitized coal. The results will benefit the high value-added utilization and application of naturally graphitized coals.

2. Geological Setting

The Yongan Coalfield is located in southwestern Fujian Province, China (Figure 1a), and the coalfield forms an important part of the late Paleozoic Yongan Basin and the late Mesozoic granite belt along the southeastern coast of China [30]. The main coal-bearing strata are in the Middle Permian Tongziyan Formation, which comprises marine deposits of terrigenous origin. The lithology is mainly mudstone and siltstone, followed by fine sandstone with thin coal seams, characterized by a thin single layer of coal and multiple layers at depth [31]. Based on the lithology and sedimentary environment, three lithological subunits from the bottom up are divided [32]. The lower subunit is composed of siltstone, carbonaceous mudstone and a thin coal seam of barrier island to lagoon facies; the middle section, consisting of thick neritic siltstone with siderite nodules, lacks a coal seam; and the upper section comprises thick layers of siltstone interbedded with carbonaceous mudstone and coal seams of marine origin [33].



Figure 1. (a) The location of Yongan Coalfield; (b) Sampling locations and structural outline of the Yongan Coalfield, South China (modified from [7]).

The multiperiod large-scale tectonic movements of the Yongan Coalfield are controlled by the Zhenghe-Dapu fault in the NE–NNE direction and the Yongan-Jinjiang fault in the NW direction (Figure 1b). Secondary faults in the same direction developed along both sides of the fault zone, and multidirectional and multigroup faults intersect to form a grid structure pattern in the study area [34]. The tectonic movements with strong intensity induced a series of structural deformations with different scales, especially extensional and compressional gliding nappe structures characterized by multilevel and multistage features [31]. The coal-bearing strata were strongly deformed by compressional stress that caused local thickening or thinning of the coal seams, which provided additional strain energy for coal graphitization [34].

In addition, regional magmatic intrusions during the Indosinian, Yanshanian and Himalayan orogenies associated with tectonic movements are common in the Yongan Coalfield, especially in the Yanshanian period [35], which led to the formation of large quantities of granitoids whose distribution was controlled by NNE-striking faults (Figure 1b). The magmatic intrusions invade coal-bearing strata in the form of dikes or dykes, and the single layer thickness varies from centimeters to meters, showing zonality and directionality and wide exposure in the Yongan Coalfield. Thermal and strong emplacement pressures caused by magmatic intrusion have a great influence on the structure pattern and mineralization of metal deposits [36] and are also the main geological controlling factor for the high degree of coal metamorphism in the Yongan Coalfield.

3. Samples and Analytical Procedures

3.1. Sampling

A total of five graphitized coal samples were collected from the upper section of the Tongziyan Formation at four coal mines in the Yongan Coalfield, of which CO1 and CO3 from the Changao mine, QK, JK and PK form the Qiongkou mine, Jiakui mine and Peikeng mine, respectively. The samples were collected in accordance with the Chinese Standard for Collecting Channel Samples GB/T 482-2008 [37] and stored in polyethylene bags immediately to reduce contamination and oxidation as much as possible. Under the observation of the naked eye, the samples were steel gray, soft, fragile and strongly deformed, with irregular friction mirror surfaces and scaly structures that provided a broken and smooth texture.

3.2. Analytical Methods

3.2.1. Proximate and Ultimate Analyses

Proximate and ultimate analyses were carried out by crushing graphitized coal samples to 80 mesh (~180 μm). Proximate analysis, including moisture content, ash yield and volatile matter, was performed in accordance with Chinese National Standard GB/T 3521-2008 [38], while the ultimate analyses, including C, H, O and N content, were conducted in accordance with Chinese National Standard GB/T 31391-2015 [39].

3.2.2. Optical Microscopy

The petrographic and reflectance analyses of macerals along with graphite microcrystals were performed on particulate pellets with randomly oriented particles using a Leica DM2500P microscope (at a magnification of $500 \times$) with a CRAIC microscope photometer system. The petrographic analysis was conducted under reflected light, polarized light with a gypsum test plate (1 λ) and cross-polarized light using a rotating microscope stage. Petrological composition statistics were undertaken using the point counting method with a total of 500 points per sample in accordance with Chinese National Standard GB/T 8899-2013 [40]. The maximum and minimum reflectances of each particle (vitrinite and flake-like graphite microcrystals) were measured under polarized light by rotating the microscope stage through 360° [7]. A minimum of 30 particles were measured for each maceral. The reflectance measurement system was linearly calibrated with standards of known reflectance (sapphire, Ro = 0.589%, gadolinium–gallium–garnet, Ro = 1.725%, cubic zirconia, Ro = 3.08%, strontium titanate, Ro = 5.36%, and silicon carbide, Ro = 7.46%).

3.2.3. Scanning Electron Microscopy

Scanning electron microscopy (SEM; ZEISS SIGMA) equipped with an energy dispersive X-ray spectrometer (EDS, OxfordX-Max20; Oxford Instruments, Abingdon, UK) was used to observe the morphology and determine the elemental distribution of graphite microcrystals. The selected sample briquettes were gold-coated before SEM–EDS analyses. SEM images were captured by a retractable solid-state backscatter electron detector with a 20.0-kV beam voltage, 10-mm working distance and a 5.0-spot size setting.

3.2.4. Raman Spectroscopy

Raman spectroscopy of graphite microcrystals was conducted on polished pellets using a Senterra Laser Raman spectrometer (Bruker, Bremen, Germany) equipped with a Leica microscope under a laser wavelength of 532 nm. A 50 × objective lens was used to focus the excitation laser beam with a diameter of ~2 μ m. The power of the laser was set to 5 mW to avoid burning of the carbonaceous materials, and the Raman analysis system was calibrated using a standard silicon wafer. Ten different spots were scanned for each graphite microcrystal in the range of 1000–3400 cm⁻¹, and each spectrum was subjected to peak fitting with Origin 8.5 software (Version Origin 8.5.0, Originlab, Massachusetts, USA) to resolve the curve using a Gaussian-curve-fitting module. The parameters obtained included the peak position, full width at half maximum (FWHM), R1 = AD1/AG (intensity ratio of bands), R2 = AD1/(AD1 + AD2 + AG) (area ratio of bands) and R3 = A2D1/(A2D4 + A2D1 + A(D1 + G) + A2D2) (area ratio of bands), which were used to characterize the structure of graphite microcrystals.

4. Results and Discussions

4.1. Geochemistry Characterization of Graphitized Coal

The geochemical data of graphitized coal samples are shown in Table 1. The organic elemental composition of coal samples shows a carbon content (daf) ranging from 89.25% to 96.88 wt.%, hydrogen content (daf) less than 0.10% in all samples except CO1 (0.94%), nitrogen content (daf) ranging from 0.14 to 0.27% and oxygen content (daf) lower than the detection limit in CO1 and QK, ranging from 2.94% to 5.76% in the other three samples, indicating that the element composition of graphitized coal is mainly carbon. Volatile matter yields (daf) range from 1.55% to 8.79% and are less than 5.0% in most samples, indicating that samples are all high rank with a metamorphic grade commensurate with anthracite or above [41]. The mean maximum reflectance of vitrinite (VR_{max}) varies from 7.01% to 8.95%; on the basis of VR_{max} values, the samples are generally coalified at the semi-graphite stage [42].

Samples			Reflecta	nce/%			I A	Proximat .nalysis/	e %	U	Ultimate Analysis/%				Maceral Composition/%			
	VR _{max}	s.d.	GM_{max}	s.d.	GM_{\min}	s.d.	$M_{\rm ad}$	A_{d}	V_{daf}	C_{daf}	H_{daf}	$O_{\rm daf}$	$N_{\rm daf}$	V	Ι	L	GM	
CO1	7.94	0.42	10.21	0.54	0.87	0.16	2.24	21.90	8.79	89.25	0.94	nd	0.14	90.11	1.68	0.90	7.32	
CO3	7.17	0.52	10.83	0.46	0.85	0.16	6.88	22.51	5.29	93.87	0.00	5.76	0.26	87.98	6.71	2.12	3.18	
QK	8.95	0.47	nd	nd	nd	nd	7.26	13.95	1.55	96.19	0.09	nd	0.27	86.15	9.74	1.73	2.39	
JK	7.01	0.43	8.49	0.44	1.33	0.25	12.90	14.54	2.61	96.88	0.00	2.94	0.15	90.21	6.11	0.00	3.68	
PK	7.32	0.39	9.75	0.47	1.25	0.19	9.62	11.64	2.85	96.66	0.01	2.98	0.15	89.37	4.55	1.82	4.26	

Note: VR_{max} —mean maximum reflectance of vitrinite; GM_{max} —mean maximum reflectance of flake-like graphite microcrystals; GM_{min} —mean minimum reflectance of graphite microcrystals; s.d.—standard deviation; V—vitrinite; I—inertinite; L—liptinite; nd—not detected.

4.2. Petrography Characterization of Graphite Microcrystals

The petrographic composition measurements showed that all the graphitized coal samples were predominantly composed of vitrinite, with a total volume percentage of 86.15%–90.21%, with minor quantities of inertinite and very rare liptinite, graphite microcrystals with a proportion of 2.39%–7.32% (Table 1). Although the volume ratio of graphite microcrystals is relatively low, as a new type of maceral widely existing in graphitized coal, graphite microcrystals provide reliable mineralogical evidence for the transformation of coal to graphite.

Under the microscope, graphite microcrystals show the occurrence of microcrack filling and cell cavity filling, and the former is the most common (Figure 2). The microcrackfilled graphite microcrystals are attached to or grow along the inner wall of the fracture, and their size is controlled by the morphology and dimension of microcracks, showing flake, needle-like and mosaic morphology and occurrence by a cluster aggregate (Figure 2a-e). The cell-cavity-filled graphite microcrystals are limited by volume, and most of them occur as aggregates (Figure 2f,g). As shown in Figure 2a, graphite microcrystals are characterized by bright white under reflected-light microscopy, which is slightly distinguished from the original macerals (e.g., vitrinite, inertinite, and liptinite). Notable optical anisotropy is exhibited under reflected single-polarized light observation (Figure 2b,c). Using polarized light and with a retarder plate of 1λ (Figure 2d,e), the graphite microcrystals show the color of primary yellow and secondary blue and only one kind of color along the microcrack, indicating the consistent arrangement direction of graphite microcrystals [26]. The two kinds of colors (primary yellow and secondary blue) exchange with each other when the stage is rotating for 90° , similar to the mosaic structure shown in coke [13]. Graphite microcrystals filled in the cell cavity of fusinite with a smaller size and showed the same color in different cell cavities, indicating the consistent arrangement of graphite microcrystals in a small range of aggregates (Figure 2f,g).

As shown in Figure 3, at least three morphologies of graphite microcrystals of flake-like graphite microcrystals, needle-like graphite microcrystals and graphite microcrystal aggregates were observed in the microcracks of graphitized coal. Flake- and needle-like graphite microcrystals are common in microcracks with large spaces, and graphite microcrystal aggregates are mainly at the edges of microcracks or small cell cavities. The morphology of graphite microcrystals observed by polarized light and with a retarder plate of 1λ is clearer than single-polarized light observation, which provides more details combined with the two kinds of colors and is a better method to identify graphite microcrystals. The length of the isochromatic region under polarized light and with a retarder plate of 1λ ranges between 10 µm and 50 µm, and the flake-like graphite microcrystals show a flow structure in the microcrack and a lower filling degree of microcracks (Figure 3a–d). However, both the needle-like graphite microcrystals and graphite microcrystal aggregates had a relatively dense structure (Figure 3e–h).

Due to the strong tectonic deformation of graphitized coal, microcracks are extremely developed, the flake-like graphite microcrystals are common in different graphitized coal samples, and the size of the flake-like graphite microcrystals is large enough to meet the reflectance measurement. As shown in Table 1, the mean maximum reflectance of the flake-like graphite microcrystals ranges between 8.49% and 10.83%, higher than the mean maximum reflectance of vitrinite in the same sample. However, the mean minimum reflectance of flake-like graphite microcrystals ranges between 0.85% and 1.33%; that is, a higher bireflectance value of flake-like graphite microcrystals is characterized, coinciding with the extremely strong optical anisotropy observed in Figure 3. Based on the observation of the occurrence and types of graphite microcrystals, the formation of graphite microcrystals is probably by the methods of vapor deposition as described by "gas graphite" [16], similar to pyrolytic carbon. A similar phenomenon of pyrolytic carbon can be observed in the data published by Li et al. [15] for graphitized coal and in Yuan et al. [5] for a set of coal-based graphite samples.



Figure 2. Occurrence characteristics of graphite microcrystals in graphitized coal samples. (a) Filmlike graphite microcrystals as microcrack filling in sample CO1, non-polarized light; (b) graphite microcrystals attached fracture wall in sample JK, reflected single-polarized light; (**c**–**e**), graphite microcrystals as fracture-filling in PK, reflected single-polarized light for (**c**) and polarized light and with a retarder plate of 1λ for (**d**,**e**), (**e**) is the same field of view as (**d**) but after stage rotation of 90°; (**f**,**g**) graphite microcrystals as cell-infillings in sample QK, plane-polarized light for (**f**) and polarized light and with a retarder plate of 1λ for (**g**).



Figure 3. Morphology of graphite microcrystals in graphitized coal samples. (**a**) Flake-like graphite microcrystals (FG), needle-like graphite microcrystals (NG) and graphite microcrystal aggregates (GA) in sample PK, reflected single-polarized light; (**b**) the same field of view as a, polarized light and with a retarder plate of 1λ ; (**c**) FG infilling the fracture in sample CO1, reflected single-polarized light; (**d**) the same field of view as (**c**) polarized light and with a retarder plate of 1λ ; (**e**) GA infilling the cell, plane-polarized light in sample CO3; (**f**) the same field of view as (**e**), polarized light and with a retarder plate of 1λ ; (**g**) FG and GA infilling the cell in sample QK, reflected single-polarized light; (**h**) the same field of view as (**g**) polarized light and with a retarder plate of 1λ .

4.3. Mineralogy Characterization of Graphite Microcrystals

The graphite microcrystals infilling the microcrack under the observation of SEM are shown in Figure 4. A clear boundary between the cracks and the coal matrix is observed, and the flake-like graphite microcrystals with irregular morphology and uneven surfaces are attached to microcracks with a width of $5-20 \mu m$ (Figure 4a,c,e). After local enlargement, it was observed that the graphite microcrystals were attached to the inner wall of the fracture in the form of bubble film, showing an obvious flow structure, and several nanoscale pores were seen on the surface of the graphite microcrystals (Figure 4b,d,f). Several voids with different sizes and shapes between the graphite microcrystals exist, showing a low degree of filling. These characteristics are indicative of cooling crystallization after softening and melting of carbonaceous materials, coinciding with the occurrence observed under the optical microscope (Figure 3). The morphology of graphite microcrystals shows the embryonic form of lamellae, indicating an intermediate state of carbon crystallization.



Figure 4. Occurrence of graphite microcrystals in graphitized coal samples under SEM. (**a**) graphite microcrystals as fracture-filling in sample CO1; (**b**) enlargement of rectangle in (**a**) with flowing and pore structure; (**c**) graphite microcrystals as fracture-filling in sample CO3; (**d**) enlargement of rectangle in (**c**) with several pore structure in the boundary of fracture; (**e**) graphite microcrystals as fracture-filling in sample CO1; (**f**) enlargement of rectangle in (**e**) with flake and flowing structure and several pores.

Under the observation of SEM, flake-like graphite microcrystals with a higher crystallization degree were also observed in the graphitized coal, showing a nearly parallel arrangement and loose stacking in the bedding direction (Figure 5a). A smooth and flat surface of graphite microcrystals was observed under local enlargement, with a diameter ranging between 1 μ m and 3 μ m and tabular shape, and interlayer pores were also developed between the graphite microcrystal particles (Figure 5b). In addition, irregular flake-like graphite microcrystals with a diameter larger than 5 μ m occurred in clusters with a rough edge (Figure 5c). Elongated flake-like graphite microcrystals stacked at random were also observed (Figure 5d), both of which had a flat surface. As shown in Figure 5e,f, the EDS of graphite microcrystals shows that the element composition is almost pure



carbon, the existence of rare O elements may be related to the oxygen functional groups at the edge or defects of the graphite microcrystal structure, and minor Si elements are mainly clay minerals adhered to the surface of graphite microcrystals.

Figure 5. SEM images of graphite microcrystals in graphitized coal samples. (**a**) Flake-like graphite microcrystals in sample CO1; (**b**) enlargement of rectangle in (**a**); (**c**) irregular flake graphite microcrystals in sample CO3; (**d**) flake-like graphite microcrystals in sample QK; (**e**) EDS spectrum of point in (**c**); (**f**) EDS spectrum of point in (**d**).

4.4. Raman Characterization of Graphite Microcrystals

Figure 6 shows the Raman shape and profile of graphite microcrystals in graphitized coal samples, and the first-order Raman spectral parameters are listed in Table 2. The pronounced and well-resolved band in the first-order Raman spectral profiles is the G band located in the position of 1582–1583 cm⁻¹ (Figure 6a,b and Table 2), which coincides with the pure-carbon graphite that shows only one band in their Raman spectra located at approximately 1582 cm⁻¹ [43] and is also called the graphite band in the literature [27]. The G band is usually attributed to the E_{2g} vibrational mode of a graphene plane or polyaromatic carbon atoms [44,45], indicating the existence of a polyaromatic structure in carbonaceous matter. Another well-resolved band is the D1 band in the position of 1350–1351 cm⁻¹; however, the intensity of the D1 band is prominently lower than that of the G band, which characterizes the formation of graphite microcrystals during the graphitization process [46] or crystal growth from coal to graphite [47]. The D1 band is usually attributed to in-plane defects in the polyaromatic layers or edge of the sp² graphene plane [44,48,49], and it disappears in pure graphite [27,43]. Moreover, a third poorly

defined band, D2, is clearly distinguished as a shoulder on the right side of the G band at approximately 1622–1624 cm⁻¹ in the spectra of almost all graphite microcrystal samples (Figure 6a,b and Table 2). The D2 band is always induced by defects and indicates a perfect structure of graphite microcrystals. Generally, another two disordered bands (D3 and D4 bands) at ~1500 cm⁻¹ and 1350 cm⁻¹ were observed in graphitized coal samples [46]; however, the two bands disappeared in graphite microcrystals, indicating that the aliphatic moieties on the carbon skeleton and amorphous carbon were almost removed.



Figure 6. (a) Raman spectra of graphite microcrystals in graphitized coal; (b) peak fitting of Raman spectrum in the first-order region of sample CO1; (c) peak fitting of Raman spectrum in the second-order region of sample CO1.

Fable 2. First-order Raman spectra	l parameters o	f graphite microcrystals c	lerived from peak fitting
------------------------------------	----------------	----------------------------	---------------------------

Samulas		D1/	cm ⁻¹			G/c	m ⁻¹			R1	R2			
Samples	Position	n s.d.	FWHM	s.d.	Positior	n s.d.	FWHM	s.d.	Position	n s.d.	FWHM	s.d.	- 111	1.2
CO1	1351	1.48	34	1.97	1583	1.86	22	1.52	1622	1.34	13	1.66	0.39	0.64
CO3	1351	1.26	37	1.39	1582	1.25	20	1.19	1624	1.09	7	0.81	0.21	0.74
QK	1351	1.55	34	1.84	1583	2.03	20	1.87	1624	0.75	9	0.97	0.36	0.60
JK	1351	2.18	35	1.08	1583	1.17	21	1.59	1623	1.16	11	1.62	0.35	0.62
PK	1350	1.13	33	1.52	1582	1.28	20	1.64	1622	0.92	8	1.06	0.21	0.74

The full width at half maximum (FWHM) for the D1 and G bands ranges from 33 to 37 cm⁻¹ and 20 to 22 cm⁻¹, respectively (Table 2), and both show a narrow value similar to semi-graphite and graphite samples [27]. The values of R1 (intensity ratios) obtained from the D1 and G bands are used to assess the degree of disordering of the graphite crystalline

structure, and the value of R1 ranges from 0.21 to 0.39 in graphite microcrystals, indicating a higher structure crystallographic order [27]. The parameter R2 (area ratio of the G band and all the first-order Raman spectra) is an indicator for determining the improvement in the order degree of structure. The R2 of graphite microcrystals ranges from 0.60 to 0.74, which coincides with the lower intensity of the defect band (D1 and D2 bands), indicating graphite microcrystals with a higher percentage of graphene planes. The weaker D1 band intensity and narrow FWHM of the G band in graphite microcrystals are related to the high condensation of aromatic rings and the shortening of alkyl chains [28,50], suggesting a highly internal crystallographic structure. Moreover, the coexistence of a higher G band and lower D1 and D2 bands indicate a heterogeneous structure of graphite microcrystals and a state of transformation from coal to pure graphite. Actually, the structure coincides with the results that graphite microcrystals are the transition products from coal to graphite.

The bands in the second-order region (2200-3400 cm⁻¹) of Raman spectra originate from the overtone and combination of the first-order vibration modes, providing additional and useful information of structural and crystallographic order [9]. Figure 6 shows the Raman shape and profile of graphite microcrystals in graphitized coal samples, and the second-order Raman spectral parameters are listed in Table 3. The most prominent feature in second-order Raman spectra is the 2D1 band located in the position of 2701–2707 cm⁻¹ which is assigned to the overtone of the D1 band in the first-order Raman spectra [51,52]. The 2D1 band is related to the number of graphene layers and represents the sensitivity of the π - π bond in the graphitic structure [53], but it does not reflect any disorder or defect structure of the graphite crystal as the D1 band [54]. The higher intensity of the 2D1 band indicates that graphite microcrystals with a higher composition of π - π bonds and better crystallinity, demonstrating that layered graphite structures are gradually produced. The 2D1 band split into two adjacent overlapping bands in graphite indicates a triperiodic organization [55,56]; however, it does not appear in the present study, suggesting that the evolution of graphitized coal may not reach pure graphite but a middle transition from coal to graphite.

Samples -		2D4	/cm ⁻¹			2D1/	′cm ^{−1}			D1+G	G/cm ⁻¹			2D2/	cm ⁻¹		D 2
	Positi	ons.d.	FWH	M s.d.	Positi	on s.d.	FWH	M s.d.	Positio	on s.d.	FWH	M s.d.	Positi	on s.d.	FWH	M s.d.	- K3
CO1	2460	2.26	60	1.26	2701	1.96	69	1.36	2940	2.16	65	1.09	3242	2.26	28	0.93	0.83
CO3	2461	1.85	54	1.58	2707	2.25	82	1.86	2947	1.85	70	1.26	3248	1.92	37	1.16	0.78
QK	2455	1.61	56	1.86	2703	1.54	69	1.08	2945	1.67	66	1.65	3246	2.16	38	1.35	0.84
JK	2464	2.08	51	1.67	2704	1.71	78	0.94	2947	1.39	64	1.38	3246	1.66	29	0.86	0.86
PK	2454	2.59	59	2.24	2705	1.63	80	1.39	2946	2.04	75	1.24	3245	1.59	33	0.97	0.86

Table 3. Second-order Raman spectral parameters of graphite microcrystals derived from peak fitting.

In addition, there are three bands in the second-order Raman spectrum with a weaker intensity compared with the 2D1 band. As shown in Table 3, the 2D4 band located in the position range between 2555 and 2464 cm⁻¹ is attributed to the overtone of the D4 band, and the 2D2 band range between 3242 and 3248 cm⁻¹ is the overtone of the D2 band, both of which are related to the defects between the graphene layer. The disordered structure is represented by the D1 + G band at 2940–2947 cm⁻¹ and is always attributed to the combination of the D1 and G bands [57]. The lower intensity of the three bands above in graphite microcrystals coincides with the semi-graphite and graphite that undergo graphitization processes [46], indicating that graphite microcrystals are products of graphitization. In contrast to the first-order Raman spectra, the band position is relatively fixed but fluctuates in a relatively narrow range in second-order Raman spectra, as does the FWHM, mainly because second-order Raman spectra are the overtones or combinations of bands in the first-order region, and the distance between bands in the second-order region is larger than that in the first-order region.

Based on the attribution and characteristics of second-order Raman bands in the present study, the parameter R3 obtained from the area ratio of 2D1 to all the second-order

Raman bands is proposed to evaluate the degree of ordering of the crystalline structure. As shown in Table 3, graphite microcrystals with R3 values ranging between 0.78 and 0.86 indicate a high area ratio of the 2D1 band. Lünsdorf et al. [58] proposed that there is no single Raman parameter that shows a steady change throughout the transformation from low maturity materials through maturation to meta-anthracite and graphite; however, Li et al. [28] studied different coal ranks and concluded that for the specific maturation stages, it may be meaningful. Moreover, the increase in the intensity of the 2D1 band in the second-order Raman spectrum suggests that the evolution degree has reached the graphitization stage [2]. Compared with band intensity, the band area involves more information about the morphology of the Raman spectrum, such as FWHM and band intensity. In the current study, both of the graphite microcrystals have higher R3 values, similar to the parameters of R1 and R2, and the parameter R3 indicates a relatively high degree of structural order. Furthermore, as a fast and non-destructive approach to characterize carbonaceous materials, R3 may be an indicator for assessing the graphitization degree of graphitized coal.

5. Conclusions

Graphite microcrystals in graphitized coal are direct mineralogical evidence of coal graphitization. The microstructure characteristics of in situ graphite microcrystals in graphitized coal of Yongan Coalfield, Fujian Province, China, were investigated by optical microscopy, scanning electron microscopy and micro-Raman spectroscopy. The following conclusions can be drawn:

- (1) Graphite microcrystals are characterized by filling microcracks and cell cavities in graphitized coal, with the morphology of flake, needle and aggregates. The volume proportion of graphite microcrystals is between 2.39% and 7.32%, and the optical anisotropy is stronger than that of coal macerals. Under polarized light with a retarder plate of 1λ , graphite microcrystals show the color of primary yellow and secondary blue, and the two kinds of color appear alternately when rotating the microscope stage. The isochromatic zone of flake-like graphite microcrystals with a diameter of $10-50 \mu$ m shows an arrangement order along the microcracks;
- (2) The morphology of graphite microcrystals filled with microcracks shows a rough and irregular edge, flow-like or bubble film-like structures along with several pores, indicating a formation mode similar to vapor deposition as cooling crystallization after softening and melting of carbon-containing substances. Moreover, flake-like graphite microcrystals that developed interlayer pores with a clear outline of loose stacking were also observed. The elemental composition was almost pure carbon, and a small amount of oxygen was related to oxygen-containing functional groups or structural defects;
- (3) The micro-Raman spectra of graphite microcrystals show low-intensity D1 and D2 bands and high-intensity G bands in the first-order region and a higher intensity of the 2D1 band and a lower intensity of the other three bands in the second-order region. The parameters R1 and R2 range from 0.21–0.39 and 0.60–0.74, respectively, and the parameter R3 proposed in this paper ranges between 0.78 and 0.86, both of them indicate a higher percentage of graphene plane with a highly internal crystallo-graphic structure.

Author Contributions: Software, J.L.; writing—original draft, J.L. and Y.Q.; supervision, Y.Q. and Y.C.; formal analysis, J.L. and J.S.; data curation, J.L. and Y.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the National Natural Science Foundation of China (No. 42130802).

Data Availability Statement: Not applicable.

Acknowledgments: Special thanks are given to Ningning Zhong and Qingyong Luo of China University of Petroleum (Beijing) for their help in using reflected-light microscopy and Ruijin Deng

of Fujian Administration of Coal Geology for sample collection. We are also particularly grateful to the editors and two anonymous reviewers for providing useful suggestions and comments on the manuscript.

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

References

- 1. Dai, S.; Ren, D. Effects of magmatic intrusion on mineralogy and geochemistry of coals from the Fengfeng–Handan Coalfield, Hebei, China. *Energy Fuels* **2007**, *21*, 1663–1673. [CrossRef]
- 2. Li, K.; Rimmer, S.M.; Liu, Q.; Zhang, Y. Micro-Raman spectroscopy of microscopically distinguishable components of naturally graphitized coals from central Hunan Province, China. *Energy Fuels* **2019**, *33*, 1037–1048. [CrossRef]
- 3. Wang, L.; Cao, D.; Peng, Y.; Ding, Z.; Li, Y. Strain-induced graphitization mechanism of coal-based graphite from Lutang, Hunan Province, China. *Minerals* **2019**, *9*, 617. [CrossRef]
- 4. Wu, Y.; Li, K.; Wang, Z.; Hu, M.; Cao, H.; Liu, Q. Fluctuations in graphitization of coal seam-derived natural graphite upon approaching the Qitianling granite intrusion, Hunan, China. *Minerals* **2021**, *11*, 1147. [CrossRef]
- 5. Yuan, L.; Liu, Q.; Li, K.; Quan, Y.; Li, X.; Mathews, J.P. The evolution of coal, examining the transitions from anthracite to natural graphite: A spectroscopy and optical microscopy evaluation. *Front. Earth Sci.* **2022**, 1–13. [CrossRef]
- 6. Li, J. Composition and Optical Proporty Evolution of Macerals in Meta-Anthracite from Yongan, Fujian, China. Master's Thesis, China University of Mining and Technology, Xuzhou, China, 2019.
- 7. Li, J.; Qin, Y.; Chen, Y.; Luo, Q.; Deng, R.; Guo, S.; Zhong, N.; Chen, Q. Differential graphitization of organic matter in coal: Some new understandings from reflectance evolution of meta-anthracite macerals. *Int. J. Coal Geol.* **2021**, 240, 103747. [CrossRef]
- 8. Cao, D.; Zhang, H.; Dong, Y.; Wu, G.; Ning, S.; Mo, J.; Li, X. Research status and key orientation of coal-based graphite mineral geology. *Front. Earth Sci.* 2017, 24, 317–327.
- 9. Zhang, S.; Liu, Q.; Zhang, H.; Ma, R.; Li, K.; Wu, Y.; Teppen, B.J. Structural order evaluation and structural evolution of coal derived natural graphite during graphitization. *Carbon* **2020**, *157*, 714–723. [CrossRef]
- 10. Chen, H.; Wang, S.; Zhang, X.; Zhao, Y.; Zhang, H. A study of chemical structural evolution of thermally altered coal and its effect on graphitization. *Fuel* **2021**, *283*, 119295. [CrossRef]
- 11. Shi, Y.; Zang, W.; Nan, D.; Huang, Z.; Liu, X.; Zheng, Y.; Shen, W. Preparation of graphitized Taixi coal and its electrochemical properties. *J. China Coal Soc.* **2012**, *37*, 1925–1929.
- 12. Shen, K.; Cao, X.; Huang, Z.H.; Shen, W.; Kang, F. Microstructure and thermal expansion behavior of natural microcrystalline graphite. *Carbon* **2021**, *177*, 90–96. [CrossRef]
- 13. Suarez-Ruiz, I.; Crelling, J.C. *Applied Coal Petrology: The Role of Petrology in Coal Utilization;* Academic Press: New York, NY, USA, 2008; pp. 180–186.
- 14. Taylor, G.; Teichmüller, M.; Davis, A.; Diessel, G.F.K.; Littke, R.; Robert, P. Organic Petrology; Gebruder Borntraeger: Berlin, Germany, 1998; pp. 162–174.
- 15. Li, K.; Rimmer, S.M.; Liu, Q. Geochemical and petrographic analysis of graphitized coals from Central Hunan, China. *Int. J. Coal Geol.* **2018**, *195*, 267–279. [CrossRef]
- 16. Stach, E.; Mackowsky, M.-H.; Teichmüller, M.; Taylor, G.H.; Chandra, D.; Teichmüller, R. *Stach's Textbook of Coal Petrology*; Gebruder Borntraeger: Berlin, Germany, 1982.
- 17. Qin, Y. *Micropetrology and Structural Evolution of High-Rank Coals in China;* China University of Mining and Technology Press: Xuzhou, China, 1994.
- Qin, Y.; Jiang, B. Coalification jumps, stages and mechanism of high-rank coals in China. In *Geology of Fossil Fuels–Coal*; CRC Press: Boca Raton, FL, USA, 2020; pp. 99–122.
- 19. Beyssac, O.; Goffé, B.; Chopin, C.; Rouzaud, J.N. Raman spectra of carbonaceous material in metasediments: A new geothermometer. J. Metamorph. Geol. 2002, 20, 859–871. [CrossRef]
- 20. Oberlin, A. Carbonization and graphitization. Carbon 1984, 22, 521–541. [CrossRef]
- 21. Zheng, Z.; Zhang, J.; Huang, J.Y. Observations of microstructure and reflectivity of coal graphites for two locations in China. *Int. J. Coal Geol.* **1996**, *30*, 277–284. [CrossRef]
- Mathews, J.P.; Fernandez-Also, V.; Jones, A.D.; Schobert, H.H. Determining the molecular weight distribution of Pocahontas No. 3 low-volatile bituminous coal utilizing HRTEM and laser desorption ionization mass spectra data. *Fuel* 2010, *89*, 1461–1469. [CrossRef]
- 23. Liu, Q.; Yuan, L.; Li, K.; Cui, X.; Yu, L. Structure characteristics of different metamorphic grade coal-based graphites. *Earth Sci.* **2018**, *43*, 1663–1669.
- 24. Li, K.; Liu, Q.; Hou, D.; Wang, Z.; Zhang, S. Quantitative investigation on the structural characteristics and evolution of high-rank coals from Xinhua, Hunan Province, China. *Fuel* **2021**, *289*, 119945. [CrossRef]
- 25. Li, J.; Qin, Y.; Chen, Y.; Song, Y.; Wang, Z. HRTEM observation of morphological and structural evolution of aromatic fringes during the transition from coal to graphite. *Carbon* **2022**, *187*, 133–144. [CrossRef]
- 26. Marsh, H. Introduction to Carbon Science; Butterworth Publishers: London, UK, 1989.

- 27. Kwiecinska, B.; Suarez-Ruiz, I.; Paluszkiewicz, C.; Rodriques, S. Raman spectroscopy of selected carbonaceous samples. *Int. J. Coal Geol.* **2010**, *84*, 206–212. [CrossRef]
- 28. Li, K.; Rimmer, S.M.; Presswood, S.M.; Liu, Q. Raman spectroscopy of intruded coals from the Illinois Basin: Correlation with rank and estimated alteration temperature. *Int. J. Coal Geol.* **2020**, *219*, 103369. [CrossRef]
- 29. Wopenka, B.; Pasteris, J.D. Structural characterization of kerogens to granulitefacies graphite: Applicability of Raman microprobe spectroscopy. *Am. Mineral.* **1993**, *78*, 533–557.
- 30. Zu, F.; Shu, L.; Li, C. Evolution features of depositional and tectonic setting from late Paleozoic to Meso–Cenozoic in the Yong'an Basin. *Int. Geol. Rev.* 2012, *50*, 126–148.
- 31. Chen, Q.; Deng, R.; He, Z.; Wang, R. Occurrence Characteristics and Coal Prospecting Mode of Deep Coal Resources in Permian Coal-Bearing Area of Fujian Province; Geological Publishing House: Beijing, China, 2016; pp. 35–41.
- 32. Shu, L.; Faure, M.; Wang, B.; Zhou, X.; Song, B. Late Palaeozoic–early Mesozoic geological features of South China: Response to the Indosinian collision events in Southeast Asia. *Compt. Rendus Geosci.* **2008**, *340*, 151–165. [CrossRef]
- 33. Huang, N. The characteristics of sedimentary structure of Lower Permian series Tongzi petrofabic of Permian system in Fujian and the range of coal-finding. *J. Jiaozuo Inst. Technol.* **1998**, *17*, 34–38.
- 34. Wang, L.; Cao, D.; Ding, Z.; Chen, Q.; Deng, R.; Lin, X.; Li, Y.; Du, X. Controlling factors and metallogenic belts of coal-based graphite in the South-weatern Fujian province. *J. China Coal Soc.* **2020**, *45*, 2865–2871.
- 35. Zhang, Z.; Zuo, R. Tectonic Evolution of southwestern Fujian Province and spatial–temporal distribution regularity of mineral deposits. *Acta Petrol. Sin.* **2015**, *31*, 217–229.
- Zhang, Y.; Xu, X.; Jia, D.; Shu, L. Deformation record of the change from Indosinian collision-related tectonic system to Yanshanian subduction-related tectonic system in South China during the Early Mesozoic. *Front. Earth Sci.* 2009, 16, 234–247.
- 37. GB/T 482-2008; Sampling of Coal Seams. Standardization Administration of the P.R.C.: Beijing, China, 2008.
- 38. *GB/T* 3521-2008; Method for Chemical Analysis of Graphite. Standardization Administration of the P.R.C.: Beijing, China, 2008.
- 39. *GB/T* 31391-2015; Ultimate Analysis of Coal. Standardization Administration of the P.R.C.: Beijing, China, 2015.
- 40. *GB/T 8899-2013;* Determination of Maceral Group Composition and Minerals in Coal. Standardization Administration of the P.R.C.: Beijing, China, 2013.
- 41. GB/T 5751-2009; Chinese Classification of Coals. Standardization Administration of the P.R.C.: Beijing, China, 2009.
- 42. Kwiecińska, B.; Petersen, H.I. Graphite, semi-graphite, natural coke, and natural char classification—ICCP system. *Int. J. Coal Geol.* 2004, *57*, 99–116. [CrossRef]
- 43. Pasteris, J.D.; Wopenka, B. Raman spectra of graphite as indicators of degree of metamorphism. Can. Mineralog. 1991, 29, 1–9.
- 44. Tuinstra, F.; Koenig, J.L. Raman Spectrum of Graphite. J. Chem. Phys. 1970, 53, 1126–1130. [CrossRef]
- 45. Ammar, M.R.; Galy, N.; Rouzaud, J.N.; Toulhoat, N.; Vaudey, C.E.; Simon, P.; Moncoffre, N. Characterizing various types of defects in nuclear graphite using Raman scattering: Heat treatment, ion irradiation and polishing. *Carbon* **2015**, *95*, 364–373. [CrossRef]
- Zhang, S.; Song, B.; Cao, C.; Zhang, H.; Liu, Q.; Li, K.; Teppen, B.J. Structural evolution of high-rank coals during coalification and graphitization: X-ray diffraction, Raman spectroscopy, high-resolution transmission electron microscopy, and reactive force field molecular dynamics simulation study. *Energy Fuels* 2021, 35, 2087–2097. [CrossRef]
- 47. Bernard, S.; Beyssac, O.; Benzerara, K.; Findling, N.; Tzvetkov, G.; Brown, G.E. XANES, Raman and XRD Study of Anthracenebased Cokes and Saccharose-based Chars Submitted to HighTemperature Pyrolysis. *Carbon* **2010**, *48*, 2506–2516. [CrossRef]
- 48. Pocsik, I.; Hundhausen, M.; Koós, M.; Ley, L. Origin of the D Peak in the Raman Spectrum of Microcrystalline Graphite. J. Non-Cryst. Solids **1998**, 227–230, 1083–1086. [CrossRef]
- 49. Pimenta, M.A.; Dresselhaus, G.; Dresselhaus, M.S.; Cancado, L.G.; Jorio, A.; Saito, R. Studying Disorder in Graphite-Based Systems by Raman Spectroscopy. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1276–1290. [CrossRef]
- 50. Ferrari, A.C.; Robertson, J. Interpretation of Raman spectra of disordered and amorphous carbon. *Phys. Rev. B* 2000, *61*, 14095–14107. [CrossRef]
- 51. Nemanich, R.J.; Solin, S.A. First- and second-order Raman scattering from finite-size crystals of graphite. *Phys. Rev. B.* **1979**, *20*, 392–401. [CrossRef]
- 52. Sato, Y.; Kamo, M.; Setaka, N. Raman spectra of carbons at 2600–3300 cm⁻¹ region. Carbon 1978, 16, 279–280. [CrossRef]
- 53. Zhang, H.; Li, K.; Sun, J.; Sun, Z.; Yuan, L.; Liu, Q. The structural evolution and mutation of graphite derived from coal under the influence of natural igneous plutonic intrusion. *Fuel* **2022**, *322*, 124066. [CrossRef]
- Wang, S.; Li, T.; Wu, L.; Zhang, L.; Dong, L.; Hu, X.; Li, C. Second-order Raman spectroscopy of char during gasification. *Fuel Process. Technol.* 2015, 135, 105–111. [CrossRef]
- 55. Rodrigues, S.; Marques, M.; Suárez-Ruiz, I.; Camean, I.; Flores, D.; Kwiecinska, B. Microstructural investigations of natural and synthetic graphites and semi-graphites. *Int. J. Coal Geol.* **2013**, *111*, 67–79. [CrossRef]
- 56. Rantitsch, G.; Lämmerer, W.; Fisslthaler, E.; Mitsche, S.; Kaltenböck, H. On the discrimination of semi-graphite and graphite by Raman spectroscopy. *Int. J. Coal Geol.* 2016, 159, 48–56. [CrossRef]
- 57. Sadezky, A.; Muckenhuber, H.; Grothe, H.; Niessner, R.; Pöschl, U. Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information. *Carbon* **2005**, *43*, 1731–1742. [CrossRef]
- Lünsdorf, N.K.; Dunkl, I.; Schmidt, B.C.; Rantitsch, G.; Eynatten, H. Towards a higher comparability of geothermometric data obtained by raman spectroscopy of carbonaceous material. Part 2: A revised geothermometer. *Geostand. Geoanal. Res.* 2017, 41, 593–612. [CrossRef]

MDPI AG Grosspeteranlage 5 4052 Basel Switzerland Tel.: +41 61 683 77 34

Minerals Editorial Office E-mail: minerals@mdpi.com www.mdpi.com/journal/minerals



Disclaimer/Publisher's Note: The title and front matter of this reprint are at the discretion of the Guest Editors. The publisher is not responsible for their content or any associated concerns. The statements, opinions and data contained in all individual articles are solely those of the individual Editors and contributors and not of MDPI. MDPI disclaims responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.




Academic Open Access Publishing

mdpi.com

ISBN 978-3-7258-3089-3