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Fluctuations in Graphitization of Coal Seam-Derived Natural Graphite upon Approaching the Qitianling Granite Intrusion, Hunan, China

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Abstract: The Lutang graphite deposit in Chenzhou, Hunan province, China, is a well-known coal seam-derived graphite (graphite formed from coal during its natural evolution) deposit with proven reserves of 9.5 million tons and prospective reserves of around 20 million tons (2015 data). The graphite occurs at an andalusite bearing sericite quartz chlorite metamorphic mudstone around a c. 530 km² Qitianling granite intrusion. A set of coal seam-derived graphite samples from the Lutang graphite deposit in Hunan was examined by geochemical, crystallographic, and spectroscopic techniques to assess changes in the degree of graphitization approaching the intrusion. The carbon content, degree of graphitization, and Raman spectral parameters of series coal seam-derived natural graphite samples show a fluctuating increase with increasing proximity to the granite intrusion. The profile of geological structural features has a close spatial correlation with the variations in the degree of graphitization of series coal seam-derived natural graphite, and a strain-enhanced graphitization model is proposed. Moreover, the geographical distribution and the degree of graphitization are positively related to changes in the iron content of chlorite, suggesting a graphitization process promoted by mineral catalysis during metamorphism. A close spatial relationship exists between graphite mineral and chlorite occurrences when approaching the intrusive mass. The results of this research are important for understanding the role of tectonic stress and mineral catalysis on the genesis of coal-derived graphite.

Keywords: coal seam; graphitization; shear stress; catalysis; granite intrusion



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1. Introduction

Contact metamorphism is a typical natural process of transformation of the protolith into a new type of rock under variations of the physico-chemical environment caused by magmatic intrusion. The zone of contact metamorphism around the igneous intrusion (metamorphic aureole) varies according to the type and depth of the intrusive event, the porosity, and the thermal conductivity of the adjacent crust [1–3]. It is generally believed that the heat radiated from the contact with the intrusion is the highest in the central metamorphic aureole. Therefore, the metamorphic grade is highest in the center and diminishes with increasing distance from the contact [4–6].

Contact metamorphism of coal under the influence of intrusive magmatism is also a common geological phenomenon. The heat, emanation, and dynamic effects of the intruded rock can induce graphitization in the coal seam and organic matters in the associated rock, thus forming coal seam-derived graphite. This type of graphite is also known as natural graphite derived from coal [7,8] or microcrystalline graphite [9]. As a type of graphite ores, coal seam-derived graphite has attracted significant interest from researchers due to its economic efficiency, ease of mining, and potential utilization as a cutting-edge material.

Previous research results show that the degree of structural ordering in coal is controlled by the metamorphic rank thereof [5,10–16]. Meanwhile, much investigation on

the formation of coal seam-derived graphite using optical microscopy, X-ray diffraction (XRD), micro-Raman spectroscopy, and high-resolution transmission electron microscopy (HRTEM) has been performed. However, there is no consensus on the mechanism of graphitization of coal under natural processes at time of writing this paper. Previous studies found the precursor materials, metamorphic temperature, duration of action of heat, catalyst, fluid activity, pressure, and shear stress exert different influences on the transformation from coal to graphite [17–22]. Franklin investigated the graphitization of different origins of carbon materials at different temperatures [20]. Oberlin and Terriere pointed out that the microporous nature of anthracite is responsible for a preferential planar orientation of the polyaromatic structures in comparison with Kerogens [19]. Bonijoly et al. endorsed findings to the effect that the temperature, pressure, and shear stress caused by metamorphism and tectonics facilitate the graphitization process. Pusz et al. showed how the texture of the higher-rank anthracites is more flexible (thus conducive to rearrangement) than lower-rank anthracite during heat-treatment at up to 1000 °C [23]. Nyathi et al. stated that the more metamorphosed anthracite tends to graphitize in a manner resulting in better crystal structure than less metamorphosed anthracite during high-temperature treatment [24]. By conducting comparative experiments, Pappano and Schobert found that anthracite with mineral catalysts more readily forms a three-dimensional ordered graphite structure than demineralized anthracite in heating experiments [25].

The development of coal seam-derived graphite in geological settings is a complex process, as a highly stable graphite structure formed from amorphous coal due to the magma intruding into coal seams at depths of several kilometers. According to specific geological context, research into the coal to graphite transformation during contact metamorphism has emerged, revealing the mechanism of coal-to-graphite transformation under natural conditions [10,26]. The coal-to-graphite transformation in coal starts at the semi-anthracite rank, which contains a small amount of aromatic ring structures. It is then transformed to anthracite, meta-anthracite, and finally forms semi-graphite and graphite in a manner dependent on the degree of ordering of the polyaromatic layers. It is well accepted that with decreasing distance from the intrusive mass, the original coal is gradually transformed into anthracite, meta-anthracite, semi-graphite, and graphite.

However, we found that the degrees of graphitization of coal seam-derived natural graphite samples do not increase monotonically with decreasing distance to the intrusion, suggesting that the temperature is not the only factor controlling this natural graphitization process. Other factors, such as strain and mineral catalyzation, should also be considered; therefore, it is imperative to clarify the main conditions for participating in natural coal graphitization. Here, we present results of geochemical analysis and microstructure analysis (X-ray diffraction and Raman spectroscopy) of coal seam-derived graphite sampled at various distances from the intrusion, discussing the relationship between fluctuations in the degree of graphitization of coal seam-derived graphite with tectonic events and chemical composition.

2. Geological Setting

The Lutang coal seam-derived graphite is located at the Lutang–Shatian composite syncline on the northern margin of the middle section of the Nanling metallogenic belt that is controlled by the compound syncline (Figure 1a,b). The Qitianling granitic pluton is a batholith formed at multiple stages during the early Yanshanian period (163–146 Ma), which can be divided into three intrusive stages [27–29]. The contact boundary between the Qitianling granite body and the ore-bearing strata is NNE striking and mostly subject to dentate or branch-like intrusive contact (Figure 1c). Complicated folds and reverse faults formed due to the intense tectonic movement and magma intruding events, while different degrees of contact metamorphism occurred at different distances from the intrusive rock mass.

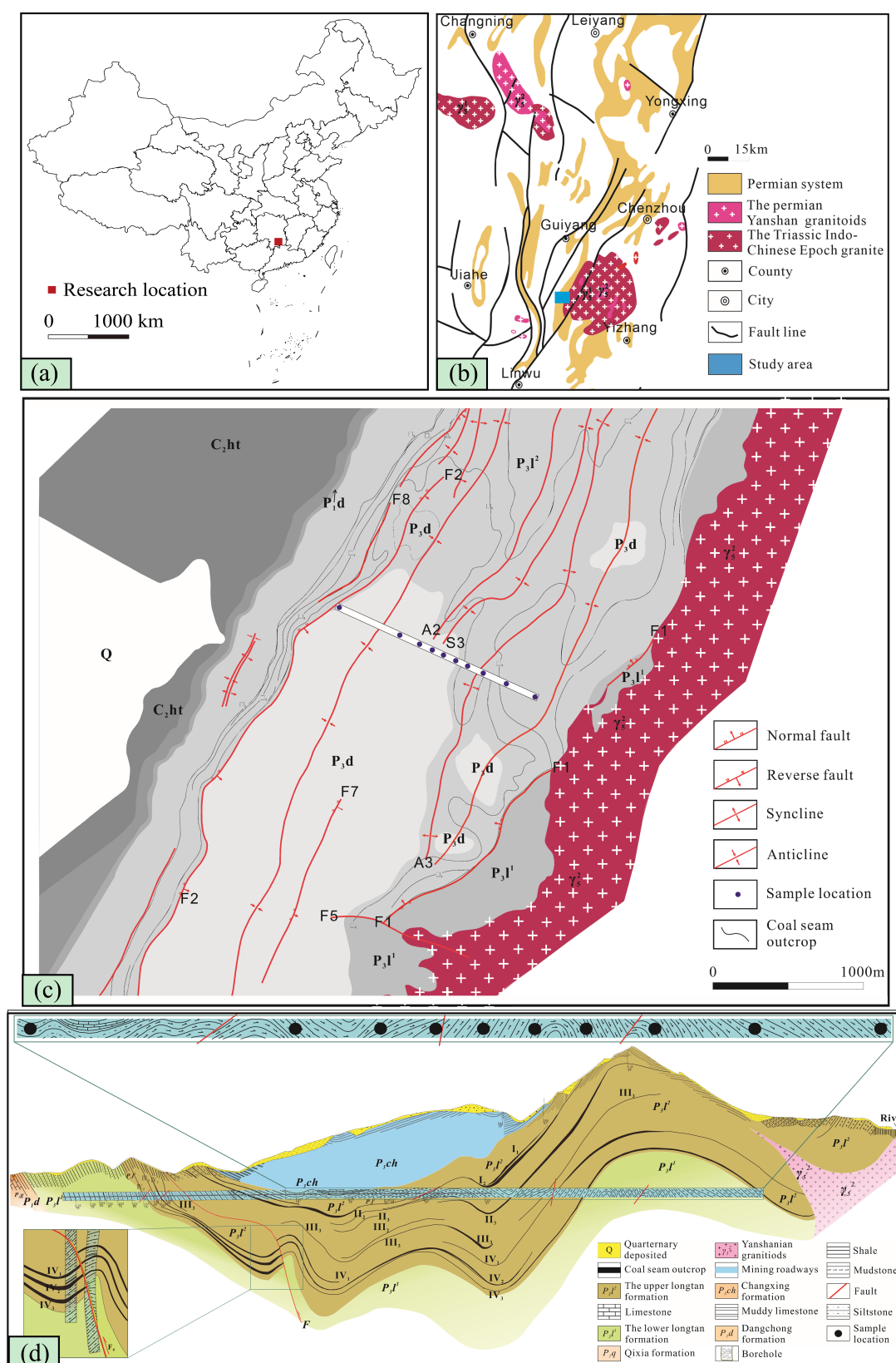


Figure 1. (a) Location of the research area; (b) geological sketch map of southern Hunan showing the general geological features of the study area (after Ma, 2002) [30]; (c) geological map of the study area with sampling positions; (d) schematic cross section through the mining area including the sampling positions. (a,b) have been redrawn and modified based on Zheng et al. (1986) [31].

In the western side of the pluton of the study area, a sequence of index minerals (cordierite, kyanite, andalusite, and tourmaline) representing different petrographic facies of contact metamorphism [32] appears. The metamorphic framework of Qitianling intrusion in this study can be divided into three metamorphic zones from west to east that include medium-weak hornfels zones, strongly hornfels, and hornfels, which consist of spotted-schist and hornfels comprising the following sequence: chlorite, biotite, cordierite, andalusite-cordierite, and garnet-andalusite [33].

The main tectonic structure is characterized by the Lutang–Shatian syncline that trends NNE in the research area. The west wing outcrops are relatively complete, and the syncline axis is gentle, while the east flank of the syncline is incompletely exposed. Affected by the compression of the intrusive rock, the east flank is relatively large and contains many secondary folds. Therefore, most of the deformation features on the western flank are characterized by broad, gentle folds, while the tectonic units at the eastern flank are marked by distinct, tight folds. In addition, the development of fault structures in the mining area destroys the continuity and integrity of the mining layer; near the intrusive rock mass, the faults are generally high-angle reverse faults, which cut graphite deposits and cause duplication and deformation of the deposits (Figure 1d).

In the mining area, the upper Permian Longtan formation is the coal-bearing stratum, which consists of a set of littoral sedimentary structures dominated by sandstone, siltstone, mudstone, and four layers of coal seams (I, II, III, IV) [34]. The coal seams were gradually transformed into graphite (coal seam-derived graphite) under the influence of the Qitianling granite intrusion. The coal seam-derived graphite strata consist of four layers divided into 11 small layers in which only five layers can be mined, and layers I₂ and IV₃ are the main mining seams [35]. Strong deformations were common in the channels and working faces during sampling.

3. Samples and Analytical Procedures

3.1. Sampling

A total of 30 graphite-seam channel samples (including ten coal seam-derived graphite and 20 non-coal/graphite roof, parting, and floor strata at the sampling site) were collected along a line approaching the intrusion from the underground working faces. Samples were numbered according to their spatial position within the mining area. From the entrance of the mine towards the granite body, all the collected samples were stored in polyethylene bags immediately in order to reduce contamination and oxidation from mine operations as much as possible. In addition, the samples were collected in accordance with the Chinese Standard for Collecting Channel Samples GB482-2008 [36].

3.2. Analytical Methods

3.2.1. Proximate and Ultimate Analyses

Proximate analyses were conducted in accordance with Chinese National Standard GB/T 3521-2008 (method for chemical analysis of graphite) [37], while the ultimate analyses were made using a Vario Macro Cube element analyzer (Elementar, Hanau, Germany) in accordance with Chinese National Standard GB/T 31391-2015 [38].

3.2.2. X-ray Diffraction

XRD analysis was performed for the coal seam-derived graphite. Each graphite sample was pretreated with a mixture of hydrofluoric acid and hydrochloric acid. The liquid-solid ratio was 2, the volume ratio of hydrochloric acid was 40%, and the reaction time was three hours at 60 °C after being washed four times [39]. Both CBGs and host rock measurements were conducted on a Rigaku D/MAX-2500PC X-ray powder diffractometer (Rigaku, Tokyo, Japan) (40 kV, 100 mA) with Cu K α graphite monochromatized radiation ($\lambda = 1.54178 \text{ \AA}$) over the scanning range $2.5^\circ \leq 2\theta \leq 70^\circ$ at a scanning speed of $2^\circ/\text{min}$. The stacking height (L_c) and lateral size of CBG crystallites were determined from (002)~ 26.8° and (100)~ 42.5° reflection peaks, respectively, using conventional Scherrer equations: $L_a = 1.84\lambda/\beta_a \cos(\theta_a)$;

$L_c = 0.89\lambda / \beta_c \cos(\theta_c)$, where β_a and β_c denote the full width at half maximum (FWHM) of fitted (100) and (002) peaks, respectively, and θ_a and θ_c are the corresponding scattering Bragg angles of each peak [40].

3.2.3. Raman Spectroscopy

A HORIBA HR800 confocal micro-Raman spectrometer (Horiba, Paris, France), equipped with an Nd-YAG laser (5 mW, 532 nm) and a BX41 50x objective lens (Olympus) was used to characterize the micro and nanostructures of graphite at room temperature. Extended scans from 600 to 3200 cm^{-1} for the Raman spectrum were conducted in situ on each graphite specimen, with a registration time of 60 s allowed for each spectrum. Meanwhile, the Raman spectrometer was equipped with a density filter to avoid the thermal decomposition of samples. Each spectral analysis was conducted with LabSpec 5 (LS5) software (Version LS5: 2.02, Horiba, Paris, France) [41,42].

3.2.4. Electron Probe

Chemical analyses of chlorite were undertaken using a Shimadzu EPMA-1600 electron probe, using natural and synthetic standard minerals, with the following standard conditions: 15 kV and 10 nA, (PAP correction procedure). Simultaneously, the analytical spot radius was set to 1.5 μm . The chlorite chemical formula was based on 14 oxygen atoms per formula unit (a.p.f.u). In order to calculate the crystallization temperature for chlorite, the WinCcac software [43] was used in which 12 empirical formulae based on previous research were established to calculate the paleotemperature.

4. Results

4.1. Proximate, Ultimate, and Microscopic Analyses

The geochemical data of series naturally graphitized coal specimens are shown in Table 1. The carbon content (daf) ranges from 92.85 to 99.67 wt%, and the H content is near or below the detection limit. The volatile matter yields of the series samples are lower than 6%, indicating that all specimens reached a metamorphic grade commensurate with anthracite (or above). As the ratio of VM/Cdaf has a low range of $0.27\text{--}6.11 \times 10^{-2}$, this points to the relatively higher coal rank and lower thermal sensitivity than compared to other lower rank coal towards combustion and pyrolysis [44,45]. As shown in Figure 2, the ash content (% d) is between 0.25% and 6%, which generally decreases when approaching the intrusion; however, it still shows a trend of decreasing volatility, with significant fluctuations therein. The carbon content (% daf) measured between 92.85% and 99.67%, showing a fluctuating increase in the sampling sites closer to the contact horizon, and similar results for naturally graphitized coals were also obtained by Wang et al. [46,47].

Table 1. Proximate and ultimate analysis of samples.

Samples NO.	Distance (m)	Proximate Analysis (%)				Ultimate Analysis (% daf)					H/C 10^{-2}	O/C	VM/Cdaf 10^{-2}
		Moist	Ash	FC	VM	S	C	H	N	O			
LT-5-16	1340	0.25	51.8	45.5	2.7	0.03	94.4	0.02	0.69	4.83	0.02	0.05	2.86
5-5	840	0.3	28.2	69.75	2.05	0.11	97.14	0	0.13	2.58	nd	0.03	2.11
5-11	760	0.76	27.8	69.66	2.54	0.21	96.48	0	0.11	3.12	nd	0.03	2.63
5-13	630	0.41	14.7	81.89	3.41	0.06	96	0.11	0.45	3.37	0.11	0.04	3.55
5-14	480	0.39	10.4	88.53	1.07	0.05	98.81	0	0.07	1.06	nd	0.01	1.08
5-16	430	0.25	8.4	89.79	1.81	0.05	98.02	0	0.09	1.84	nd	0.02	1.85
5-18	330	6	20.7	73.63	5.67	0.12	92.85	0.5	0.45	6.04	0.54	0.07	6.11
NF5-5	200	0.28	23.2	73.21	3.59	0.11	95.33	0	0.38	4.15	nd	0.04	3.77
NF5-9	150	0.82	27.8	70.97	1.23	0.03	98.3	0	0.17	1.49	nd	0.02	1.25
5-19-7-31	1	0.35	17.8	81.93	0.27	0.03	99.67	0	0.06	0.23	nd	0.01	0.27

Note: Data are ordered by decreasing distance to the intrusion horizon. Moist—moisture, air-dry basis; Ash—ash yield, dry basis; FC—fixed carbon, dry basis; VM—volatile matter, dry ash-free basis; Nd—not detected; ad—air-dry basis; d—dry basis; daf—dry ash-free basis.

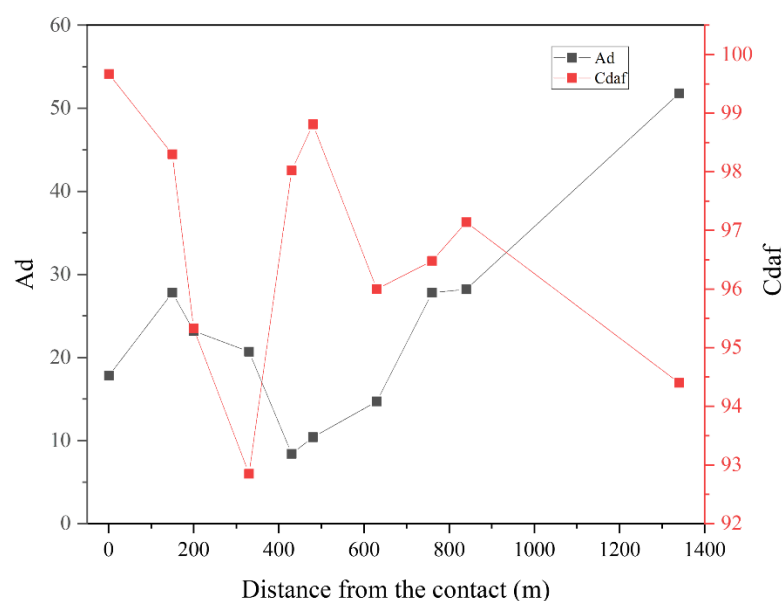


Figure 2. Contents of Ad and Cdaf versus distance from the intrusive contact horizon.

4.2. XRD Analysis

Figure 3 presents the XRD spectra of 10 series of naturally graphitized coals arranged by distance from the intrusion, with two illustrations of partially enlarged details viewed on the (002) and (100) peaks showing the data in the low-intensity region. As shown in Table 2, only one anomalous estimated d_{002} interlayer spacing (0.3454 nm), in a specimen sampled at the greatest distance from the magmatic intrusion, was characterized as anthracite ($d_{002} > 0.340$ nm, with a typical anthracite diffraction profile), as shown in Figure 3 and Table 2 [48], while other d_{002} values range from 0.3367 to 0.3393 nm, as represented by sharp peaks and narrow full width at half maxima (FWHM), evincing its graphitic characteristics [48]. The FWHM of series samples shows a fluctuating decrease with decreasing the distance from the intrusion. A similar trend was found in crystalline parameters (L_c and L_a). The values of L_c ranged from 10.7 to 21.63 nm in addition to that of the most distant specimen at 1.83 nm; with the exception of the most distant sample, the L_a values changed in a more complicated manner albeit they were all within the range of 30.82–53.58 nm. This finding indicates that tridimensional ordering occurred with decreasing distance to the contact horizon even though the permutation is not strictly or universally applicable [49,50]. Notably, the structural parameters (L_c and L_a) of LT-5-5 (the second farthest sampling site from the intrusion) are not lower than those close to the intrusion. These distinct formations might be because of anomalous thermal gradients and the catalysis of abnormal elements during their graphitization. The mechanism of the distinct formation will be further discussed in later sections.

Table 2. XRD parameters and optical reflectance of samples.

Samples	D (m)	d_{002} (nm)	FWHM (°)	L_c (nm)	L_a (nm)
LT-5-16	1340	0.3454	4.402	1.83	5.14
5-5	840	0.3367	0.523	15.43	44.09
5-11	760	0.3381	0.562	14.36	52.01
5-13	630	0.3393	0.754	10.70	34.69
5-14	480	0.3372	0.468	17.24	42.27
5-16	430	0.3375	0.574	14.06	45.94
5-18	330	0.3375	0.519	15.55	35.25
NF5-5	200	0.3374	0.548	14.72	30.82
NF5-9	150	0.3373	0.373	21.63	53.58
5-19-7-31	1	0.3379	0.461	17.50	42.57

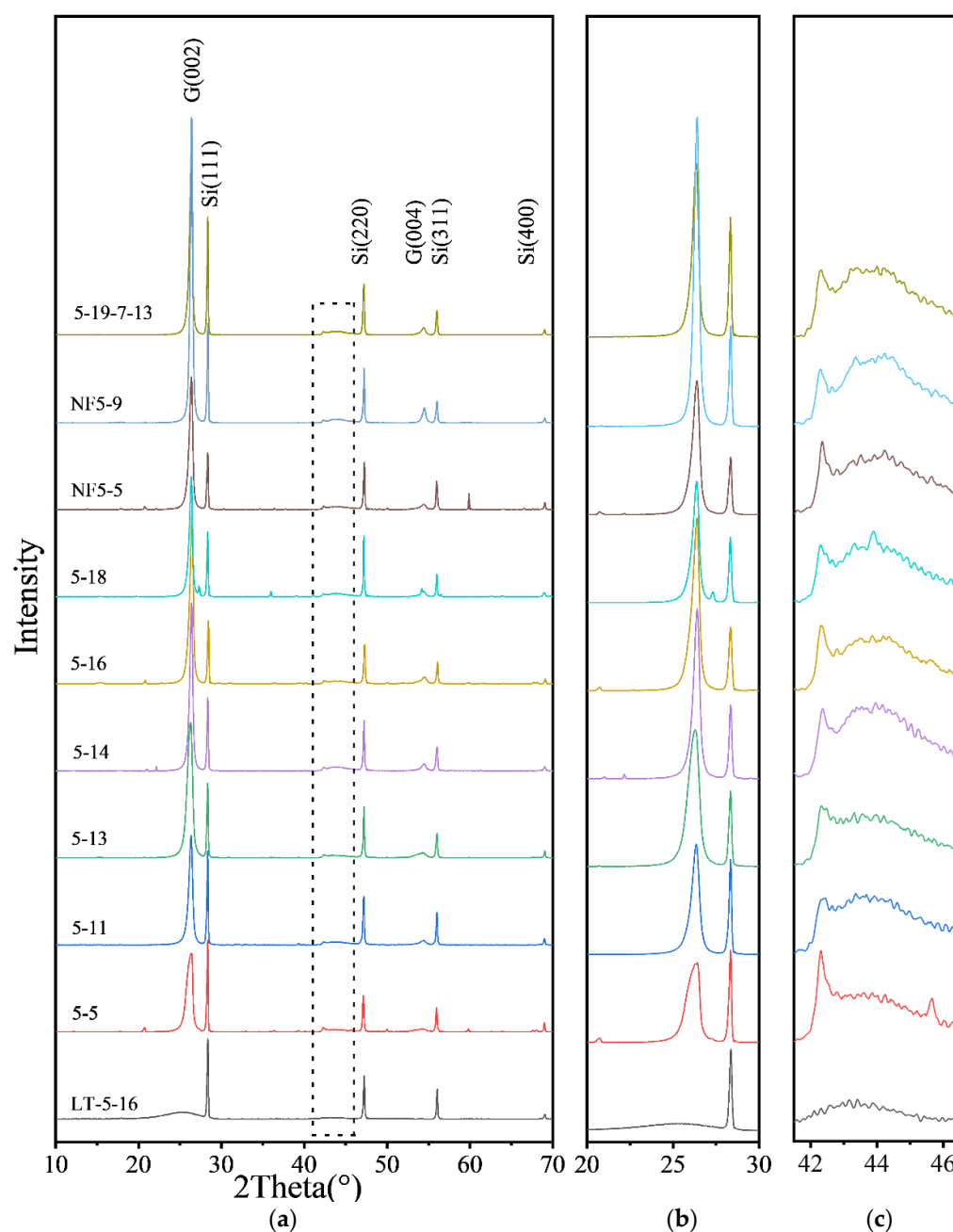


Figure 3. XRD patterns of coal seam-derived graphite in 2θ ranges (a) between 10° and 70° , (b) between 20° and 30° , and (c) between 42° and 46° .

4.3. Raman Analysis

Figure 4 shows the Raman spectral profiles of series samples, and the main Raman spectral parameters are listed in Table 3. Overall, there are three bands, the D bands at $1320\text{--}1350\text{ cm}^{-1}$, the G bands at $c. 1580\text{ cm}^{-1}$, and the D2 band at $c. 1620\text{ cm}^{-1}$ in the first-order portion [51,52]. Viewed from the top in the first-order Raman region, the narrow and relatively strong G band is considered to be the vector of highly ordered graphite (basal plane) [52], and a relatively broad defect induced by the D band represents a state of disordered stacking in the crystalline structure [53]. Both are repeating and overlapping (Figure 4), showing that the samples are in the stage of the transformation from disordered turbostratic graphite to graphite [53,54]. The D2 band separated from the shoulder of the G band becomes weaker from specimens NF-5-5 to NF-5-9. The up-turn in the D2 band suggests a hexagonal lattice involving graphene layers that are not stacked between

two other graphene layers in a manner similar to a sandwich [55], representing the lower limit of the graphite zone [56]; its intensity decreases with the increase in the degree of organization [57]. Thus, both the D band and D2 band suggest symmetry-breaking processes [58–61].

Table 3. The Raman spectral parameters derived from peak fitting of the series samples.

Sample NO.	Distance (m)	D1 Band		G Band		D2 Band		R1	R2
		Position	FWHM	Position	FWHM	Position	FWHM		
LT-5-16	1340	1345.31	74.63	1560.16	128.16	1601.47	48.22	7.17	0.12
5-5	840	1349.49	31.47	1581.99	23.65	1621.28	17.23	0.6	0.53
5-11	760	1350.13	46.23	1581.98	26.04	1621.97	29.03	0.5	0.5
5-13	630	1347.29	34.51	1576.8	24	1615.5	21.06	0.43	0.6
5-14	480	1349.59	49.74	1582.51	22.22	1615.6	34.97	0.37	0.49
5-16	430	1349.07	42.4	1579.39	21.74	1620.18	16.04	0.18	0.74
5-18	330	1349.64	35.74	1582.08	24.19	1620.09	21.5	0.44	0.58
NF5-5	200	1349.46	39.22	1582.84	24.58	1619.01	25.23	0.72	0.49
NF5-9	150	1349.19	44.41	1579.9	21.65	1620.63	16.31	0.45	0.48
5-19-7-31	1	1349.35	40.08	1582.12	23.01	1620.02	21.4	0.53	0.51

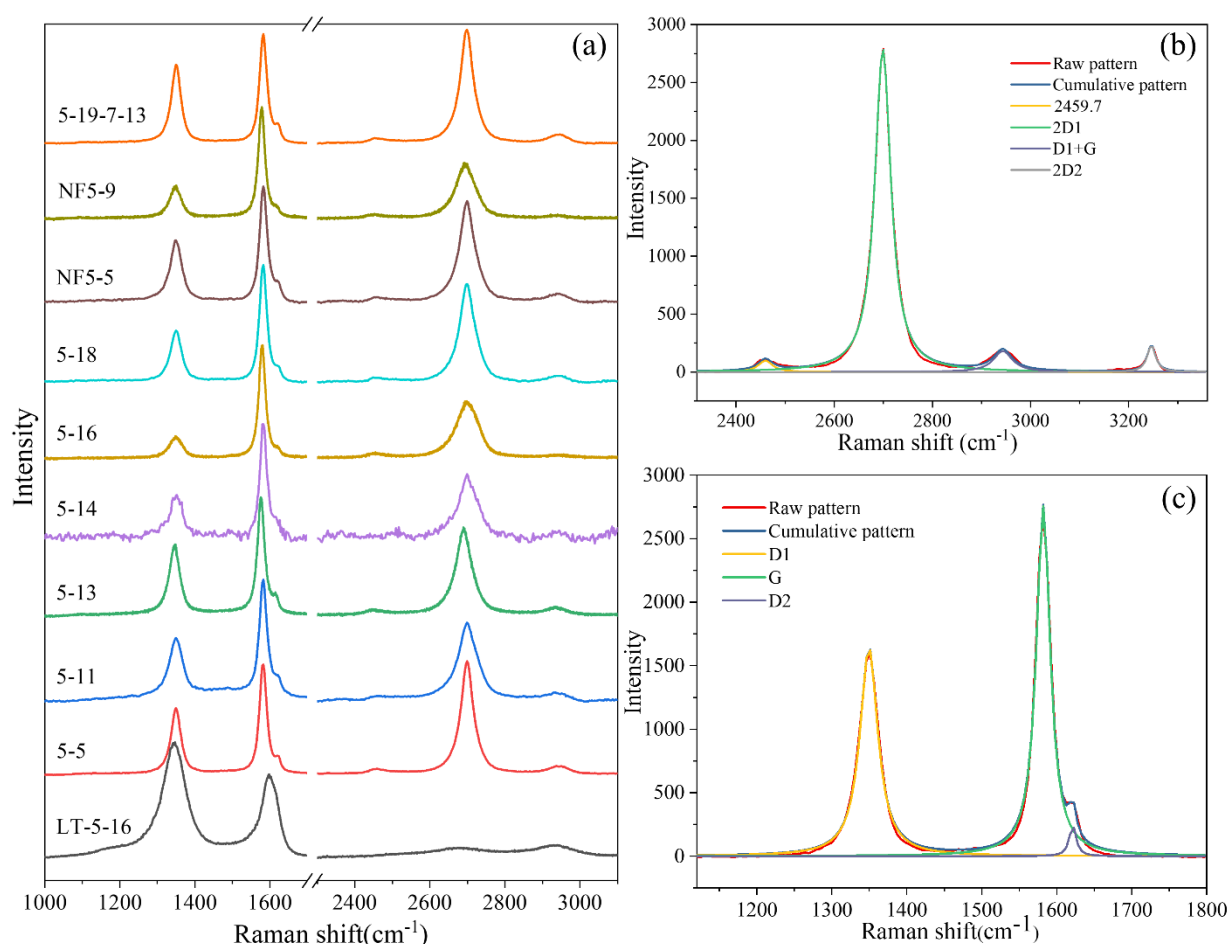


Figure 4. (a) Raman spectra of series coal seam-derived graphite samples, (b) peak fitting of Raman spectrum in the first-order region in case of sample 5-5, and (c) peak fitting of Raman spectrum in the second order region in case of sample 5-5.

The bands in the second-order Raman spectra were generally attributed to the overtone or a combination of the bands in the first-order spectrum, especially for the highly ordered carbon materials [61,62]; thus, the Raman parameter of second-order-like position, shape,

and intensities can impart similar information as the corresponding bands in the first-order region. The most conspicuous feature is the 2D band with solid intensity, except in the specimen sampled at greatest distance from the pluton, which is considered as the overtone of the D band and is believed to be related to the number of graphene layers and does not reflect any disorder or defect in the structure of the graphite crystal [63,64]. The intensity of the 2D2 band, defined as a counterpart in the second order spectra of the D2 band, is usually increased, accompanied by the 2D band as the crystallinity increases when its precursor is transformed to graphitizable carbon [65–69]. The D + G band is defined as the combination of the D band and G band in the first-order region [64,65]. It can be attributed to the larger aromatic rings present in the coal [70]. The attribution of the (2D)_R band at c. 2460 cm⁻¹ is suggested as indicative of the presence of such large aromatic rings in coal [70].

The intensity ratios and the half-height width are often used to characterize the degree of structural changes underway [7,8,10]. However, the half-height width was greatly affected by test conditions (i.e., different gratings, CCD cameras, etc.) [71]. As a function of the band intensity and the FWHM, the band area ratios are not only a combined parameter of the two parameters mentioned above but also provide the necessary information with respect to the carbon crystalline structure [60]. The parameter R_1 , which is the intensity ratio of the D and G bands, is evidence used to assess the degree of disordering of graphite crystalline structure and is suitable for use as a tool to compare different heating rates [52,72,73]. The parameter $R_2 = AG/(AD1 + AD2 + AG)$ (area ratio of bands) was used to determine the improvement in the order degree of structure [50,60,72,74].

As observed in Table 3, R_1 ranges between 0.18 and 7.17. As a vector of the disorder of crystalline structure, a disordered structure is not regularly arranged according to the distance from the rock mass, as found in the XRD analysis. The value of R_2 ranges from 0.12 to 0.74. With the exception of the most distant specimen, all other R_2 values exceed 0.4, which is interpreted as the distinction between semi-graphite and graphite [72]. Thus, the analysis above is consistent with the XRD analysis: what is also of note is the fact that the degree of structural change (represented by R_2) is not arranged in order according to distance from the heat source.

4.4. Chlorite Chemical Composition

Previous studies stated that the interlayered smectite or illite in the matrix of altered rocks might increase the concentrations of Na⁺, K⁺, and Ca²⁺ in the major element data of chlorite [75–78], which will affect the accuracy of subsequent analysis. Thus, the value of (CaO + Na₂O + K₂O) content of 0.5 wt% was selected as an upper limit herein. The chlorite chemical composition on the spatial distribution of samples is displayed in Table 4 and plotted in Figure 5. As shown in Table 4, there are lower concentrations of K₂O (0–0.08 wt%), Cr₂O₃ (0–0.39 wt%), MnO (0–0.66 wt%), CaO (0–0.69 wt%), Na₂O (0.25–2.11 wt%), and TiO₂ (0–4.46 wt%) relative to that of other major oxides. The SiO₂ content ranged from 22.39 to 35.88 wt%, and these were relatively stable with Al₂O₃ (19.58–33.55 wt%). Moreover, the concentration of MgO (1.84–11.81 wt%) was lower, but a higher FeO (7.61–41.59 wt%) was detected relative to other oxides in most specimens.

The structure calculation of chlorite was conducted by using WinCcac as proposed elsewhere [43]. The results show that the composition of Si ranged from 2.51 to 3.39 apfu, Fe: 0.60–4.02, R²⁺ (Mg + Fe + Mn): 1.38–4.41 apfu, and Fe/(Fe + Mg) mol: 0.43–0.93. Figure 5a shows that most chlorite from the Lutang graphite mining area could be classified as Type-I chlorite, which is characteristically Mg-poor and Fe-rich [79]. On the other hand, two samples that were relatively far from the intrusion belonged to Type-II (i.e., the total amount of Mg and Fe did not account for most of the number of atoms in each formula unit). Figure 5b shows that the content of MgO is negatively correlated with FeO, indicating an essential ionic substitution mechanism between Fe²⁺ and Mg²⁺ [43]; Figure 5c illustrates the trend whereby the content of Al^{VI} keeps increasing while that of (Fe²⁺ + Mg) is decreasing, suggesting that 3(Mg, Fe²⁺)^{VI} ⇌ +2(Al³⁺)^{VI} substitution dominates [43,80,81] due to

the tetrahedral vacancies usually occupied by Si and Al^{IV}, while the octahedra are often occupied by Mg²⁺, Fe²⁺, and Al^{VI} [81]. This result is consistent with Figure 5d (Al^{IV} versus Al^{VI} diagram for chlorite), which suggests that the tetrahedral Al values are negatively correlated with the octahedral Al concentrations in the specimens.

In the plot of Fe versus Si (a.p.f.u) after [82] (Figure 5e), the chlorite samples are plotted mainly in/near the ripidolite field besides two samples that are relatively far from the intrusion fall in the pennine field. Similarly, in the diagram of Si versus Fe (a.p.f.u) [83] (Figure 5f) based on the chlorite structure differences, most of the chlorite components are plotted in the sheridanite-ripidolite field, and the octahedral sites are occupied by R²⁺. In addition, as presented in the Al+-Mg-Fe classification diagram [79], most of the chlorite specimens were Fe-rich.

The non-stoichiometric composition of chlorite displays a wide range of variations that are related to the prevailing physico-chemical conditions at formation and protolith composition. Based on previous studies on the relationship of the formation temperature and composition of chlorite, i.e., chlorite geothermometers [43,78,80,84], combined with mineralogical observations (assemblages, modes, and mineral chemistry), we found that the quasi-constant chemical composition is the main feature of the sampling strata throughout the study area.

Table 4. Chemical composition (wt %) of chlorite from Lutang deposit analyzed by EPMA, along with their structural formulae and estimated formation temperatures.

Samples	5-19-7-31	NF5-9	NF5-5	5-18	5-16	5-14	5-13	5-11	5-5	LT-5-16
(%) SiO ₂	22.9	23.92	22.5	23.8	24.39	22.39	26.95	22.96	23.47	35.88
TiO ₂	4.46	0.06	0.01	0.29	0	0.15	1.56	0	0	0.58
Al ₂ O ₃	20.32	22.29	21	23.04	23.2	22.76	19.58	23	24.04	32.86
Cr ₂ O ₃	0.04	0.08	0.31	0.07	0.3	0.03	0.03	0.39	0.05	0.08
FeO	35.12	29.17	41.59	31.14	26.5	32.39	31.46	30.87	30.66	7.61
MnO	0.28	0.51	0.66	0.07	0.49	0.61	0.41	0.32	0.4	0.04
MgO	5.33	10.21	1.84	9.29	11.81	7.87	7.2	8.11	8.46	5.64
CaO	0.06	0.1	0.11	0.06	0.15	0	0.17	0.28	0.43	0.42
Na ₂ O	0.25	0.31	0.4	0.4	0.29	0.32	0.43	0.34	0.33	2.04
K ₂ O	0	0.04	0.02	0.06	0.02	0.04	0.06	0.08	0.07	0.03
Total (%)	88.76	86.69	88.44	88.22	87.15	86.56	87.85	86.35	87.91	85.18
(apfu)Si	2.5376	2.6181	2.601	2.5771	2.6108	2.5087	2.9265	2.5531	2.5488	3.3924
Ti	0.3717	0.0049	0.0009	0.0236	0	0.0126	0.1274	0	0	0.0412
Al	2.6538	2.8753	2.8611	2.9403	2.9269	3.0055	2.5059	3.0143	3.0769	3.6617
Cr	0.0035	0.0069	0.0283	0.006	0.0254	0.0027	0.0026	0.0343	0.0043	0.006
Fe(2+)	3.2546	2.67	4.0206	2.8199	2.3723	3.035	2.857	2.8707	2.7845	0.6017
Mn	0.0263	0.0473	0.0646	0.0064	0.0444	0.0579	0.0377	0.0301	0.0368	0.0032
Mg	0.8805	1.6659	0.3171	1.4996	1.8846	1.3145	1.1656	1.3444	1.3696	0.795
Ca	0.0071	0.0117	0.0136	0.007	0.0172	0	0.0198	0.0334	0.05	0.0425
Na	0.0537	0.0658	0.0897	0.084	0.0602	0.0695	0.0905	0.0733	0.0695	0.374
K	0	0.0056	0.0029	0.0083	0.0027	0.0057	0.0083	0.0113	0.0097	0.0036
Type (Zane and Weiss (1998) [79])	Type-I	Type-I	Type-I	Type-I	Type-I	Type-I	Type-I	Type-I	Type-I	Type-II
(Octahedral vacant)	0.2719	0.1115	0.1064	0.127	0.1356	0.063	0.3774	0.1531	0.179	1.4988
R2+	4.1614	4.3832	4.4024	4.3259	4.3013	4.4074	4.0603	4.2453	4.191	1.3999
Fe/(Fe + Mg)	0.7871	0.6158	0.9269	0.6528	0.5573	0.6978	0.7102	0.6811	0.6703	0.4308
Mg/(Mg + Fe ²⁺)	0.2129	0.3842	0.0731	0.3472	0.4427	0.3022	0.2898	0.3189	0.3297	0.5692
TCN _{85-Al} ^{IV} (°C)	324	307	310	315	308	330	241	320	321	321
TCN _{85-Octahedral Vacancy} (°C)	218	255	256	252	250	267	193	245	239	239
TZF _{95-Al} ^{IV} (°C)	286	285	260	290	292	301	211	293	295	295
TX _{97-Al} ^{IV} (°C)	205	252	124	249	279	252	112	245	251	251

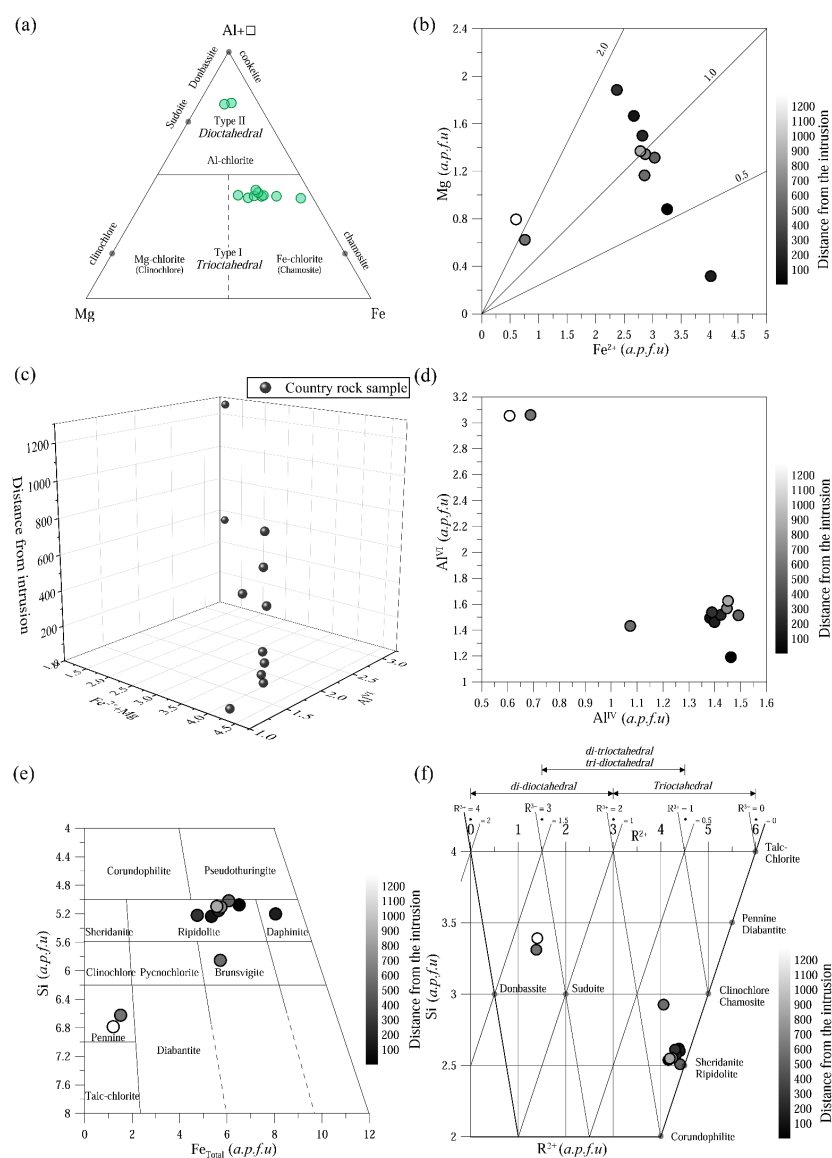


Figure 5. Chlorite chemical composition and the spatial distribution of specimens. (a) (Al+□)-Mg-Fe (after Zane and Weiss (1998) [79]; (b) Fe²⁺ vs. Mg (a.p.f.u) (after Yavuz et al. (2015)) [43]; (c) Al^{VI} vs. Fe²⁺+Mg vs. Distance from the intrusion; (d) Al^{VI} vs. Al^{IV}; (e) Fe vs. Si (a.p.f.u) (Hey and Hey (1954)) [82]; (f) R²⁺ vs. Si (a.p.f.u) (after Wiewióra and Weiss (1990)) [83].

5. Discussion

It is generally accepted that the metamorphic process from coal to graphite is mainly due to the influence of thermal energy [85,86]. With the influence of heat-treatment triggered by a magmatic intrusion, the macromolecules of coal gradually lose heteroatoms, the aromatic ring structure of the coal is rearranged and becomes stacked while the number and size of the aliphatic functional groups fixed upon the aromatic layers become lower and small. Then, a short-range ordered graphite structure gradually forms, and this evolves to a long-range ordered graphite structure. On this basis, previous studies on the evolution of graphitization under natural conditions have shown that the distance from the magma intrusion, which is the heat source, is a key factor controlling the degree of graphitization. However, in this study, it was found that in the zone near the heat source, the degree of graphitization is not strictly ordered according to distance from the intruded magma. The non-progressive extension of the structure of graphite occurs not only by heat treatment but as a result of other factors.

5.1. The Geological Strain Effect

As shown in Figure 6, with decreasing distance from the contact horizon, the order of grain size and structure is significantly higher than that of anthracite, and the carbon content (C%, daf), structural parameters (L_c and L_a), and Raman spectral parameter ($AG/AD1 + AG + AD2$) indicate fluctuating increases with increasing proximity to the Qitianling granite intrusion. Meanwhile, the Raman spectral parameter and XRD results show excellent consistency in indicating changes in graphitized structure. The trends in such fluctuations are consistent with the shape of the fold (Figure 1d). The occurrence of folding in the mining area of western Qitianling is associated with the tectonic period of igneous intrusion; thus, the strain energy generated by folding probably accelerates the ordering of polyaromatic rings in coal (Figure 7).

According to Bonijoly et al. [87], the graphitization of anthracites during their natural evolution is thermodynamically impossible with heat alone. Bustin confirmed that the strain energy could lower the temperatures for graphitization of carboniferous materials, and graphitization can occur at 600 °C under deviatoric compression in the laboratory [85,88]. This is consistent with the fact that the most graphitized samples were collected from highly deformed seams that were clearly observed at the tunnel when sampling at local mines. The stress is usually concentrated at the axis position of the fold and lowest at the middle wing of the fold; thus, the degree of graphitization of coal seam-derived graphite is highest at the fold axis and lowest at the middle of the wing (Figure 7).

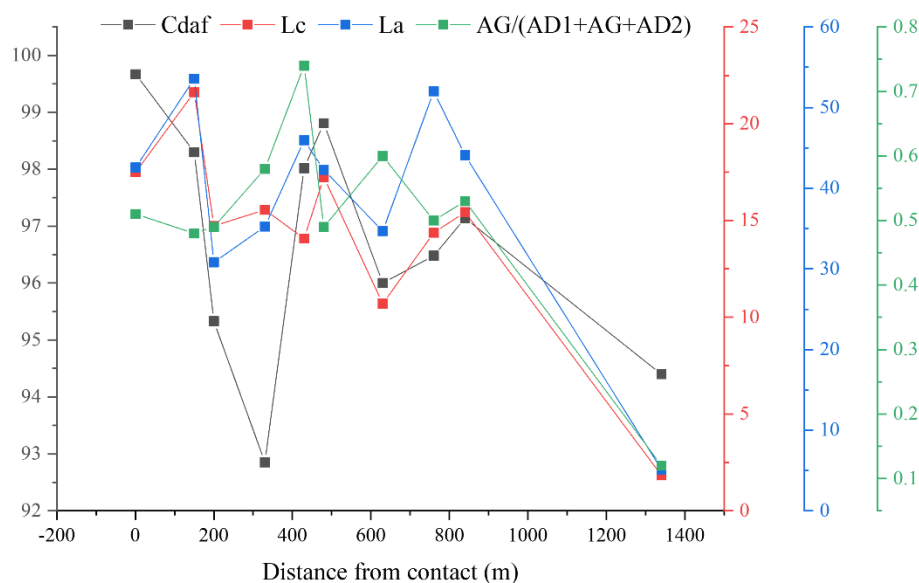


Figure 6. Relationships between Cdaf (%) content, the parameter (L_c , L_a) of grain size, Raman spectral parameter ($AG/AD1 + AG + AD2$), and distance from the contact horizon (m).

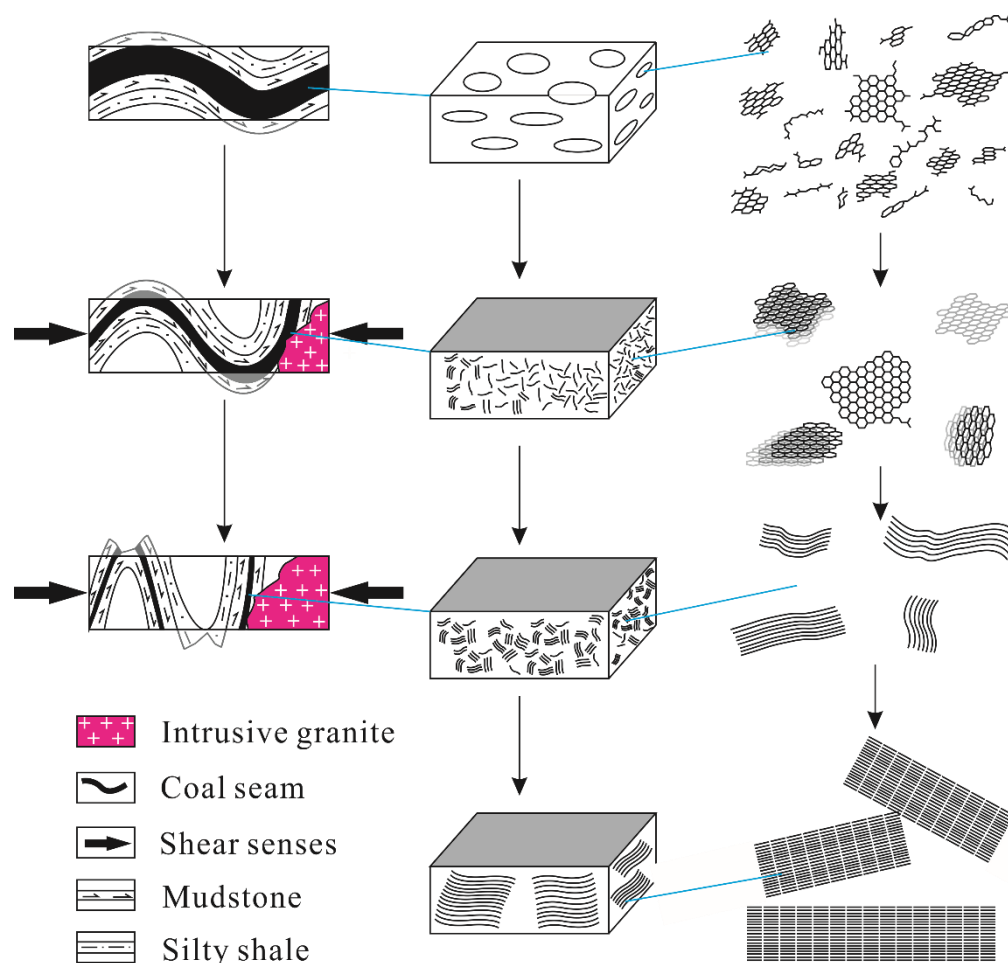


Figure 7. Strain-induced graphitization model of coal seam-derived graphite.

5.2. Natural Catalytic Graphitization by Iron-Bearing Minerals

As ubiquitous phyllosilicates in sedimentary, metamorphic, and hydrothermal environments, chlorites induce a high degree of isomorphous substitution. The chemical composition, such as Al^{IV} content and chlorite $\text{Fe}/(\text{Fe} + \text{Mg})$ ratio, is known to be a function of the physico-chemical conditions of crystallization and the bulk composition of the host rocks. According to the calculation in Table 4, the temperature of chloritization is far from reaching the lower limit of synthetic graphitization mentioned above. However, the compositional difference among the chlorite reflects protolith and fluid chemistry, which could influence the graphitization process in the period of geological activity.

As mentioned, the ionic substitution mechanisms of $\text{Fe}^{2+} \Leftrightarrow \text{Mg}^{2+}$, Tschermak $\text{Al}^{\text{IV}} \text{Al}^{\text{VI}} \Leftrightarrow \text{Si}$ (Mg^{2+} , Fe^{2+}), and di-trioctahedral $3(\text{Mg}^{2+}$, $\text{Fe}^{2+}) \Leftrightarrow +2\text{Al}^{\text{VI}}$ play an important role in the formation chlorite at the sampling tunnel. Approaching the nature of the contact, $\text{Fe}/(\text{Fe} + \text{Mg})$ ratios clearly increased, and most of the chlorite was classified as Fe-chlorite, indicating that the chlorite was mainly influenced by precursor Fe-rich minerals or the mafic-rich hydrothermal fluid.

Previous studies have found that the ore-forming temperature of coal-to-graphite in nature is about 600–900 °C, whereas the experimental temperature of coal graphitization in the laboratory exceeds 2000 °C [19,89]. In order to decrease the activation temperature for synthetic graphite, previous researchers have tried to increase the pressure and add appropriate catalysts. The catalyst is the most critical factor influencing the graphitization process of various carbons when temperature and carbon precursors are determined. Previous studies have entailed the use of certain major inorganic elements contained in the mineral matter of coals, such as silicon, iron, or aluminum, as catalysts in the graphitization

of different precursor carbon materials [19,90,91]. Since clay minerals (e.g., illite, chlorite, or kaolinite) are the main minerals present in coal [92–94], it is widely accepted that the presence of iron in the clay minerals promotes the structural ordering of carbon materials during high-temperature treatment.

As shown in Figure 8, the (002) diffraction FWHM of graphite shows a close relationship with the Fe^{2+} (total) content in chlorite. There is an increase in the value of total Fe^{2+} of chlorite and a decrease in the FWHM (d_{002}) of XRD spectra of graphite. As the structural ordering of graphite improves, the composition of Fe^{2+} is enriched. The appearance of chlorite may be altered from surrounding rock after graphitization. However, most of the coals often include various impurities (e.g., quartz, clays, or pyrite), which decompose by heat-treatment caused by intrusive events. Consequently, a catalytic graphitization process may occur, either due to iron or silica [19,90].

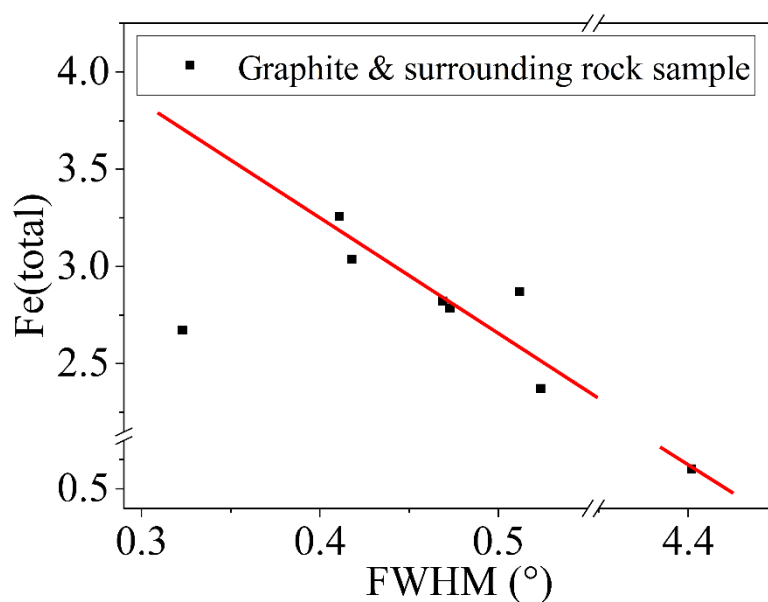


Figure 8. Relationships between the value of total Fe^{2+} of chlorite and the FWHM (d_{002}) of graphite XRD spectra.

6. Conclusions

The carbon content ($\text{C}\%$, daf), structural parameters (L_a and L_c), and Raman spectral parameter ($\text{AG}/\text{AD1} + \text{AG} + \text{AD2}$) of a series of coal seam-derived natural graphite samples exhibit fluctuating increases with decreasing distance to the Qitianling granite intrusion. After thorough analysis on the relationship between fluctuation variation degree of coal seam-derived graphite with the tectonic event and chemical composition, the following conclusions can be drawn:

(1) The strain energy generated by folding during igneous intrusion can accelerate the ordering of polyaromatic rings in coal. The stress is usually concentrated at the axis of a fold and is lowest at the middle wing of the fold; thus, the degree of graphitization of coal seam-derived graphite is maximized at the fold axis and lower at the wing of the fold.

(2) A high Fe content in the chlorite from the peripheral intrusion halo suggests a higher degree of graphitization at one sampling site. The iron ion transfer during mineral phase transformation will play a catalytic role in the formation of coal seam-derived natural graphite.

(3) The compositional variations in chlorite could be used as a guide for the exploration of coal seam-derived graphite mineralization in shallow levels of a contact metamorphic environment.

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