Effects of Rapid Igneous Intrusion Heating on the Geochemistry, Petrography, and Microcrystalline Structure of Coals from Huainan, China

Shike Li,* Yanming Zhu,* Yang Wang, and Jing Liu

ABSTRACT: Igneous intrusion into coal-bearing strata may change the geochemical, petrographic, and microcrystalline structural characteristics of coal. Here, a series of coal samples affected by igneous intrusion were analyzed by petrography, geochemistry, and X-ray diffraction. In addition, the trend observed in altered coal with normal burial maturity is compared to evaluate whether the intrusive coal follows another maturity path. A petrographic analysis shows that the \( R_0 \) value increased rapidly and lost the ability to distinguish liptinite. Pyrolytic carbon and isotropic and anisotropic coke with a fine-grained circular mosaic structure are formed at the intrusion. Moreover, the degree of structural order of coal samples increases in an approach to the intrusion. There are transition phases with different structural orders due to different degrees of metamorphism. Petrographic and geochemical data indicate that intrusive coals may follow a maturation pathway other than that from normal burial maturation, which may be related to the rapid geological thermal event related to the intrusion. However, the results of XRD data suggest that the microcrystalline structure of igneous intrusion coals is consistent with a growth in the trend of normal burial. This study of geochemical petrography and microcrystalline structure of surrounding coal seams by rapid intrusive heating of igneous intrusions not only greatly improves the natural coke industrial utilization but also provides an important theoretical basis for the generation and enrichment of coalbed methane in igneous thermal abnormal coal reservoirs.

1. INTRODUCTION

Igneous intrusions into coal seams are relatively widely distributed and may significantly alter the geochemical and microcrystalline structure characteristics of coal\(^{1-9}\) and change the mineral composition within the heating aureole around the intrusions.\(^{6,10,11}\) In addition, they may possibly enhance the coaled methane production and improve reservoir characteristics.\(^{8,12,13}\) The alteration of the physical and chemical effects of igneous intrusion on coal is mainly associated with the intrusion temperature, which has been described around the world.\(^{14,15}\) However, the changes in the alteration zone may be significantly differently affected by many factors such as temperature and heating time on coal kinetics.\(^{16-18}\) The influence of igneous intrusions on coal seam properties and chemical composition have been extensively studied by many scholars.\(^{1,3,10,15,14,19-24}\) However, it has rarely been mentioned in previous papers that the magma intrudes into low-rank coal seam and that there is a difference in the thermal maturity pathway of coal under the influence of magma and normal burial.\(^{2,20,25,26}\) Thus, the maturation path difference between the two has not yet been fully investigated, possibly due to the intrusions by magma of a series of coal samples in a low-rank coal seam being difficult to obtain. A large igneous intrusion scale was discovered during commercial mining in Zhuxianzhuang Coal Mine in Huainan, Anhui Province, China, and especially the intrusion of a coal seam was at the stage of low rank. Therefore, this is an ideal location to investigate the differences in maturity pathways. The study of properties of the surrounding coal seams by rapid intrusive heating of igneous intrusions not only greatly improves the natural coke industrial utilization but also provides an important theoretical basis for the generation and enrichment of coalbed methane in an igneous thermal abnormal coal reservoir.

Microcrystalline graphite formed in the metamorphic zone is related to the igneous heat source around graphite, semi-graphite, meta-anthracite, anthracite, and low-rank coal zones.\(^{27}\) Generally, high-rank coal is composed of polyaromatic...
layers produced by cross-linking of aliphatic or ether groups. This is accompanied by the generation and release of light hydrocarbons, aromatic ring condensation, and an increase in the aromatic layer stacking in the process of coal maturation. The chemical structure and macerals of coal are extremely sensitive to changes in temperature and pressure. High temperature and pressure may promote the development of coal to coking and graphitization. Especially high temperature and pressure geological activities, such as igneous intrusion or tectonic activities, can provide coal with sufficiently high activation energy in comparison to normal geothermal gradients. Laboratory tests have shown that natural coke can be formed in the presence of stress at temperatures greater than 300 °C.

Coal macerals affected by igneous intrusion usually clearly show an increase in vitrinite reflectance, carbon content, and fixed carbon, and thermally metamorphic structures such as devolatilization vacuoles, coke texture, and pyrolytic carbon are formed in the alteration aureole. While the volatile hydrogen and nitrogen contents are reduced, the ability to recognize liptinite is also reduced. There has been a great deal of previous research on the natural coke influenced by igneous intrusion. However, it is rare to find a systematic description of coal body changes and the geochemical variations of coal from low-rank coal to coke in the literature. To help improve the understanding of coal seam changes caused by intrusion events, in this study the changes in coke chemical composition and the evolution of coal macromolecular structure under magmatism are mainly studied through optical microscopy and proximate, elemental, and geochemical analyses.

2. PROCEDURES

2.1. Sampling. Freshly exposed and unweathered coal samples in the underground mine were found just days after the discovery of igneous intrusions during mining activities. The sampling position started from the contact position of the intrusion and coal. Samples were taken every 0.5 m within the first 6.3 m, and the sample numbers were denoted TRJ-1–TRJ-7 and 44-1–44-8 according to the distance from the igneous intrusion. Among them, a few samples such as 44-1 and 44-2 were not sampled at an exact interval of 0.5 m because the location of coals was not easy to obtain. After that, samples were taken every 1 m between 6.3 and 9.3 m, with sampling numbers 44-9–44-11 respectively. When the distance was greater than 9.3 m, coals were sampled every 2 m, and the sampling numbers are 44-12–44-14 (Figure 1). In addition, MD-1 and MD-5 samples unaffected by contact metamorphism were collected to gather background information. The magmatic intrusion thickness cannot be measured in an underground mine, but on the basis of data from the mine, the total sampling distance is approximately 1.5 times the thickness of the igneous intrusion.

2.2. Analytical Procedures. Proximate experiments and an ultimate analysis have been demonstrated to be the basic methods to investigate the chemical analysis for coals. A proximate analysis (volatile matter (Vdaf), fixed carbon (FCdaf), ash (A) and moisture (Mad)), an ultimate analysis (C, H, O, and N), and total sulfur content analyses were performed on the coal samples at the Jiangsu Geology and Mineral Design and Research Institute in China that were both una...
The asymmetric (002) band can be divided into two parts, with sample 44-10 in Figure 2 as an example. The broad band in the range of 20° on the left can be attributed to a highly disordered material of amorphous carbon. The narrow band in the range of 26° on the right is crystallite carbon. Here, the mean interlayer spacings (d_{002}) were determined from the (002) peak position by applying the Bragg equation. The crystallite size parameters of crystallite height (L_c) and crystallite width (L_a) were calculated by measuring the fwhm values of the (002) and (100) peaks, respectively, using the Scherrer equation, with values of K = 0.9 and 1.84 for L_c and L_a, respectively. Moreover, the average stacking number of aromatic layers was calculated by \( \langle N \rangle = L_c / d_{002} \), from the procedure by Laggoun-Defarge et al. The relationship \( DOG = (3.440 - d_{002}) / (3.440 - 3.354) \) was used to determine the graphitization degree. The probability \( p \) of random orientation between any two adjacent layers is given by \( d_{002} = 3.354 + 0.086p \), which is based on the assumption that the nongraphite carbon interlayer spacing is 3.440 Å and nongraphite carbon (3.440 Å). The broadening of diffraction peaks due to instrumental factors was corrected by a silicon standard. Furthermore, the XRD patterns exhibit wide asymmetric (002) and (100) bands.

### 3. RESULTS AND DISCUSSION

#### 3.1. Geochemistry of Coked Coal.

Due to the coal seam being altered to a certain extent by intrusion, the properties of coal were related to the distance from the igneous intrusion. The coal rank for the Huaibei (No. 8) coalbed is highly volatile bituminous. The original, unaltered, background reflectance levels for coals range between 0.66% and 0.72% (average 0.69%; Table 1). However, the vitrinite reflectance of sample 44-14 at the farthest distance location from the intrusion in the transect is 1.60% (Table 1 and Figure 1). Closer to the intrusion, the value of \( R_m \) increases dramatically from 1.60% for the sample 44-14 to 5.73% in contact with the intrusion, corresponding to anthracite. These \( R_m \) data also indicate that the alteration halo is confined to 15.3 m from the intrusion. Figure 3 shows a sharp decrease in vitrinite reflectance with the distance from the dike intrusion and displays an obvious concave-up pattern. The dike contact point vitrinite reflectance values vary with each contact point, probably due to local variations in the degree of convective heat dissipation.

The proximate analyses \( (M_{ad}, A_d, V_{daf}, \text{and } FC_d) \) of the coal samples approaching the intrusion are given in Table 1. Some of these parameters show the expected variations. The most obvious change in volatile matter content overall decreases from 16.24% to 4.98% close to the intrusion (Table 1 and Figure 4). In comparison with the unaltered coal with an average volatile matter content of 29.76%, the decrease is large.

### Table 1. Vitrinite Reflectance and Proximate Analyses for Coal Samples Affected and Unaffected by Magma Collected from the Zhuxianzhuang Coal Mine

| sample  | dist (cm) | \( R_m \) (%) | \( A_d \) (wt %) | \( M_{ad} \) (wt %) | \( V_{daf} \) (wt %) | \( FC_d \) (wt %) |
|---------|-----------|---------------|-----------------|-----------------|-----------------|-----------------|
| TRJ-1   | 50        | 5.73          | 18.36           | 0.45            | 4.98            | 77.57           |
| TRJ-2   | 100       | 5.40          | 30.35           | 0.84            | 12.54           | 60.91           |
| TRJ-3   | 150       | 5.29          | 24.42           | 1.30            | 7.41            | 69.98           |
| TRJ-4   | 200       | 5.20          | 21.26           | 1.49            | 7.25            | 73.04           |
| TRJ-5   | 250       | 5.20          | 21.26           | 2.49            | 9.13            | 64.18           |
| TRJ-6   | 300       | 4.15          | 21.42           | 3.28            | 5.76            | 74.05           |
| TRJ-7   | 350       | 4.22          | 35.43           | 1.91            | 8.97            | 58.78           |
| 44-1    | 370       | 4.01          | 20.50           | 2.14            | 6.79            | 74.11           |
| 44-2    | 390       | 3.86          | 17.47           | 2.00            | 6.47            | 77.19           |
| 44-3    | 410       | 3.56          | 17.94           | 1.56            | 6.29            | 76.90           |
| 44-4    | 430       | 3.40          | 18.03           | 1.41            | 6.74            | 76.44           |
| 44-5    | 490       | 3.16          | 17.22           | 2.30            | 6.75            | 77.20           |
| 44-6    | 530       | 3.15          | 14.51           | 2.58            | 5.40            | 80.87           |
| 44-7    | 580       | 3.10          | 20.45           | 1.48            | 9.34            | 72.12           |
| 44-8    | 630       | 2.91          | 28.21           | 1.64            | 8.48            | 65.70           |
| 44-9    | 730       | 2.91          | 30.48           | 1.78            | 9.75            | 62.74           |
| 44-10   | 830       | 2.91          | 17.32           | 1.60            | 6.81            | 77.05           |
| 44-11   | 930       | 2.56          | 23.98           | 1.58            | 8.83            | 69.31           |
| 44-12   | 1130      | 2.18          | 19.39           | 1.20            | 7.01            | 74.96           |
| 44-13   | 1330      | 1.80          | 33.37           | 1.64            | 10.12           | 59.89           |
| 44-14   | 1530      | 1.60          | 19.71           | 1.32            | 16.24           | 67.25           |
| MD-1    | unaltered coal | 0.66    | 7.76            | 1.60            | 28.78           | 65.69           |
| MD-5    | unaltered coal | 0.72    | 4.43            | 1.70            | 30.74           | 66.20           |
The fixed carbon (dry) content ranges from approximately 59% to over 80% (Table 1 and Figure 4), but it increased significantly in comparison to the unaltered coal sample with an average fixed carbon (dry) content of 65.96%. In addition, the moisture content overall initially increases from 1.32% to 3.28% and then decreases to 0.45% as the intrusion is approached (Table 1). However, the variation in ash (dry) is less pronounced, ranging from <15% up to 35% in this transect (Table 1). This is a significant increase in comparison to the average of 6% for the unaltered coal sample. The reason for the increase in ash yield percent is that the carbonate formed by the gradual cooling of the hydrothermal fluid after the igneous intrusion fills the cell cavity.

### 3.2. Petrography of Coked Coal

Coals in this transect show an increase in carbon content and a decrease in hydrogen, nitrogen, oxygen, and sulfur content near the intrusion. The carbon content increases from 86% to 94%, the hydrogen content decreases from 4.22% to 1.23%, the nitrogen content decreases slightly overall from 1.72% to 0.9%, the oxygen content decreases from about 7% to about 2%, and the sulfur content shows a minor decrease from 0.36% to 0.06%. Here, there is an abnormally high sulfur point in sample 44-12 (Table 2 and Figure 5). The decrease in sulfur content close to the intrusion is related to thermal elimination of the organic sulfur and possibly sulfate decomposition by the thermochemical reduction of sulfate. Similarly, the atomic ratios decrease near the intrusion in the transect (Figure 6). However, sample 44-7 shows abnormally low element and atomic values, but it has higher carbon and sulfur values in comparison to the other samples.

Unaltered coal samples MD-1 and MD-5 were collected from the No. 8 coal seam in addition to the altered coal samples, both of which are at the stage of low rank with $R_0$ values of 0.66–0.72% (Table 1). Petrographically, the unaltered coal samples of No. 8 are mainly inertinite (mostly semifusinite and fusinite) macerals (51–51.4%), followed by vitrinite (collotelinite and colloideternite) ranging from 37.9% to 40%, and a small amount of macerals part of liptinite ranging between 8.4% and 10.1%. Liptinite is represented as being dominated by sporinite and rarely by cutinite. As shown

![Figure 3. Variation of $R_m$ with distance from the magmatic intrusion.](image_url)

![Figure 4. Variation in proximate analyses ($M_{ad}$, $A_{ad}$, $V_{daf}$, and $FC_d$) with the distance from the intrusive contact for coal samples. The red scatter diagram represents the relationship between $M_{ad}$ and distance, the orange scatter diagram represents the relationship between $A_{ad}$ and distance, the blue scatter diagram represents the relationship between $V_{daf}$ and distance, and the green scatter diagram represents the relationship between $FC_d$ and distance.](image_url)
in Figure 7a, the photomicrographs of MD-1 coal sample indicate a relatively pure sample without any thermal alteration structure. However, coal samples in close vicinity to the igneous intrusion show obvious thermal alteration characteristics: that is, the liptinite macerals disappear and vitrinite gradually becomes coked. Due to the larger range of igneous intrusion, the vitrinite reflectance of the 44-14 (\( R_0 = 1.6\% \)) coal sample 15 m away from the igneous intrusion is higher those that of unaltered coal samples MD-1 and MD-5 (\( R_0 = 0.66\% \) and \( R_0 = 0.72\% \), respectively), suggesting that the sample collected at the farthest distance from the intrusion is also within the range of the alteration halo. Since the vitrinite reflectance of the 44-14 coal sample has exceeded the rank at which liptinite is visible and liptinite macerals cannot be distinguished within the distance of the whole alteration halo, the fluorescence disappeared.37 Near the intrusion, vitrinite appears to be increasingly coked and isotropic coke can be

Table 2. Ultimate Analyses and Atomic Ratio Coal Samples Affected and Unaffected by Magma Collected from the Zhuxianzhuang Coal Mine

| sample | C_{daf} (%) | H_{daf} (%) | N_{daf} (%) | S_{daf} (%) | O_{daf} (%) | O/C   | H/C   | N/C   |
|--------|-------------|-------------|-------------|-------------|-------------|-------|-------|-------|
| TRJ-1  | 94.23       | 1.23        | 0.91        | 0.06        | 3.56        | 0.028 | 0.157 | 0.008 |
| TRJ-2  | 87.81       | 1.23        | 0.96        | 0.12        | 9.25        | 0.079 | 0.168 | 0.009 |
| TRJ-3  | 92.57       | 1.26        | 1.15        | 0.22        | 4.72        | 0.038 | 0.163 | 0.011 |
| TRJ-4  | 93.58       | 1.25        | 1.16        | 0.25        | 3.67        | 0.029 | 0.160 | 0.011 |
| TRJ-5  | 88.31       | 1.48        | 1.48        | 0.26        | 7.97        | 0.068 | 0.201 | 0.014 |
| TRJ-6  | 93.70       | 1.63        | 1.68        | 0.26        | 2.66        | 0.021 | 0.209 | 0.015 |
| TRJ-7  | 90.80       | 1.83        | 1.52        | 0.32        | 5.37        | 0.044 | 0.242 | 0.014 |
| 44-1   | 94.22       | 1.95        | 1.41        | 0.20        | 2.16        | 0.017 | 0.248 | 0.013 |
| 44-2   | 93.50       | 2.04        | 1.35        | 0.24        | 2.82        | 0.023 | 0.262 | 0.012 |
| 44-3   | 93.41       | 2.43        | 1.39        | 0.30        | 2.40        | 0.019 | 0.312 | 0.013 |
| 44-4   | 91.52       | 2.61        | 1.56        | 0.32        | 3.91        | 0.032 | 0.342 | 0.015 |
| 44-5   | 91.59       | 2.08        | 1.48        | 0.35        | 4.43        | 0.036 | 0.273 | 0.014 |
| 44-6   | 93.78       | 1.87        | 1.46        | 0.38        | 2.44        | 0.020 | 0.239 | 0.013 |
| 44-7   | 95.44       | 2.36        | 1.58        | 0.29        | 0.24        | 0.002 | 0.297 | 0.014 |
| 44-8   | 88.91       | 2.59        | 1.74        | 0.26        | 6.39        | 0.054 | 0.350 | 0.017 |
| 44-9   | 89.79       | 2.64        | 1.79        | 0.26        | 5.40        | 0.045 | 0.353 | 0.017 |
| 44-10  | 90.98       | 2.54        | 1.45        | 0.36        | 4.60        | 0.038 | 0.335 | 0.014 |
| 44-11  | 89.75       | 2.78        | 1.60        | 0.33        | 5.44        | 0.045 | 0.372 | 0.015 |
| 44-12  | 90.21       | 2.79        | 1.38        | 0.54        | 4.96        | 0.041 | 0.371 | 0.013 |
| 44-13  | 86.79       | 2.72        | 1.74        | 0.37        | 8.21        | 0.071 | 0.376 | 0.017 |
| 44-14  | 86.43       | 4.22        | 1.72        | 0.36        | 7.18        | 0.062 | 0.586 | 0.017 |
| MD-1   | 84.11       | 4.56        | 1.54        | 0.41        | 9.34        | 0.083 | 0.651 | 0.016 |
| MD-5   | 82.78       | 4.70        | 1.64        | 0.26        | 10.60       | 0.096 | 0.681 | 0.017 |

Figure 5. Variation in composition of C, H, O, N, and S with the distance from the intrusive contact for coal samples. The red line chart represents the relationship between C and distance, the orange line chart represents the relationship between H and distance, the blue line chart represents the relationship between O and distance, the green line chart represents the relationship between N and distance, and the brown line chart represents the relationship between S and distance.

Figure 6. Variation in atomic ratios with the distance from the intrusion.
seen in sample 44-8 with the vitrinite reflectance \( R_0 = 2.91\% \) (Figure 7b). Most of the coke may be described as a fine-grained circular mosaic structure (Figure 7b), on the basis of a comparison with commercial coke textures described by Crelling.\(^{38}\) However, the distorted maceral component arrangement of sample 44-14 (Figure 7c) may be caused by local strain near the boundary. Degradofusinite and pyrofusinite are the main forms of the inertinite macerals in this type of sample. Degradofusinite can be easily identified in the least metamorphosed sample, 44-12 (Figure 7d), but with an increase in metamorphism, the degradofusinite becomes more difficult to identify. Striped pyrofusinite (Figure 7e) and the well-preserved regular rectangular cell structure pyrofusinite appeared in sample 44-2. Close to the intrusion, the structure of pyrofusinite may be modified, changing from a striped shape to circular cell shapes of varying sizes and regular rectangles. In addition, devolatilization vacuoles occur in sample 44-14 with a distance of 16 m. On approach to the intrusion, the devolatilization vacuoles become more prevalent and obvious, as shown in Figure 7i of sample TRJ-1. Another distinct difference in petrography is the formation of pyrolytic carbon. The morphology and relative abundance of pyrolytic carbon depend on the distance from the dike intrusion. Here, pyrolytic carbon merely appears in samples from TRJ-1 to TRJ-4 within a distance of 2 m from the intrusion. The isotropic pyrolytic carbon appears in sample TRJ-4, as shown in Figure 7g. However, large flakes of laminated anisotropic pyrolytic carbon appeared in sample TRJ-1, indicating a higher formation temperature (Figure 7h). Notable concentrations of pyrolytic carbon increased on approach to the intrusion.

### 3.3. Petrographic and Geochemical Variations Associated with the Intrusion.

Zhuxianzhuang coal mine No. 8 coal in Huainan with igneous intrusion petrographic data show that vitrinite is gradually coked, the liptinite disappeared in coal samples with \( R_0 > 1.35\% \), and degradofusinite and pyrofusinite are the main forms of the inertinite. New components formed during the coking stage lead to strong heterogeneity of the coal samples. In comparison with the structure formed by commercial coke, a typical fine-grained circular mosaic structure and devolatilization vacuoles appear near the igneous intrusion, indicating that the temperature is close to 500 °C.\(^{3,21}\) In addition to differences in macerals composition, the reflectance values of the coal samples near the intrusion increase significantly and show a concave upward trend as reported for the Illinois Basin\(^{39}\) and the Raton Basin.\(^{12}\)

The influence of an intrusion on the surrounding coal was determined by the intrusion type, temperature, and thickness. The background coal seam is highly volatile, and the \( V_{daf} \) value decreases significantly adjacent to the intrusion. Similarly, the appearance of devolatilization vacuoles indicates that the volatiles are released and formed by pyrolytic carbon, which is the condensation stage of aromatization residual products.\(^{21}\)

The relationship between volatile matter and \( R_0 \) (Figure 8) shows that no matter whether magma intrudes into the coal seam or there is normal burial coal the \( V_{daf} \) value is affected, and \( V_{daf} \) decreases with an increase in coal rank. This indicates the loss of volatile products, which may be the result of residual product condensation caused by aromatization.\(^{37}\) Most importantly, Figure 8 shows a significantly different relationship between the intrusion samples and normally buried coal in comparison with the data for German coals,\(^{40}\) Illinois Basin coals,\(^{12}\) and graphitized coal of Hunan, China.\(^{39}\) It can be clearly observed from Figure 8 that the volatile content of intrusive coals in the range of \( R_0 < 2.5\% \) is within or below the normal burial coal range, while when \( R_0 > 2.5\% \) the volatile content is significantly higher than that for the normal burial coals. It has been suggested that a volatile content of coal being higher than that for the normal burial process may

---

**Figure 7.** Micrographs of petrography compositions of an unaltered sample (a) and thermal samples (b–i) near the intrusion.
be caused by the volatile content being trapped in the coal alteration zone. In summary, this shows that igneous intrusion may affect the volatile content of coal samples in the range of $R_0 > 2.5\%$ to the largest extent but has no obvious effect on coal samples with $R_0 < 2.5\%$. Rimmer et al.\(^3\) believed that the maturation pathway of coal with a rapid high-temperature igneous intrusion may be different from that of normal buried coal. Similarly, the relationship between C content and $R_0$ for coal samples (Figure 9) shows that the C content data of most of the coal samples in this study are concentrated in the normal burial coalification curve of Teichmüller et al.\(^4\) and the contents of only a few of the coal samples are higher or lower than that of the normal burial. Figure 9 also shows two other suites of igneous intrusion data in the Tanjung Enim area of Sumatra\(^{41}\) and Illinois Basin\(^{41}\) (Rahman et al.). The data of Sumatra coals are within or above the normal trend, while the data of Illinois Basin are within or below the normal trend. This result is consistent with the conclusion drawn by Amijaya and Littke\(^4\) that the intrusive coal samples follow maturation trends, which is similar to the trend observed in normal burial diagenesis.

The evolution trend diagram of elemental composition (Figure 10) shows that coal samples affected by intrusion may have maturation pathways different from those of the normal buried coals.\(^5\) In the Seylor plot, basically all coal sample data points deviate from those of the normal burial coals. For a given C content, all coals seem to have a lower H content, which may make it easier to remove the hydrogen element under the condition of rapid heating of the igneous intrusion. For the Illinois Basin, the data points of coal samples are basically within the range of normal burial coal at low ranks, which deviate from those of normal burial coal at high ranks. However, most of the Sumatra data are concentrated on normal burial coal, which implies a different maturation pathway for these coals. Rahman and Rimmer\(^21\) believe that the maturation pathway is controlled by conditions related to the intrusive events, such as the size of the intrusive body, heating rate, continuous heating time, and other conditions.

### 3.4. Microstructure Changes Determined by X-ray Diffraction Analysis

Figure 10. Distribution diagram of percentages of H and C for coal samples. The intrusion coals for our samples are compared with those Rahman et al. and are adapted with permission from 10.1016/j.coal.2014.06.020 and those of Rimmer et al. and are adapted with permission from 10.1016/j.coal.2009.06.002. The normal coalification trend of Van Krevelen et al. is shown in gray.

Figure 9. Variation in the value of C content (%) with $R_0$. The burial coalification trends of Teichmüller et al. is adapted with permission from 10.1016/S0070-4571(08)71074-4, those of intrusive samples studied by Rahman et al. are adapted with permission from 10.1016/j.coal.2014.06.020, and those Amijaya, Littke et al. are adapted with permission from 10.1016/j.coal.2005.07.008 and are shown for comparison.
at around 45°. The samples MD-1 and MD-5 of normal coal seams unaffected by intrusion are located at a distance greater than 15 m away from the igneous intrusion and belong to a low coal rank. Thus, their XRD patterns exhibit wide asymmetric (002) and (100) bands (Figure 11). According to the XRD crystallographic analysis (002) and (100) reflections are visible in all samples (MD-1, MD-5) affected by magma. The progressive changes in XRD parameters close to the igneous intrusion are located at a distance greater than 0.337 nm and the d002 spacing range of <0.337 nm belongs to the graphite zone. Several authors' have used the layer spacing parameter d002 as a standard representing the graphite crystal structure, which is equally applicable to highly ordered graphite coal samples formed under contact metamorphism. According to the experimental results, the value of 002 reflectance in Table 1, MD-1 and MD-5 are both in the stage of low rank. The samples from 44-9 to 44-14 are within the anthracite range. Moreover, samples from 44-6 to 44-8 belong to the meta-anthracite category, samples 44-4 and 44-5 are in the range of semigraphite stage, and the samples from TRJ-1 to 44-3 belong to the graphite zone (Figure 12).

Previous studies' classified highly ordered graphite coal samples formed under contact metamorphism using d002 < 0.336 nm. The d002 value in the range of 0.336–0.337 nm represents a transitional stage between semigraphite and highly ordered graphite coal samples. In this study, samples 44-2 and 44-3 in the transition stage belong to the prophase of high-graphite coal. The d002 value of samples TRJ-1–44-1 is less than 0.336 nm, which belongs to highly ordered graphite coal. Moreover, the d002 values of samples 44-4–44-14 are all greater than 0.337 nm, and their 002 reflection bands are more asymmetrical (Figure 11), which are classified as ordered graphite coal. However, the sample MD-5 obviously deviates from the correlation (Figure 13b), which is far from the graphite stage, probably caused by the highly inhomogeneous crystal structure. The asymmetry of the 002 reflection band in the XRD pattern in Figure 11 is precisely caused by structural defects in the graphite crystal structure and crystal structure. Previous research defined this asymmetry as the AI value, that is, the ratio of the left fwhm and the right fwhm of the 002 reflection band, as shown in Figure 13a. The relationship between AI and d002 shows a good negative correlation in the coal samples affected by igneous intrusion (R² = 0.87) except for sample MD-5. However, in the highly ordered graphite coal samples TRJ-1–44-3, the AI values have not yet fully reached 1, suggesting that the 002 reflection bands is still slightly asymmetric. Probably there is a dislocation along the parallel stacking of the aromatic layers as previously reported by Zhang et al. The evolution of graphitized crystallite of coal samples under magmatic contact metamorphism may be consistent with the four-stage evolution process of graphitization proposed by Oberlin. In the first stage, only a single basic structural unit exists in the microstructure of carbonaceous materials. BSU refers to a minimum structural unit consisting of five to six pairs of stacking layers. In the second stage, the BSUs are interconnected to form distorted columns. Subsequently, in the third stage, adjacent columns merge into distorted wrinkled layers. The distorted layers harden and become flat and perfect in the final fourth stage. In addition, the growth trend of the other XRD parameters L002, L010, N, and p affected by the igneous intrusion agrees well with the growth
trend of graphite crystallite size during the normal buried graphitization process. However, apart from structural changes, there is a lack of good correlation between crystallographic parameters (XRD) and chemical parameters in these coal samples, as shown in Figure 14. In fact, if samples with an H/C atomic ratio larger than 0.35 are not included in the correlation, a good correlation between $d_{002}$ and H/C can be observed ($R^2 = 0.83$, Figure 14). This lack of correlation was also reported by Marques et al., Li et al., and Marques et al. It was considered that some coal samples have low H/C but have almost no graphite order. This was also different from the results reported in this study and may be related to the environment of the sample or the nature of the sample itself.

4. CONCLUSIONS

Geochemical and microcrystalline structures of coal in direct contact with the intrusions in the Zhuxianzhuang mining area of Huainan undergo unique specific changes on approach to the intrusion. On approach to the intrusion, $R_0$ values showed a significant upward concave-up growth trend, increasing from the background reflectance levels for coals ranging between 0.66% and about 5.73%. The liptinite disappears when the $R_0$ value increases more than 1.35%. In addition, the contents of FC and $C$ increase and the percentages of $H$, $O$, $N$, and $S$ decrease, but the change trend of geochemical data is not obvious in comparison with the normal buried coalification trend. The relationship trend between VM (%) and $R_0$ indicates that an igneous intrusion has a greater effect on the volatile content with $R_0 > 2.5\%$ in comparison to normal burial coal. The distribution of carbon content with $R_0$ is basically consistent with that of normal burial coal. However, the element distribution diagram shows that the evolution of elements is different from that of normal burial coal.

The XRD parameter $d_{002}$ can clearly classify the degree of ordering of graphite coal samples formed under contact metamorphism. The degree of structural order of coal samples increases on approach to the intrusion. In addition, there are transitional stages with different structural orders. The AI values of the XRD pattern (002) reflections have a good correlation with $d_{002}$, and asymmetry still exists even in highly ordered coal samples. Moreover, the growth trend of the other XRD parameters $L_a$, $L_c$, $N$, and $p$ is consistent with the growth trend of normal graphite crystallite size, indicating that the

| sample | $d_{002}$ (Å) | DOG | fwhm (002) (deg) | $L_a$ (Å) | $L_c$ (Å) | $\langle N \rangle$ | $p$ | AI |
|--------|---------------|-----|-----------------|-----------|-----------|-----------------|-----|----|
| TRJ-1  | 3.32972       | 1.660 | 2.320          | 8.17      | 35.22     | 11              | 0.81 |    |
| TRJ-2  | 3.3298       | 1.630 | 1.945          | 8.52      | 42.01     | 13              | 0.78 |    |
| TRJ-3  | 3.3148       | 1.456 | 3.090          | 8.23      | 26.44     | 8               | 0.75 |    |
| TRJ-4  | 3.3181       | 1.418 | 2.475          | 9.72      | 33.01     | 10              | 0.74 |    |
| TRJ-5  | 3.3219       | 1.374 | 3.422          | 9.94      | 23.87     | 7               | 0.66 |    |
| TRJ-6  | 3.3464       | 1.088 | 2.321          | 7.98      | 35.18     | 11              | 0.67 |    |
| TRJ-7  | 3.3467       | 1.085 | 3.031          | 7.86      | 26.93     | 8               | 0.65 |    |
| 44-1   | 3.3547       | 0.992 | 2.125          | 7.77      | 38.41     | 11              | 0.0081 | 0.61 |
| 44-2   | 3.3632       | 0.893 | 2.575          | 9.51      | 31.70     | 9               | 0.1070 | 0.60 |
| 44-3   | 3.3693       | 0.822 | 3.425          | 9.74      | 23.83     | 7               | 0.1779 | 0.65 |
| 44-4   | 3.3724       | 0.786 | 3.563          | 10.71     | 22.91     | 7               | 0.2140 | 0.59 |
| 44-5   | 3.3739       | 0.769 | 3.351          | 14.89     | 24.35     | 7               | 0.2314 | 0.41 |
| 44-6   | 3.3949       | 0.525 | 2.842          | 11.54     | 28.70     | 8               | 0.4756 | 0.39 |
| 44-7   | 3.3985       | 0.482 | 3.234          | 11.45     | 25.22     | 7               | 0.5174 | 0.38 |
| 44-8   | 3.4065       | 0.389 | 3.651          | 8.17      | 22.34     | 7               | 0.6105 | 0.38 |
| 44-9   | 3.4126       | 0.318 | 3.726          | 8.94      | 21.89     | 6               | 0.6814 | 0.35 |
| 44-10  | 3.4361       | 0.046 | 3.441          | 9.84      | 23.69     | 7               | 0.9547 | 0.40 |
| 44-11  | 3.4394       | 0.007 | 3.312          | 11.67     | 24.62     | 7               | 0.9930 | 0.25 |
| 44-12  | 3.4736       | 0.622 | 10.68          | 22.49     | 6        | 1.3907         | 0.16 |
| 44-13  | 3.4514       | 3.194 | 8.56           | 25.52     | 7        | 1.1326         | 0.21 |
| 44-14  | 3.4514       | 2.829 | 8.95           | 28.81     | 8        | 1.1326         | 0.20 |
| MD-1   | 3.4574       | 3.468 | 9.56           | 23.50     | 7        | 1.2023         | 0.26 |
| MD-5   | 3.5226       | 3.622 | 10.35          | 22.48     | 6        | 1.9605         | 0.26 |

*Definitions: DOG, graphitization degree; fwhm, full width at half-maximum; $L_a$ and $L_c$, microcrystalline structure size; $\langle N \rangle$, aromatic layer stacking number; $p$, random orientation; AI, asymmetry index.*

Figure 12. Grouping of graphitized coal samples based on $d_{002}$ and $R_0$ values.
magmatic rapid heating coal crystallite structure is consistent with the normal trend of normal burial coal. The study of the properties of surrounding coal by rapid intrusive heating of igneous intrusions not only greatly improves the natural coke industrial utilization but also provides an important theoretical basis for the generation and enrichment of coalbed methane in an igneous thermal abnormal coal reservoir.

**AUTHOR INFORMATION**

**Corresponding Authors**

Shike Li — Key Laboratory of Coalbed Methane Resources and Reservoir Formation Process, Ministry of Education, China University of Mining and Technology, Xuzhou 221008, People’s Republic of China; School of Resources and Geosciences, China University of Mining and Technology, Xuzhou 221116, People’s Republic of China; orcid.org/0000-0003-0884-7057; Email: xxxx@xx.com

Yanming Zhu — Key Laboratory of Coalbed Methane Resources and Reservoir Formation Process, Ministry of Education, China University of Mining and Technology, Xuzhou 221008, People’s Republic of China; School of Resources and Geosciences, China University of Mining and Technology, Xuzhou 221116, People’s Republic of China; orcid.org/0000-0003-0884-7057; Email: ymzhucumt@126.com

**Authors**

Yang Wang — Key Laboratory of Coalbed Methane Resources and Reservoir Formation Process, Ministry of Education, China University of Mining and Technology, Xuzhou 221008, People’s Republic of China; School of Resources and Geosciences, China University of Mining and Technology, Xuzhou 221116, People’s Republic of China

Jing Liu — Key Laboratory of Coalbed Methane Resources and Reservoir Formation Process, Ministry of Education, China University of Mining and Technology, Xuzhou 221008, People’s Republic of China; School of Resources and Geosciences, China University of Mining and Technology, Xuzhou 221116, People’s Republic of China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c07287

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This research was supported by the Postgraduate Research & Practice Innovation Program of Jiangsu Province (Grant KYCX21_2318) and National Natural Science Foundation of China (42072199 and 42172156).

**REFERENCES**

(1) Gröcke, D. R.; Rimmer, S. M.; Yoksoulian, L. E.; Cairncross, B.; Tsikos, H.; Van Hunen, J. No evidence for thermogenic methane release in coal from the Karoo-Ferrar large igneous province. *Earth Planet Sc Lett.* 2009, 277, 204–212.

(2) Kisch, H. J.; Taylor, G. H. Metamorphism and alteration near an intrusive-coal contact. *Econ Geol.* 1966, 61, 343–361.

(3) Rimmer, S. M.; Yoksoulian, L. E.; Hower, J. C. Anatomy of an intruded coal, I: Effect of contact metamorphism on whole-coal geochemistry, Springfield (No. 5) (Pennsylvanian) coal, Illinois Basin. *Int. J. Coal Geol.* 2009, 79, 74–82.

(4) Rimmer, S. M.; Crelling, J. C.; Yoksoulian, L. E. An occurrence of coked bitumen, Raton formation, Purgatoire River valley, Colorado, USA. *Int. J. Coal Geol.* 2015, 141, 63–73.

(5) Stewart, A. K.; Massey, M.; Padgett, P. L.; Rimmer, S. M.; Hower, J. C. Influence of a basic intrusion on the vitrinite reflectance and chemistry of the Springfield (No. 5) coal, Harrisburg, Illinois. *Int. J. Coal Geol.* 2005, 63, 58–67.

(6) Finkelman, R. B.; Bostick, N. H.; Dulong, F. T.; Senftle, F. E.; Thorpe, A. N. Influence of an igneous intrusion on the inorganic
geochemistry of a bituminous coal from Pitkin County, Colorado. *Int. J. Coal Geol.* 1998, 36, 223–241.

(7) Golab, A. N.; Carr, P. F. Changes in geochemistry and mineralogy of thermally altered coal, Upper Hunter Valley, Australia. *Int. J. Coal Geol.* 2004, 57, 197–210.

(8) Golab, A. N.; Hutton, A. C.; French, D. Petrography, carbonate mineralogy and geochemistry of thermally altered coal in Permian coal measures, Hunter Valley, Australia. *Int. J. Coal Geol.* 2007, 70, 150–165.

(9) Mastalerz, M.; Drobiak, A.; Schimmelmann, A. Changes in optical properties, chemistry, and micropore and mesopore characteristics of bituminous coal at the contact with dikes in the Illinois Basin. *Int. J. Coal Geol.* 2009, 77, 310–319.

(10) 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.

(11) Peverar, D. R.; Williams, V. E.; Mustoe, G. E. Kaolinite, smectite, and K-rectorite in bentonites: Relation to coal rank at Tulameen, British Columbia. *Clay Clay Miner.* 1980, 28, 241–254.

(12) Cooper, J. R.; Caffee, J. C.; Rimmer, S. M.; Whittington, A. G. Coal metamorphism by igneous intrusion in the Raton Basin, CO and NM: implications for generation of volatiles. *Int. J. Coal Geol.* 2007, 71, 15–27.

(13) Saghafi, A.; Pinetown, K. L.; Grobler, P. G.; Van Heerden, J. H. P. CO₂ storage potential of South African coals and gas entrapment enhancement due to igneous intrusions. *Int. J. Coal Geol.* 2008, 73, 74–87.

(14) Caffee, J. C.; Dutcher, R. R. A petrologic study of a thermally altered coal from the Purgatoire River Valley of Colorado. *Geol. Soc. Am. Bull.* 1968, 79, 1375–1386.

(15) Bostick, N. H.; Pawlewicz, M. J. Paleotemperatures based on vitrinite reflectance of shale and limestone in igneous dike aureoles in the Upper Cretaceous Pierre shale, Walsenburg, Colorado. 1984.

(16) Murchison, D. Organic petrology in the 19th, 20th, and 21st centuries: the Newcastle contribution. *Int. J. Coal Geol.* 2005, 62, 5–31.

(17) Barker, C. E.; Pawlewicz, M. J. Calculation of vitrinite reflectance from thermal histories and peak temperatures: a comparison of methods; Academic Press and American Chemical Society: 1994; pp 216–229.

(18) Hood, A.; Gutjahr, C. C. M.; Heacock, R. L. Organic petrology; Academic Press and Schweizerbart Science Publishers: 1998.

(19) Caffee, J. C. Coal Carbonization. In Applied Coal Petrology; Academic Press and Elsevier: 2008; pp 173–192.

(20) 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.

(21) Teichmüller, M.; Teichmüller, R. Diagenesis of coal (coalification). In Developments in sedimentology; Elsevier: 1979; Vol. 25, pp 207–246.

(22) Amijaya, H.; Littke, R. Properties of thermally metamorphosed coal from Tanjung Enim Area, South Sumatra Basin, Indonesia with special reference to the coalification path of macerals. *Int. J. Coal Geol.* 2006, 66, 271–295.

(23) Van Krevelen, D. W. Graphical-statistical method for the study of structure and reaction processes of coal. *Fuel* 1950, 29, 269–284.

(24) Gonzalez, D.; Montes-Morón, M. A.; Garcia, A. B. Graphite materials prepared from an anthracite: a structural characterization. *Energy Fuels.* 2003, 17, 1324–1329.

(25) Lu, L.; Sahajwalla, V.; Kong, C.; Harris, D. Quantitative X-ray diffraction analysis and its application to various coals. *Carbon* 2001, 39, 1821–1833.

(26) Wang, G. F. Carbonaceous material in the Ryoke metamorphic rocks, Kinki district, Japan. *Lithos.* 1989, 22, 305–316.

(27) Nakamura, Y.; Akai, T. Microstructural evolution of carbonaceous material during graphitization in the Gyoja-yama contact aureole: HRTEM, XRD and Raman spectroscopic study. *J. Miner. Petrol. Sci.* 2013, 108, 131–143.

(28) Nakamura, D. Comparison and interpretation of graphitization in contact and regional metamorphic rocks. *Isr. Arc.* 1995, 4, 112–127.

(29) French, B. M. Graphitization of organic material in a progressively metamorphosed Precambrian iron formation. *Science* 1964, 146, 917–918.

(30) Grew, G. S. Carbonaceous material in some metamorphic rocks of New England and other areas. *Journal Geology.* 1974, 82, 50–73.

(31) Kwiecinska, B.; Suarez-Ruiz, I.; Paluszkewicz, C.; Rodrigues, S. Raman spectroscopy of selected carbonaceous samples. *Int. J. Coal Geol.* 2014, 100, 45–55.
(51) Landis, C. A. Graphitization of dispersed carbonaceous material in metamorphic rocks. *Contrib Mineral Petr.* 1971, 30, 34–45.

(52) Kwiecińska, B.; Petersen, H. I. Graphite, semi-graphite, natural coke, and natural char classification—ICCP system. *Int. J. Coal Geol.* 2004, 57, 99–116.

(53) Zhang, S.; Liu, Q.; Zhang, H.; Ma, R.; Li, K.; Wu; Teppen, B. J. Structural order evaluation and structural evolution of coal derived natural graphite during graphitization. *Carbon* 2020, 157, 714–723.

(54) Oberlin, A. Carbonization and graphitization. *Carbon* 1984, 22, 521–541.

(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.

(56) 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.