ABSTRACT: Thermally altered coals affect the safety and efficiency of coal mining and utilization, but most studies of thermally altered coal have focused on the whole coal instead of on different macerals. Thermally altered coals have complex and special maceral components; not only intrinsic macerals but also newly formed macerals such as pyrolytic carbon can be observed. The shape and texture of intrinsic macerals also change significantly after thermal alteration, especially for vitrinite. Therefore, employing an in situ testing method to study the macerals in thermally altered coals is necessary. Herein, a confocal Raman imaging microscope was used. Results show that macerals become coked in samples adjacent to the sill, and circular mosaic texture is the most common texture observed in this series of samples. In samples away from the sill, inertinite is isotropic, while in samples closest to the sill, anisotropic inertinite can be found. The Raman spectra of inertinite and vitrinite (mosaic texture) are significantly different. For vitrinite, the D and G peaks are closer, and the height of D is lower than for inertinite. The Raman spectra of thermally altered coal include 13 bands after curve fitting. Curved-fitted results show that for vitrinite, polycondensation provides the nucleation of mesophase spheres, and newly formed aromatics take part in the growth of mesophase spheres. However, for inertinite, excessive amorphous carbon and substituents, such as aromatic alkyl and aryl–alkyl ether, form cross-linked structures and hinder the anisotropic development of inertinite.

1. INTRODUCTION
Coal is not only one of the most widely used fuels but also extensively used industrial feedstocks. However, coal is a non-renewable resource and will be depleted within decades according to the current reserve-to-production ratio. To utilize coal for a longer time, mining deeper to increase coal reserves and improving efficiency to conserve coal are two important approaches. Thermally altered coal, affected by the direct contact of igneous intrusions, is one of the difficulties in the efficient utilization of coal. Compared with coal subjected to normal coalification, thermally altered coal has higher risks of both post-mining spontaneous combustion and gas outburst and higher contents of toxic elements and polycyclic aromatic hydrocarbons. In other words, thermally altered coal may cause a series of problems during coal mining, storage, transportation, and utilization. Therefore, further research of thermally altered coal should be carried out to ensure production safety and to improve utilization efficiency.

A considerable amount of literature has focused on petrology of thermally altered coal. These studies suggest that the shape and texture of intrinsic macerals (vitrinite, inertinite, and liptinite) change significantly, and newly formed optical components such as pyrolytic carbon can be observed in thermally altered coal. The reflectance, birefringence, and anisotropy of macerals increase significantly.
2. RESULT AND DISCUSSION

2.1. Petrological Analysis. The results of petrological analysis are summarized in Table 1. With samples approaching the sill contact zone, the contents of vitrinite and inertinite decreased and liptinite became unrecognizable, while natural coke increased. The content of natural coke continuously increased with samples approaching the sill except SL5 and SL7, in which the content of natural coke reduced slightly.

The morphology of vitrinite also reflects the transformation from vitrinite to coke. As shown in Figure 1, vitrinite with a smooth surface is the most common maceral in sample SL1 (Figure 1a), while in samples adjacent to the sill, vitrinite coked to form circular mosaic texture (Figure 1b) and lenticular texture (Figure 1c). Inertinite, mostly fusinite and macrinite, decreased from 17.8 to 5.2% with samples approaching the sill. Because the roof of the coal seam was obscured by the sill, it is not possible to determine whether the reduction of the inertinite was due to the change in the sedimentary environment or the effect of the sill. However, it is determined that the optical characteristics of the inertinite were affected by the sill. As shown in Figure 1d, optically anisotropic fusinite can be observed in samples close to the sill, while in samples away from the sill, fusinite has no anisotropy. Figure 1g shows a macrinite with anisotropic edges in SL6, and this anisotropic edge of inertinite is present from SL5. In SL7, optically anisotropic fusinite (Figure 1d) is observed both at the edges and in the interior, so we think that the anisotropy of inertinite first starts at the edges under the influence of stress and then the anisotropy gradually progresses to the interior. Liptinite is rare in samples used; it may be because the intrinsic content of liptinite in the coal seam is rare or because liptinite becomes difficult to identify during the thermal alteration. As shown in Figure 1e,f, the observable liptinite included meta-sporinite and meta-cutinite. Although most of the natural coke can be described as mosaic texture, incipient anisotropic coke and pyrolytic carbon can also be found (Figure 1h,i), but the content is very low.

Circular mosaic is the most common mosaic texture, and Table 2 shows the contents of various circular mosaic textures. The total content of circular mosaic textures sharply increased from SL1 to SL2, but the increased circular mosaic textures were only fine circular mosaic textures in this range. Medium circular mosaic textures obviously increased in SL3 and SL5. Coarse circular mosaic textures increased in SL4. As known, a larger-area circular mosaic texture is composed of more aromatics arranged in similar directions. In the range from SL3 to SL5, the content of medium and coarse circular mosaic textures increased, suggesting that many aromatics may take part in the arrangement of mosaic texture in this range.

2.2. Raman Spectra. 2.2.1. Raw Spectra. As mentioned above, with samples approaching the sill, vitrinite became coked and mosaic texture was mainly transformed from vitrinite; hence the Raman spectra of mosaic texture in this work are analyzed and discussed as the spectra of vitrinite. The Raman spectra are shown in Figure 2, and only one inertinite spectrum and one vitrinite (or mosaic texture) spectrum of every sample are shown in Figure 2 as examples. As shown in Figure 2, the first-order region Raman spectra are characterized by two peaks usually named D and G. Adjacent to the sill, the two peaks separated away, and the valley (V) between the two peaks tended to be wider and flatter. In samples far from the sill, the peaks in inertinite spectra are significantly sharper than those in vitrinite, while in samples near the sill, this difference gradually faded away.

To describe the characteristics of these Raman spectra quantitatively, several parameters were used, and the results are summarized in Figure 3. The total area is the integral of the entire first-order region. The intensities of D, G, and V are expressed as HD, HG and HV, respectively, and their comparison with each other is in the form of ratios, for example, HD/HG. The Raman shifts of D, G, and V are denoted by PD, PG, and PV, respectively, and their comparison with each other is in the form of differences, for example, PD−PG.

Raman parameters of vitrinite and inertinite, such as PG, PV/ PD, and PD−PG, have similarly shaped curves in Figure 3, indicating that these parameters have similar evolutionary trends. However, the values of these parameters are significantly different, especially parameters related to the D peak. The HD/ HV and HD/HG values of inertinite were always larger than those of vitrinite, suggesting that inertinite had higher D peaks.
In addition, it is notable that the gap of HD between inertinite and vitrinite was significant in samples SL3, 4, and 5, but the gap reduced in SL6 and 7. The position of the D peak (PD) also showed a great gap, indicating that the D peak of inertinite was obviously far from the G peak than vitrinite.

The total area is the integral of the entire first-order region Raman spectra, and previous studies had pointed out that the total area was related to aromaticity and electron-rich structures. Results of the total area in this work showed a trend that the area adjacent to the sill decreased. However, both vitrinite (mosaic texture) and inertinite in SL6 had significantly high values, and area of vitrinite also increased in the range of SL2 to SL4. The intensity of the G peak shows almost the same trend as the total area because both the total area and HG reflect the Raman scattering ability. It has been proved that aromaticity and electron-rich structures can affect the Raman scattering ability; increase in aromaticity (sp³ carbons condense into sp² carbons) or electron-rich structures such as C=O enhance Raman scattering ability.

Parameters HD/HG, HV/HG, and HD/HV reflect the relative intensity of D, G, and V, respectively. For this suite of thermally altered coals, the HD/HG showed a decreasing tendency first and then increasing as the sample approached the igneous intrusion. With samples close to the sill, the values of HV/HG decreased while those of HD/HV increased, indicating that the intensity of the valley between D and G decreased. However, it should be noted that the HV increased from SL4 to SL5. More importantly, there are multiple parameters in the range from SL4 to SL5 that also exhibited anomalous trends, such as PG and PV. PD, PG, and PV are the position of D peak, G peak, and the lowest point of the valley, respectively. Except for SL5, PG tended to increase while PD tended to decrease, so the distance between the two peaks was gradually increasing, which is consistent with previous studies. Adjoining to the igneous intrusion, the values of PV tended to increase from SL1 to SL6, that is, the lowest point of the valley was closer to the G peak and farther from the D peak. However, for SL7, PV sharply decreased and resulted in the steepening of the D peak, which can also be observed from the spectra in Figure 2.

In summary, vitrinite and inertinite in thermally altered coal can be clearly distinguished based on the original Raman spectra because for vitrinite, two peaks were closer and the relative intensity of D was lower than that for inertinite. Overall, the evolutionary trend of the thermally altered coal is similar to the results obtained from previous studies. However, no parameter changed as a straight line, and clearly, abnormal intervals can be observed. Especially, in combination with the petrological analysis results in Section 2.1 and the staged evolution of thermally altered coal in our previous work, we considered that macerals in thermally altered coal also have multiple different evolutionary stages. To discuss the staged evolution of macerals, more information should be obtained from curve-fitted Raman spectra.

2.2.2. Curve Fitting. By comparing the Raman spectra of thermally altered coal with those of the previous literature, it was found that the method originally used for char Raman spectra was also suitable for thermally altered coal in this work. Meanwhile, considering that both thermally altered coal and char have gone through a rapid and high-temperature heating process than coals subjected to burial metamorphism, so, in this work, an improved curve fitting method based on char Raman spectra is applied to thermally altered coal (as shown in Figure 2). About 13 bands are divided for every Raman spectrum, and
the positions and assignments of these bands are summarized in Table 3.

As shown in Figure 3, oTO and R1 bands are very small. Because the oTO band is assigned to the out-of-plane transverse optical phonon mode near the Γ point of the Brillouin zone, and only curved graphene planes cause the oTO-phonon mode to be Raman active,\textsuperscript{51−53} but the graphene plane is rare in thermally altered coal, so the oTO band is small. The R1 band is assigned to the alkanes or cyclic alkanes, and these structures are usually few in high-rank coals.\textsuperscript{60} The S1 band is assigned to C−H on aromatic rings, while S and S2 bands reflect substituents linked with aromatics. The S band includes C\textsubscript{aromatic}−C\textsubscript{aliphatic}, aromatic (aliphatic) ethers, and C−C on hydro-aromatic rings. The S2 band is caused by aryl−alkyl ether and para-aromatic-like structures. The D and G bands are the two most dominant bands, and the main difference between D and G bands is that the G band is Raman active for any aromatic rings but the D band is only sensitive for aromatics with not less than six rings.\textsuperscript{61} It is notable that the D band also represents graphite defects, but our previous work showed that crystalline graphite in these thermally altered coal samples was rare and amorphous structures were dominant.\textsuperscript{23} So, in this work, the D band is thought to be mainly caused by aromatics with not less than six rings. Three bands, V1, V, and V2, existed in the valley between D
and G, and these three bands are attributed to amorphous carbon structures. The D2 band always existed with the presence of the D band and was attributed to the defect of graphite. R2 and R3 bands represent the carbonyl group C=O and ester −COOR, respectively.

2.2.3. Structural Evolution of Different Macerals. Figure 5 summarizes the relative intensity of bands and shows the structural evolution with samples adjacent to the sill. It should be noted that all values in Figure 5 are normalized mean values, and except IG, the intensities of the other bands are presented as ratios, reflecting the relative content of chemical structures to which these peaks are attributed for a constant aromaticity.

As seen in Figure 5, with samples close to the sill, IG tended to increase, while the relative intensities of other bands assigned to amorphous carbon structures, oxygen-containing functional groups, and substituents tended to decrease. Meanwhile, the
intensities of oTO and D2 bands respectively related to graphite layer curvature and defects, also tended to decrease. All these phenomena indicated that the chemical structural evolution of both vitrinite and inertinite showed a general trend that the content of aromatic structures increased as the sample approached the intrusion, while the content of other structures, such as amorphous carbon structures and substituents, decreased.

It should be noted that there were outliers that differ from the general trends: only one outlier, SL3, in vitrinite but two outliers, SL3 and SL5, in inertinite. IG in SL5 was low, and this result corresponds to the results in Section 2.2, indicating that aromaticity of SL5 was indeed lower than that of other samples. Additionally, the intensities of R bands, especially the R3 band, were significantly high in SL5, that is, the content of oxygen-containing functional groups was high. Herein, the abnormality in SL5 may be caused due to oxidation, which is consistent with the NMR and high resolution transmission electron microscopy results in our previous work.

In addition to the difference in anomalies, there was another obvious difference between vitrinite and inertinite. The difference is that from SL1 to SL5, inertinite had lower contents of amorphous carbon structures and substituents than vitrinite, as well as aromatics with not less than six rings, but in SL6 and SL7, inertinite had lower contents. Moreover, an important phenomenon is that the content of aromatics with not less than six rings and the contents of amorphous carbon structures and substituents are positively correlated. For instance, ID/IG of vitrinite decreased from SL2 to SL4, indicating that the proportion of aromatic structures with not less than six rings to all aromatic structures declined. Also, in the range from SL2 to SL4, the relative intensities of $R_3$, $S_3$, $S_2$, $V_1$, $V_2$, and $V_3$ obviously decreased, that is, the contents of structures like alkanes, cyclic alkanes, arylyingalkyl, and sp$^3$–sp$^3$ amorphous carbon structures decreased. Considering that the aromaticity was elevated in this range, we thought that reduced alkyl, alkanes, and so forth transformed into small aromatic fragments by aromatization, diluting the intensity of the D band. Another evidence for aromatization is the intensity of the S band, which did not decrease in this range and even slightly increased in SL3. Because the S band was associated with the hydro-aromatic ring and the aromatization of alkanes first forms hydrogenated aromatic rings which then dehydrogenate to form aromatic rings, so the intensity of S band first increased in SL3 and then declined in SL4.

### 2.3. Relationship between Structural Evolution and Petrologic Characteristics

From the results above, we can find that the petrologic variations of samples and chemical structural characteristics are related. Samples with abrupt changes in the content of macerals also showed significant chemical structure changes. This suggests that the petrologic evolution of thermally altered coal is caused by the evolution of the chemical structure. One of the most obvious relationships is that the IG variation of vitrinite is consistent with the change in the content of the natural coke, indicating that the aromatic structure was the main component of the mosaic texture formed by the coked vitrinite. Vitrinite or mosaic texture features of each sample are also correlated with the evolution of aromatic structures. From SL1 to SL2, vitrinite was heavily coked and formed mosaic textures, especially fine circular mosaic textures. Also, in this range, the main chemical structural variation was the increase in aromatic size by polycondensation (ID/IG increased). Considering that the petrologic characteristic was the formation of numerous fine circular mosaic textures and the precursor of this texture was mesophase spheres, whose chemical structure was spherically stacked aromatics, the polycondensation may provide the nucleation of mesophase spheres, and many fine circular mosaic textures formed in this range. From SL2 to SL4, the content of mosaic texture still increased, and the increase in content of fine circular mosaic textures was slowed down, while medium and coarse mosaic texture had a significant increase in this range. The results in Section 2.2 indicated that the chemical variation from SL2 to SL4 was dominated by the synthesis of new aromatic structures, suggesting that the newly formed aromatic structures were involved in the growth of the mesophase spheres. Because of low content of aromatics, less natural coke was also observed in SLS, especially fine circular mosaic textures. Medium circular mosaic textures obviously increased in SLS, which may be the result from fusion of fine circular mosaic textures. For samples SLS-7, the chemical structure changes occurred inside the existing mosaic textures because the temperature was too high and the structure solidified quickly. So, there was no significant increase in the content of the mosaic textures.

As shown in Figure 5, the major difference between inertinite and vitrinite is the substituents and amorphous carbon structures in the range from SL1 to SLS. Although aromatics
with not less than six rings in inertinite were also more than vitrinite, excessive substituents and amorphous carbon formed cross-linked structures, which hindered the anisotropic development of inertinite. From SL5 to SL7, the chemical structure changes in inertinite and vitrinite are basically the same, and the inertinite also exhibited anisotropy under a microscope in samples close to the sill. This indicates that although inertinite did not melt as vitrinite, anisotropy and similar chemical structural changes also occurred as inertinite approached the sill.

3. CONCLUSION

In this work, petrologic characteristics of a set of thermally altered coal affected by a sill were analyzed, and a confocal Raman imaging microscope was employed to obtain the Raman spectra of inertinite, vitrinite, and mosaic texture derived from the vitrinite. By analyzing the chemical structure information reflected by the Raman spectrum and combining the coal petrological characteristics of macerals, the following conclusions are obtained.

1. Adjacent to the sill, macerals became coked. Vitrinite not coked was common in samples away from the sill; with samples close to the sill, vitrinite coked to form circular mosaic texture and lenticular texture. Inertinite in samples away from the sill is isotropic, while in samples closest to the sill, strain anisotropic inertinite can be found. Circular mosaic texture is the most common natural coke in the samples used.

2. The original Raman spectra of inertinite and vitrinite in thermally altered coal are significantly different. For vitrinite, the D peak and G peak were closer and the relative intensity of D was lower than inertinite. The Raman spectral curve fitting method of thermally altered coal used in this work distinguished 13 bands, and the bands assigned to functional groups and substituents linked with aromatic structures are abundant.

3. Petrologic characteristics of thermally altered coal result from the chemical structural evolution of macerals. For vitrinite, polycondensation provided the nucleation of...
mesophase spheres, and newly formed aromatics took part in the growth of mesophase spheres. Inertinite were not always inert in samples used in this work. The chemical structural evolution of inertinite was similar to that of vitrinite in samples close to the sill, and inertinite also showed the petrologic characteristic of anisotropy.

4. SAMPLING AND METHODOLOGY
The tested samples were collected from the Shuoli no. 5 coal seam in Anhui province, China. A quartz porphyry sill intruded the coal seam along the roof, and a suite of thermally altered coal samples, SL1 to SL7, was collected from the floor to the sill. SL7 was the sample closest to the sill and directly in contact with the sill. Unfortunately, the thickness of the sill was not measured because only the lower part of the sill can be observed in the tunnel. Details of the sampling information and the general properties of samples can be found in our previous work.23

All samples were crushed to 20 mesh, and then, pellets of these samples were prepared for petrological analysis according to a standard procedure (GB/T 16773-2008). Samples were examined petrologically, and not less than 500 counts per pellet were performed to quantify vitrinite, liptinite, and inertinite contents and optical texture of natural coke. Circular mosaic textures are the most common optical texture, which can be further subdivided into fine, medium, and coarse circular mosaic textures according to the classification system proposed by John C. Crerrell in Applied Coal Petrology.65 The mean maximum of reflectance of vitrinite (Ro) was measured using a Zeiss Universal reflected light microscope fitted with a 40×-oil-immersion objective and 100× ocular lenses according to a standard procedure (GB/T 6948-2008).

The Raman spectra of the macerals were obtained using a confocal Raman imaging microscope (WITec alpha300 R), which was equipped with a 100× objective lens (Zeiss EC Epiplan-Neofluar Dic 100×/0.9) to focus the laser beam (excitation line λ = 532 nm) on the sample surface. To reduce the experiment system error, the Raman spectrometer was calibrated by using a silicon standard. Because a high laser power can induce high thermal emission and thermal degradation on the coal surface, different experimental conditions (laser power, integration time, and number of accumulations) were tested to obtain the best experimental conditions. Conditions used in this work were: laser power 0.8 mW, integration time 3 s, and number of accumulations 5. The first-order Raman spectrum (800 to 2000 cm⁻¹) was applied and analyzed in this work, and not less than 10 points were tested for every maceral in every thermally altered coal samples.

AUTHOR INFORMATION

Corresponding Author
Shaoqing Wang — College of Geoscience and Surveying Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China; orcid.org/0000-0001-5158-7751; Email: wangzq@cumtb.edu.cn

Authors
Hao Chen — College of Geoscience and Surveying Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China
Jinsong Deng — College of Geoscience and Surveying Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China

Xiaomei Zhang — College of Geoscience and Surveying Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China
Yu Liu — College of Geoscience and Surveying Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China
Xiaoguang Li — State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c03922

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully thank the National Natural Science Foundation of China (research project no. 42072196). The authors also wish to acknowledge the support by the Institute of Geology and Geophysics, Chinese Academy of Sciences.

REFERENCES

(1) BP plc. By Statistical Review of World Energy 2021; Whitehouse Associates: London, 2021.
(2) Shi, Q.; Qin, B.; Liang, H.; Gao, Y.; Bi, Q.; Qu, B. Effects of Igneous Intrusions on the Structure and Spontaneous Combustion Propensity of Coal: A Case Study of Bituminous Coal in Daxing Mine, China. Fuel 2018, 216, 181−189.
(3) Zhou, B.; Yang, S.; Wang, C.; Cai, J.; Xu, Q.; Sang, N. Experimental Study on the Influence of Coal Oxidation on Coal and Gas Outburst during Invasion of Migmatic Rocks into Coal Seams. Process Saf. Environ. Prot. 2019, 124, 213−222.
(4) Wang, L.; Cheng, L.-B.; Cheng, Y.-P.; Yin, G.-Z.; Cai, C.-C.; Xu, C.; Jin, K. Thermal Effects of Migmatic Sills on Coal Seam Metamorphism and Gas Occurrence. Bull. Volcanol. 2014, 76, 803.
(5) An, Y.; Liu, L.; Wang, M.; Zheng, S.; Guo, Y.; Zhang, S.; Lai, C. Source and Enrichment of Toxic Elements in Coal Seams around Mafic Intrusions: Constraints from Pyrites in the Yuandian Coal Mine in Anhui, Eastern China. Minerals 2018, 8, 164.
(6) Wang, R.; Liu, G. Variations of Concentration and Composition of Polycyclic Aromatic Hydrocarbons in Coals in Response to Dike Intrusion in the Huainan Coalfield in Eastern China. Org. Geochem. 2015, 83−84, 202−214.
(7) Rimmer, S. M.; Yokoulan, L. E.; Hower, J. C. Anatomy of an Intruded Coal, I: Effect of Contact Metamorphism on Whole-Coal Geochemistry, Springfield (No. S) (Pennsylvanian) Coal, Illinois Basin. Int. J. Coal Geol. 2009, 79, 74−82.
(8) Rahman, M. W.; Rimmer, S. M. Effects of Rapid Thermal Alteration on Coal: Geochemical and Petrographic Signatures in the Springfield (No. S) Coal, Illinois Basin. Int. J. Coal Geol. 2014, 131, 214−226.
(9) Śmigdowski, L.; Duber, S.; Matuszewska, A. An effect of igneous intrusion on the structure, texture and microtexture of coal from the Soinica coal mine, Upper Silesian Coal Basin, Poland. Geol. Q. 2015, 59, 507−516.
(10) Jiang, J.; Cheng, Y. Effects of Igneous Intrusion on Microporosity and Gas Adsorption Capacity of Coals in the Haizi Mine, China. Sci. World J. 2014, 2014, 976582.
(11) 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.
(12) Singh, A. K.; Singh, M. P.; Sharma, M.; Srivastava, S. K. Microstructures and Microtextures of Natural Cokes: A Case Study of Heat-Affected Coking Coals from the Jharia Coalfield, India. Int. J. Coal Geol. 2007, 71, 153−175.
(53) Osipov, V. Y.; Baranov, A. V.; Ermakov, V. A.; Makarova, T. L.; Chungong, L. F.; Shames, A. I.; Takai, K.; Enoki, T.; Kaburagi, Y.; Endo, M.; et al. Raman Characterization and UV Optical Absorption Studies of Surface Plasmon Resonance in Multishell Nanographite. *Diamond Relat. Mater.* 2011, 20, 205−209.

(54) 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.

(55) Li, Z.; Fredericks, P. M.; Rintoul, L.; Ward, C. R. Application of Attenuated Total Reflectance Micro-Fourier Transform Infrared (ATR-FTIR) Spectroscopy to the Study of Coal Macerals: Examples from the Bowen Basin, Australia. *Int. J. Coal Geol.* 2007, 70, 87−94.

(56) 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.

(57) Pimenta, M. A.; Dresselhaus, G.; Dresselhaus, M. S.; Cançado, L. G.; Jorio, A.; Saito, R. Studying Disorder in Graphite-Based Systems by Raman Spectroscopy. *Phys. Chem. Chem. Phys.* 2007, 9, 1276−1290.

(58) 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.

(59) He, X.; Liu, X.; Nie, B.; Song, D. FTIR and Raman Spectroscopy Characterization of Functional Groups in Various Rank Coals. *Fuel* 2017, 206, 555−563.

(60) O’Keefe, J. M. K.; Bechtel, A.; Christianis, K.; Dai, S.; DiMichele, W. A.; Eble, C. F.; Esterle, J. S.; Mastalerz, M.; Raymond, A. L.; Valentim, B. V.; et al. On the Fundamental Difference between Coal Rank and Coal Type. *Int. J. Coal Geol.* 2013, 118, 58−87.

(61) Ferrari, A. C.; Robertson, J. Interpretation of Raman Spectra of Disordered and Amorphous Carbon. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2000, 61, 14095.

(62) Schwan, J.; Ulrich, S.; Batori, V.; Ehrhardt, H.; Silva, S. R. Raman Spectroscopy on Amorphous Carbon Films. *J. Appl. Phys.* 1996, 80, 440−447.

(63) Vidano, R.; Fischbach, D. B. New Lines in the Raman Spectra of Carbons and Graphite. *J. Am. Ceram. Soc.* 1978, 61, 13−17.

(64) Zhang, Y.; Li, Z. Raman Spectroscopic Study of Chemical Structure and Thermal Maturity of Vitrinite from a Suite of Australia Coals. *Fuel* 2019, 241, 188−198.

(65) Crelling, J. C. Chapter 7—Coal Carbonization. *Applied Coal Petrology* Suárez-Ruiz, I., Crelling, J. C. B. T.-A. C. P., Eds.; Elsevier: Burlington, 2008; pp 173−192.