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Influences of magmatic intrusion on the macromolecular and pore structures of coal: Evidences from Raman spectroscopy and atomic force microscopy

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HIGHLIGHTS

- The macromolecular order of coal was characterized by Raman micro-spectroscopy.
- The pore types and nano-structure of coal was determined by Atomic force microscopy.
- Quantitative results provide useful information for the utilization of high-rank coal.

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ABSTRACT

Magmatic intrusion into coal-bearing sequences can significantly affect the rank of the intruded coal and change the macromolecular and pore structures. Here, we use Raman microscope and Atomic force microscope (AFM) to obtain quantitative information on these transformations. Six coal samples of different ranks taken from a magmatic intrusion zone of Huainan Coalfield, China, were studied. The Raman spectra were fitted with a combination of 8 Lorentzian bands and 1 Gaussian band. We found that the macromolecular structures in coals of different ranks have significant relationships with Raman spectral parameters, particularly the band area ratios (I_{D1}/I_G, I_{D2}/I_G, I_{D3}/I_G, I_{D4}/I_G and I_G/I_{All}). With the increase of coal rank, I_{D1}/I_G, I_{D2}/I_G, I_{D3}/I_G and I_{D4}/I_G show trends of decreasing intensity, suggesting an enhanced orientation of aromatic hydrocarbons. Observations by Atomic force microscopy indicate that the pore parameters (e.g. amount, size, shape) are quite different for different ranks of coals. The pore size of low-rank bituminous coal is much larger than high-rank anthracite and pore abundance is higher in the former. In addition, there is also good correspondence between the surface topography of coal grains and coal rank.

1. Introduction

Influences of magmatic intrusion on the transformation of physicochemical properties in coal are observed in many coalfields [1–4]. The degree to which the coal physicochemical properties were altered depends on the temperature of the intruded magma, the duration of magmatic-derived heat, and the distance between intruded magma and coal [5,6]. Magmatic intrusion could cause dramatic changes in elemental compositions (e.g. volatilization of high-volatile elements, addition of magmatic-derived elements), macromolecular structures and physical properties (e.g. pore and fracture) in coal [7–9]. Typically, in a coalfield that was subjected to additional magmatic intrusion, a spectrum of coal ranks from bituminous coal, to semi-anthracite, and to anthracite and meta-anthracite can be formed. Many authors believe that graphitization, proceeding from meta-anthracite through semi-graphite to graphite, is the last stage of coalification [10–12]. The structural properties (e.g. macromolecular structure and pore structure) of coal have received much attention because they can provide useful information concerning the pyrolysis, liquification and gasification behavior of coal [13,14], and can help understand the coalification process. However, determination of the quantitative constraints on coal structural properties is a challenge due to the heterogeneous nature of coal [15]. The organic matrix of coal is thought to be a three-dimensional macromolecular network [16]. This network is made up of stacked aromatic clusters where aromatic rings are linked by aliphatic and hetero-aliphatic bridges [17].

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Nomenclature

AFM	atomic force microscope	I_{D1}/I_G, I_{D2}/I_G, I_{D3}/I_G and I_{D4}/I_G	band area ratios
FWHM	full width at half maximum	σ	standard deviation
λ_0	Raman spectral wavelength (nm)	R_a	average absolute deviation of the roughness irregularities
D_i, G	Raman peak position or band	R_q	standard deviation of the distribution of surface heights
I_{Di}, I_G	integrated area under D*i* or G band		

Table 1
Basic information of Huainan coals with their ultimate and proximate analysis.

	ZJ-1	ZJ-2	PS-1	PS-2	PS-3	PS-4
Coal mine	Zhuji	Zhuji	Pansan	Pansan	Pansan	Pansan
Macro-lithotype	Semi-dull	Semi-dull	Semi-bright	Semi-bright	Tegular, semi-dull	Mylonitic, semi-bright
Coal rank	Bituminous	Bituminous	Semi-Anthracite	Anthracite	Meta-anthracite	Meta-anthracite
Elemental composition (wt.%, daf)						
C	85.6	82.4	90.9	91.8	93.4	94.7
H	5.39	5.80	2.87	2.49	2.33	1.81
O	7.05	9.67	2.23	2.15	1.26	1.20
N	1.48	1.68	1.24	1.26	1.29	1.05
S	0.46	0.49	0.78	0.93	0.20	0.48
Proximate analysis (wt.%)						
Moisture (M_{ad})	1.49	1.34	1.74	2.13	1.64	1.97
Ash (A_{ad})	21.23	19.19	16.90	8.82	23.66	14.08
Volatile matter (V_{ad})	32.99	36.41	5.10	7.31	7.82	3.90
O/C	0.08	0.12	0.03	0.03	0.02	0.01
H/C	0.06	0.07	0.02	0.03	0.01	0.02

ad: air dried basis. daf: dried ash free basis.

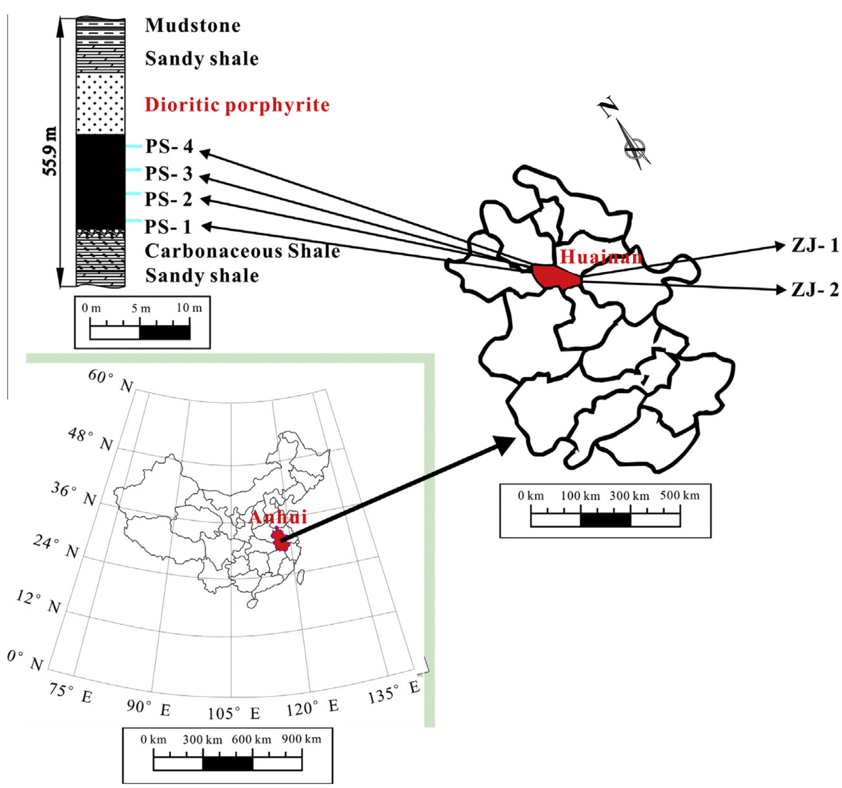

Fig. 1. Geographical and stratigraphic locations of studied Huainan Early Permian coals.

Raman spectroscopy is a powerful technique, characterized by high sensitivity in determination of both the crystal structure of carbonaceous materials and the macromolecular structure of coal [18–20]. For example, Van Doorn et al. [21] employed Raman