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Thermal behavior and Raman spectral characteristics of step-heating perhydrous coal: Implications for thermal maturity process

Dun Wu[a,b,c], Binyu Chen[a], Ruoyu Sun[d], Guijian Liu[a,c,*]

[a] School of Earth and Space Sciences, University of Science and Technology of China, CAS Key Laboratory of Crust-Mantle Materials and Environment, Hefei, Anhui 230026, China

[b] Exploration Research Institute, Anhui Provincial Bureau of Coal Geology, Hefei, Anhui 23008, China

[c] State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, The Chinese Academy of Sciences, Xi'an, Shaanxi 710075, China

[d] Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, China

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ABSTRACT

Perhydrous coal (PHC) had been widely investigated; however, a systematic research on the relationship between the structure of PHC and its thermal reactivity was rarely reported in the previous studies. The PHC was widely developed in the Carboniferous-Permian coal-bearing strata in the northern and eastern regions of the Huainan coalfield. In this study, we chose No. 13-1 PHC as the research object. Based on the macroscopic observation of No. 13-1 PHC of the borehole #9-3 and its logging response, a typical PHC sample was selected and pyrolyzed using a thermogravimetric analyzer (TGA) to acquire a set of coal samples after pyrolysis with wide range of random vitrinite reflectance (% VRo) from 0.86 to 7.79%. The thermal evolution process of PHC before and after pyrolysis was investigated by atomic force microscopy (AFM) and Raman spectroscopy. Research results show that: 1) in the experimental temperature range, the reflectance (VRo) range of PHC varied greatly; 2) with the increase of pyrolysis temperature, the Raman spectra of PHC changed significantly in the D band of disordered structure and the G band of ordered structure and the orderliness of its macromolecule particle arrangement was increasing gradually; 3) the relationship between the thermal reactivity of PHC and its Raman structure parameters was established, the FWHM of G-band can be used as indicators of the degree of thermal evolution of PHC; 4) compared with the G FWHM of normal coal with different rank, the thermal reaction temperature of PHC was advanced. Under the premise of comparable reaction temperature, the thermal maturity of PHC was gradually higher than that of bituminous coal, and slightly lower than anthracite, indicating that the actual PHC thermal maturity was suppressed by a higher amount of hydrogen.

1. Introduction

Compared to the conventional coal, perhydrous coal (PHC) has a high atomic hydrogen/carbon (H/C) ratio (> 0.83) [1]. Because PHC has a higher H content, its calorific value is higher. Thus, it was widely exploited in thermal power generation [2–5]. The existing research results of PHC mainly focused on the following aspects:

(1) Petrographic characteristics. The study of Arenillas et al. [1] and Costa et al. [2] showed that PHC dominantly composed of humic macerals. This PHC not only had high hydrogen content (5.7–7.4%, dry ash-free basis), but also had high calorific value (7700–8830 kcal/kg, ash-free basis). The degree of coalification of PHC was usually low, only reaching to subbituminous coal.

(2) Chemical structure. Detail studies on chemical composition of PHC [3,4] showed that the molecular structure unit of PHC was largely composed of aromatic structures with 1–2 rings, followed by a very small concentration of aromatic rings of large size. In addition, they found that the enrichment of *H* content in PHC changed the proportion of different functional groups in PHC, and affected its chemical structure.

(3) Thermal behavior. In order to understand the thermal behavior of PHC during pyrolysis and combustion, many researchers [1,2,5,6] had investigated the thermal reaction properties of PHC under different experimental conditions by TG/MS techniques. The main results showed that the higher *H* content in PHC caused the coal to produce a lot of hydrogen-containing free radicals during heat treatment, leading to the increase of yield of light components (H_2O

* Corresponding author at: School of Earth and Space Sciences, University of Science and Technology of China, CAS Key Laboratory of Crust-Mantle Materials and Environment, Hefei, Anhui 230026, China.

E-mail addresses: wudun@ustc.edu.cn (D. Wu), lgj@ustc.edu.cn (G. Liu).

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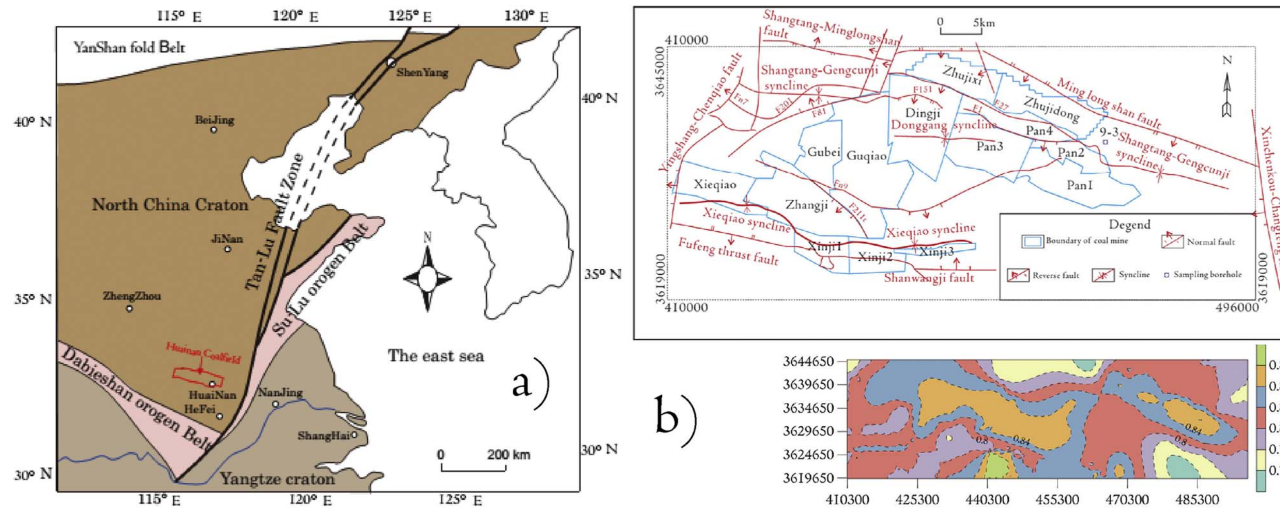

Fig. 1. (a) The simplified regional geographical map. (b) The structure outline map of Huainan Coalfield and the contour map of the atomic H/C ratio of No, 13-1 PHC.

and hydrocarbon).

(4) Thermodynamics. According to the study of thermodynamics of PHC (inertinite-rich), Wang et al. [7] focused on its thermal reaction during pyrolysis and combustion, found that the maximum temperature of volatile components loss in PHC was closely related to its softening temperature, and when temperature increased to 200 °C, it began to decompose, leading to the production of a certain amount of small-molecule gases (H_2 and H_2O), which suggests that PHC might show positive thermal reactivity during the heat treatment. By coincidence, we conducted the thermodynamic study of Huainan PHC, and found that its main pyrolysis temperature range was 300–600 °C, and its apparent activation energy was calculated with values ranging from 78 to 307 kJ/mol [8].

In the past few years, Raman spectroscopy has become the most widely used tool to investigate the quantitative structural characterization of natural solid organic matter (graphite, coals, solid bitumen and carbonaceous materials (CM)) [9–14] and artificial solid bitumen [15], because of its many advantages (non-destructive microstructure identification, high spatial resolution, the short spectrum-acquisition time as well as close connection with the degree of metamorphism of CM). On the other hand, the Raman spectral parameters (the position and intensity of peak, band area and FWHM) can be used as indicators for thermal maturity of CM. Of note, Wilkins et al. [10] used a new thermal maturity evaluation tool, RaMM (Raman Maturity Method), to establish the equivalent Raman spectra of vitrinite and inertinite in coal. The advantage of this method was that with the exception of the avoidance of exinite, it did not necessitate identification of maceral type; measured assemblages ranging from all inertinite to all vitrinite were appropriate. Besides, compared with the optical microscopy or electron beam method, Raman spectroscopy was more sensitive to the ordering degree of carbon crystal structure of CM. Beyssac et al. [13] used Raman method to characterize a series of CM with different ranks and quantify the thermal maturity of CM based on the area of the defect bands (R2 ratio). On this basis, they found a linear relation of the R2 ratio and the metamorphic temperature ($T = -445 \times R2 + 641$ (°C)) in the range of 330–650 °C (Standard deviation $\sigma = \pm 50$ °C). However, for PHC, under the condition of stepwise pyrolysis, whether the relation between the thermal evolution temperature of PHC and its Raman parameters was in line with Beyssac's formula needs further study.

From the above, pyrolysis played an important role in the study of thermal behavior of coal and was conducive to understanding the thermal maturation process of PHC. Raman spectroscopy can help us understand the structural characteristics of PHC. However, the systemic studies on the quantitative characterization of the degree of PHC pyrolysis, the Raman spectral characteristics of PHC and the correlation between the thermal maturity process of PHC and the types of coal metamorphism were greatly lacking. Therefore, we used Raman spectroscopy to characterize the ordering degree of carbon crystal structure of PHC under the condition of gradually increasing temperature to achieve the purpose of quantitatively characterizing the degree of coal pyrolysis in this study. The No. 13-1 PHC was a type of coal broadly generating in Carboniferous-Permian coal-bearing strata in the northern and eastern regions of the Huainan coalfield. In order to acquire a set of pyrolysate samples with different ranks in the process of PHC pyrolysis, a typical No. 13-1 PHC sample was pyrolyzed by step-heating method, after this their Raman spectra were measured, and the relationship between the Raman parameters of PHC and its thermal maturity evolution was investigated. To this end, the point of this study is: 1) investigating the thermal behavior features of PHC; 2) ascertaining the Raman spectral evolution characteristics of PHC during pyrolysis; 3) accurately acquiring all kinds of Raman spectral parameters and optimizing the appropriate parameters to characterize the thermal maturity of PHC; 4) demonstrating the relationship between the thermal maturity processes of PHC and the metamorphism processes of coal; 5) providing a feasibility of PHC reflectance as a new indicator of thermal maturity of coal.

2. Geological setting and sample description

2.1. Regional geology

The Huainan Coalfield was located in the southeast margin of North China Plate. It bordered in the west of the southern branch of the Tan-Lu faulted, in the north of Dabie orogenic belt and in the south of Bengbu uplift (Fig. 1a). It was the imbricate-type thrust-nappe structure basin, developing widely Carboniferous-Permian coal-bearing strata. The final structural outline of this Coalfield was based on the result of the combined effect of regional tectonic movement in different periods, which not only controlled the occurrence form of sedimentary coal seams, but also changed the degree of coal metamorphism. Yang et al. [16] showed that the coal rank of this Coalfield was relatively low, only reaching the level of gas coal and coking coal, and the type of coal metamorphism was considered as geothermal metamorphism of coal superimposed by telemagmatic metamorphism. However, the researches of several authors [17–19] indicated that the large-scale magmatic intrusion occurred in this coalfield during the early Cretaceous, which also led to the increase of degree of coal metamorphism in local areas, and the coal rank reached the level of bituminous coal.