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Raman spectral characteristics of magmatic-contact metamorphic coals from Huainan Coalfield, China

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ABSTRACT

Normal burial metamorphism of coal superimposed by magmatic-contact metamorphism makes the characteristics of the Raman spectrum of coal changed. Nine coal samples were chosen at a coal transect perpendicular to the intrusive dike, at the No. 3 coal seam, Zhuji Coal Mine, Huainan Coalfield, China, with different distances from dike-coal boundary (DCB). Geochemical (proximate and ultimate) analysis and mean random vitrinite reflectance (R_0, %) indicate that there is a significant relationship between the values of volatile matter and R_0 in metamorphosed coals. Raman spectra show that the graphite band (G band) becomes the major band but the disordered band (D band) disappears progressively, with the increase of metamorphic temperature in coals, showing that the structural organization in high-rank contact-metamorphosed coals is close to that of well-crystallized graphite. Evident relationships are observed between the calculated Raman spectral parameters and the peak metamorphic temperature, suggesting some spectral parameters have the potentials to be used as geothermometers for contact-metamorphic coals.

1. Introduction

Contact-metamorphism features a high heating rate with a relatively short duration of intense heat surrounding the intrusive body [41]. Many researchers have investigated the effects of magmatic intrusion on the thermal maturity of sedimentary organic matter (SOM) [10,11,13,15,17,21]. For example, Murchison and Raymond [42] showed that there is a close relationship between the regional vitrinite reflectance of SOM and the degree of magmatism by studying intrusive coal beds from the Midland Valley in Scotland. Querol et al. [45] and Ward [63] found that the sill intrusion into coal seams could cause significant gradient of coal ranks and geochemical and mineralogical parameters. Further, Gurba and Weber [26] reported that the intrusive coal thermal aureole was ~0.8 to 1 times of the thickness of the sill within the Gunnedah Coal Basin, and concluded that the thickness of the sill is the dominant factor controlling the extent of thermal aureole. These studies mainly focused on large intrusive sills (tens of meters thickness) that caused geologically instantaneous heating in the vicinity of magmatic contacts. However, in numerous sedimentary basins, magmatic intrusion took place in meter or even centimeter scales [6,16,23,24,38,44,53]. Although meter-scale magmatic intrusions have relatively narrow thermal aureoles, they are still able to significantly increase the maturation degree and alter the molecular structure in coals.

Up to now, most researchers mainly focus on the petrological and geochemical characteristics rather than microstructure of coals subjected to the magmatic heat [35,37,56]. We have earlier studied the microstructure of contact-metamorphosed coals in two different coal sequences affected by a dike intrusion, and indicated that the degree of ordering in coal crystalline structure is controlled by the metamorphic ranks [66,67]. However, the correlation between the crystallinity of contact-metamorphosed coal and metamorphic temperature is still not well constrained. This relationship in carbonaceous material in metasediments has been widely studied by diverse analytical techniques such as X-ray diffraction [19,32,40,43], Fourier transform infrared spectroscopy (FTIR) [54,55], and high-resolution transmission electron microscopy [34]. More recently, Raman spectroscopy, a high resolution and non-destructive method that is extremely sensitive to the degree of structural amorphousness, has been widely exploited to quantitatively characterize both crystallized graphite and amorphous carbon (e.g., coal, activated carbon, and soot) [20,25,33,46,49]. Therefore, its application in contact-metamorphosed coals is worthy of a deep investigation.

Magmatic rocks are extensively distributed in the Lower Permian No. 3 coal seam, Huainan Coalfield, China [27]. Coal samples were chosen at a coal transects perpendicular to the intrusive dike. Our primary

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purpose is to set up the empirical relationships between the degrees of structural order in magmatic-contact metamorphosed coals quantified by Raman spectroscopy and the maximum metamorphic temperature inferred from random vitrinite reflectance.

2. Materials and methods

2.1. Geological settings

The Huainan Coalfield is located in northern Anhui Province at the southeast corner of the North China Plate (Fig. 1). It is an elongated territory with a mean length of 180 km (W-E), and mean width of 15–25 km (N-S). The Zhuji Coal Mine situated in the northeastern Huainan Coalfield, covers an area of 54.13 km^2 with coal reserve of approximately 950 million tons. The geological structure of the Zhuji Mine primarily consists of broad shallowly-plunging folds and sporadic faults (Fig. 1). The coal-bearing Permian sequences in the Zhuji Mine are divided into the Shanxi, Lower Shihezi and Upper Shihezi Formations (Fig. 2) [57]. Detailed information on the thickness of each coal seam and the stratigraphic and lithological features of the coal-bearing strata can be found in Sun et al. [57].

Approximately 44% recoverable reserves of No. 3 coal seam in the Zhuji Coal Mine were engulfed by intruded magma (Fig. 1). Mineral composition and texture analyses indicate that the intruded dikes in No. 3 coal seam are classified as basic gabbro, having an isotopic age of ~118 Ma [68]. In general, these dikes have a north-west orientation and are positioned at the central and eastern sections of the coal mine (Fig. 1).

2.2. Sample collection and preparation

Samples were taken from the No. 3 coal seam in the Zhuji Coal Mine, Huainan Coalfield. This coal seam of ~2 m thickness was cut through by a ~3 m thick gabbroid dike. The dike/coal boundary (DCB) is irregular, with mixed coke/gabbros zones. As shown in Fig. 2, nine channel coal samples (~200 g each) were collected in the middle of afresh coal face perpendicular to the dike. These samples are numbered in an order of increasing distances from DCB (i.e., #1 is the closest and #9 is furthest).

The polished sections of all coal samples were formulated in terms of international standards [31], after which we check carefully the polished section under the microscope to ensure that these polished sections do not contain polishing defects. Besides, each coal sample was manually crushed in a quartz mortar by using a grinding rod. The pulverized samples were passed through a 200 mesh screen before drying in a desiccator at 60 °C for 12 h. Before performing Raman spectroscopy, the dried samples were demineralized by HF + HCl + $HClO_4$ as described in Wu et al. [67].

2.3. Analysis

Proximate analysis was performed in terms of ASTM Standards [3]. And ultimate analysis was followed by the national standards of China GB/T 476-2008. The results are listed in (Table 1). For each polished section, 50 particles were collected under white light by using 500× magnification to improve the accuracy of experimental results, after which its petrologic analysis was examined. Random vitrinite reflectance (R_0, %) measurements were determined by a Zeiss Universal microscope (oil immersion) equipped with a photometer in accordance with the Chinese standard (GB/T 6948-1998) (Table 1).

A microscope spectrometer (Jobin Yvon Labram HR800) equipped with a 50× lens was used to focus the excitation laser beam (514.5 nm exciting line of a Spectra Physics Ar-laser) on the samples, and Raman signals were collected in the backscattered direction. During measurement, each sample was regularly mounted on a glass slide where 10–15 particles were collected and analyzed randomly to compensate for the structural heterogeneity of coals. The laser power at the sample surface was set at about 1 mW. Spatial resolution was 1 μm and wavenumber resolution was 1 cm^{-1}. The average acquisition time for each spectrum was 45 s. The spectra were recorded in the range of 600–3500 cm^{-1}, including the first-order (600–2400 cm^{-1}) and second-order regions (2400–3500 cm^{-1}) (Fig. 3).

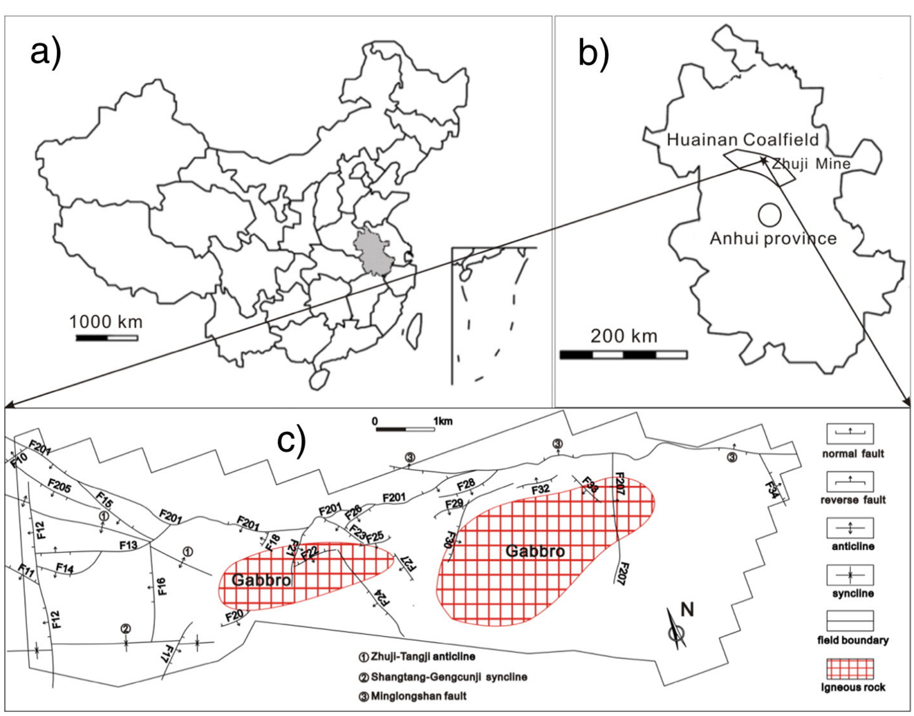

Fig. 1. Maps showing the location of study area and planar graph of magmatic dikes of No.3 coal seam.