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Influence of magmatic intrusions on organic nitrogen in coal: A case study from the Zhuji mine, the Huainan coalfield, China

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ABSTRACT

Although the influence of magmatic intrusions on coal has been studied extensively at many locations, data on changes of organic nitrogen forms in coal in response to this kind of geological instantaneous heating is still scarce. To fill this information gap, a total of five coal samples, including four coal samples collected along a coal transect approaching a magmatic intrusion and one unaltered coal sample, were collected from the No. 3 coal seam of the Zhuji mine in the Huainan coalfield, China and were analyzed for organic nitrogen forms using X-ray photoelectron spectroscopy (XPS), together with the determination of coal quality parameters and elemental composition. Due to the effect of magmatic intrusion, ash yield and carbon content of the coals increase, whereas moisture, volatile matter, oxygen, nitrogen and total sulfur decrease. The N-5 peak is dominant in unaltered and moderately altered coals, but disappears entirely in the coals adjacent to the magmatic intrusion due to the strong thermal influence. The N-Q peak mainly represents “protonated” quaternary nitrogen in unaltered and moderately altered coals. The N-Q peak can be transformed to the N-6 peak through the deprotonation of “protonated” quaternary nitrogen resulting from the loss of oxygen groups under the thermal influence of the magmatic intrusion. Closer to the magmatic intrusion, the N-Q peak is assigned to “graphitic” quaternary nitrogen, which increases sharply and becomes the predominant form eventually. Magmatic intrusion is responsible for the conversion of less stable nitrogen forms to more stable forms in coal.

1. Introduction

The chemical forms of organic nitrogen (N_{org}) in a coal matrix have attracted much scientific attention because this kind of coal-bound nitrogen is the main source of N_2O and NO_x , which are classified as harmful gas emitted into the atmosphere [1–3]. Moreover, the chemical forms of N_{org} in a coal matrix can help understand the history of coalification process as a valuable tracer [4,5].

Recent advances in X-ray photoelectron spectroscopy (XPS) [4], X-ray absorption near-edge structure spectroscopy (XANES) [5] and solid-state nuclear magnetic resonance (NMR), such as $^{13}C\{^{14}N\}$ SPIDER [6], have provided useful non-destructive spectroscopic techniques for the study of composition and functional groups of organic compounds. XPS allows for comprehensive and quantitative structural information obtained from solid materials, and has been employed widely to investigate organic nitrogen forms in coal [4,5,7–9]. The XPS N 1s spectra from coal can generally identify three types of the peak, including the N-5, N-6 and N-Q peaks, corresponding to nitrogen expressing a mean

binding energy of 400.6 eV, 398.8 eV and 401.6 eV, respectively [4,5,7–9]. The N-5 peak has been associated with pyrrolic nitrogen atom bonded to one H atom and two C atoms in a five-membered ring [4,8] (Fig. 1). However, the chemical environment of the nitrogen atom in pyridine-N-oxide is similar to pyrrolic nitrogen [10]. Hence, considering the accuracy of XPS measurements, pyridine-N-oxide (Fig. 1) cannot be distinguished from pyrrolic nitrogen [4,8]. Although amine and amide moieties are widespread in less mature coal, especially in lignites, there is no need to include amino-N to reach an acceptable fit in the N-5 peak in most cases [8]. The N-6 peak is assigned unambiguously to pyridinic nitrogen atom bonded only to two C atoms [4,8] (Fig. 1). The N-Q peak, namely quaternary nitrogen, can be attributed to more than one specific form. In coals with C_{daf} below ~90 wt%, quaternary nitrogen mainly reflects a structure of pyridinic nitrogen associated with oxygen groups such as hydroxyl or carboxyl groups, which is protonated via formation of H-bridges, and is called “protonated” quaternary nitrogen [8,10] (Fig. 1). With increasing maturity, this species decreases because of the loss of oxygen groups. In

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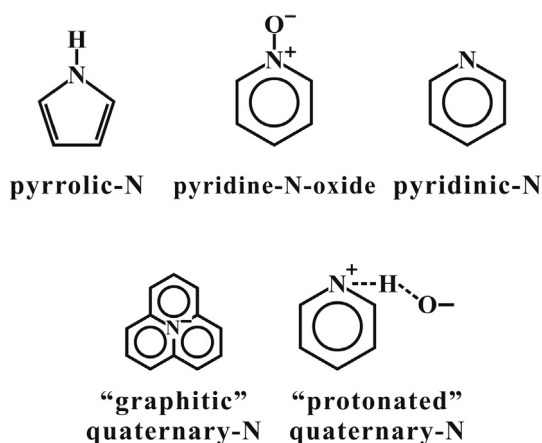


Fig. 1. Structures of major nitrogen forms presenting in coal. Modified from the literature reported by (Boudou et al. [4]; Pels et al. [8]).

coals with C_{daf} above ~ 90 wt%, the N-Q peak represents a structure of N-C₃ in which each N atom is bonded covalently to three C atoms, and is referred to as “graphitic” quaternary nitrogen [4] (Fig. 1). The “graphitic” quaternary nitrogen expresses remarkable thermal stability. However, several studies have reported that N-C₃ could also occur in low-rank coals, such as lignites [4,11]. The N-Q peak in some materials may also indicate the presence of ammonium salts. Nevertheless, ammonium salt is typically absent or negligible in bituminous and higher rank coals [4]. In addition, some other possible nitrogen forms, such as nitrogen oxide, could be found in coals, but their concentrations are very low [5,8].

Previous research has indicated that pyrrolic, pyridinic and quaternary nitrogen are the major constituents in coals, whereas changes in their quantity occur in different coal rank [4,8,9,12]. Low-rank coals are dominated by pyrrolic nitrogen, with subordinate pyridinic and quaternary nitrogen [5,7,8,10,12]. It has been reported that within the “oil window” rank range, pyrrolic nitrogen is the most abundant form in vitrinite-rich coals, steadily decreasing with coal rank, while pyridinic and quaternary nitrogen show variation with rank [9]. Boudou et al. [4] investigated changes of organic nitrogen from anthracite to semi-graphite, and found that a strong relative increase of quaternary nitrogen occurred with increased rank, at the expense of pyridinic and pyrrolic nitrogen.

There are numerous examples of coals that have been affected by magmatic intrusions [13–20]. This kind of thermally altered coals have been investigated extensively [13–21]. Magmatic intrusions increase maturity of the coal near magmatic intrusions, and may lead to significant changes in physical and chemical properties, including the petrology, geochemical composition, stable isotopic feature, microstructure, and microconstituents [13,15–17,19–24]. Moreover, the extent to which the coal physicochemical properties were altered depends on the temperature of intrusion, the duration of magmatic derived heat, the distance of the coal from the intrusion, lithology of the surrounding rocks, and other local factors [17,25]. Although there is significant data on the changes in organic and inorganic constituents of coals influenced by magmatic intrusions, the variations of organic nitrogen forms in coals in response to geological rapid heating due to magmatic intrusions are largely unknown.

The Huainan coalfield, the site of the largest magmatic intrusions into the Permo-Carboniferous coal measures [18,19], is located in the northern Anhui Province and is a major coal deposit in eastern China. Therefore, a large amount of thermal altered coal has been found in many mines, such as the Zhuji mine. The coal quality and rare earth elements of the magmatic intruded coal and the structural characteristics of thermally metamorphosed coal have been studied in the Zhuji mine [15,19,26]. In addition, Wang and Liu [18] recently investigated variations in concentration and composition of polycyclic aromatic

hydrocarbons in coals affected by intrusions from the Zhuji mine. In the current project, changes in N_{org} forms in coals in response to magmatic intrusions were investigated for the first time. The XPS technique was used to observe N_{org} forms in magmatic intrusion-influenced coal samples, which were collected from a transect approaching a magmatic intrusion from the No. 3 coal seam of the Zhuji mine.

2. Samples and methods

The geological background for the Huainan coalfield has been well described in the literature [13,18,19,26–28]. The Huainan coalfield is located in northern Anhui province, China. The coalfield has an elongated outline with a length of 180 km and a width of 15–25 km, and it covers an area of 3200 km². Within the coalfield, multiple coal sequences accumulated during the Permian period. The Permian strata of the Huainan coalfield comprise the Shanxi, Lower Shihezi and Upper Shihezi formations in chronological order, and all coal seams occur in the first three formations. The Zhuji mine, located near the northeast border of the Huainan coalfield, covers an area of 45 km².

Freshly exposed and unweathered coals (2–2.5 kg each) were sampled from the No. 3 coal seam of the Zhuji mine in the Huainan coalfield. In this mine, the No. 3 coal seam was partially intruded by an Early Triassic dike. The crystallized diorite porphyry dike, with a thickness of ~ 0.9 m, had been encountered during mining. Four grab samples of coal (ZJ-1 to ZJ-4) were collected at closely spaced intervals close to the intrusion-coal boundaries and identified in terms of distance from the contact (Fig. 2). One unaltered coal sample (ZJ-UA) from the same seam in this mine was also collected. The unaltered coal in the Zhuji mine is bituminous in rank [26].

All samples were stored in sealed polyethylene bags to avoid potential contamination and alteration. Before analysis, the coal samples were air-dried, crushed and passed through a 200-mesh sieve to homogenize. Coal quality parameters, including moisture (M_{ad}), ash yield (A_{ad}) and volatile matter (V_{daf}), were performed according to Chinese National Standard GB/T 212-2001. Elemental compositions, including carbon (C_{daf}), nitrogen (N_{daf}), oxygen (O_{daf}) and total sulfur ($S_{t,ad}$), were determined by an elemental analyzer (Elementar Vario EL cube, Germany). All experiments were accomplished at Laboratory of Environmental Geochemistry and Instruments’ Center for Physical Science of USTC. Each sample was measured in triplicate to demonstrate precision and reproducibility.

XPS analysis was conducted at the Instruments’ Center for Physical Science of USTC according to Chinese National Standard GB/T 19500-2004. In order to minimize bias due to surface oxidation, coal samples were crushed to $< 212 \mu\text{m}$ in an agate mortar to expose new fresh surfaces. Powdered samples were then pressure-mounted onto conducting indium foil. XPS analysis was performed using a Thermo-VG Scientific ESCALAB 250 X-ray photoelectron spectrometer, using Al K α radiation as the excitation source running at 15 kV and operating in CAE mode with 30 eV pass energy. To calibrate possible deviations caused by electric charge of the samples, the C 1s level binding energy at 284.6 eV was taken as internal standard. The repeatability of peak position of XPS measurement can be achieved within ± 0.1 eV. The software XPSPEAK was used in the spectra curve resolution and data treatment. The Gaussian-Lorentzian mixing ratio was typically 30% Lorentzian and 70% Gaussian functions, FWHM was fixed at 1.7 eV and the N peaks were defined but not fixed [9,12]. Three peaks in the XPS spectra for nitrogen forms were initially considered for our coal samples, corresponding to N-5, N-6 and N-Q.

3. Results and discussions

3.1. Changes in coal quality

The results of coal quality and elemental composition are shown in Table 1. ZJ-1 from the transect approaching a dike is similar to ZJ-UA,

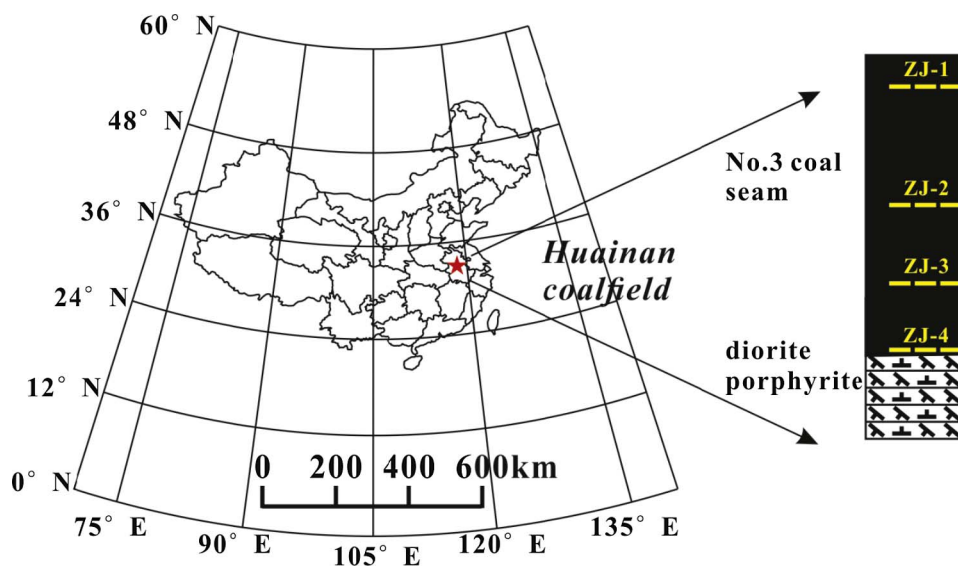


Fig. 2. Geological profile of the No. 3 coal seam in the Zhuji mine, the Huainan coalfield showing the relative locations of the magmatic intrusion and coal samples.

the unaltered coal, in coal properties, indicating that ZJ-1 may not be thermally altered by the magmatic intrusion. The trends in coal quality parameters (M_{ad} , V_{daf} and A_{daf}) and elemental composition (C_{daf} , O_{daf} , N_{daf} and $S_{t,ad}$) for the four samples collected along the transect are illustrated in Fig. 3. In most cases reported in the literature, magmatic intrusions may result in significant increases in A_{ad} and C_{daf} contents, accompanied by decreases in M_{ad} , V_{daf} , O_{daf} , N_{daf} and $S_{t,ad}$ contents [17,18,20,23,29]. In the current work, the A_{ad} and C_{daf} contents show a continuous increase toward the intrusion. Conversely, the M_{ad} , V_{daf} , O_{daf} , N_{daf} and $S_{t,ad}$ contents exhibit a obvious decrease. The N/C ratios show a decreasing trend toward the intrusion (Table 1). Meyers and Simoneit [31] proposed that the reduced N/C ratios in coals with proximity to the intrusion indicate that extensive destruction of organic matter and preferential loss of organic nitrogen. However, it is noted that the N_{daf} content and N/C ratio in ZJ-2 are higher than these in other coals. Zheng et al. [30] found that organic nitrogen content in the coals influenced by magmatic intrusions was higher than that in unaltered coals. Similarly, the maximum N/C ratios in the coals at some distance from magmatic intrusions have also been observed by Meyers and Simoneit [31] and Schimmelmenn et al. [32]. Schimmelmenn et al. [32] suggested that the maxima in N_{daf} content and N/C ratio in the coal at a farther distance indicate that reactive nitrogenous compounds had been liberated at higher temperature closer to the intrusion, migrated along the heated coal seam, and recombined with organic matter in a zone of intermediate temperature.

3.2. Changes in nitrogen forms

Fig. 4 shows the N 1s XPS spectra of samples from this study and the results of curve resolution into different components. The distribution of organic nitrogen forms in coals and elemental concentrations

calculated from XPS spectra are listed in Table 2. XPS is a surface-sensitive spectroscopy technique. It is worth mentioning that the total nitrogen content from XPS analysis is in general agreement with elemental analysis results for our coals (Table 3), indicating that the surface composition of nitrogen in our samples is possibly comparable to that of the bulk [5,10,33–35].

The N 1s spectra of ZJ-1 is similar to ZJ-UA, the unaltered coal (Fig. 4), and is dominated by the N-5 peak whose percentage is approximately one half of the entire coal (Fig. 5). Similar findings were also observed in previous studies for other coals [36,37]. Boudou et al. [4] suggested that the N-5 peak is dominant and hardly varies in coals with C_{daf} below ~90 wt%. The N-5 peak corresponds to pyrrolic and pyridine-N-oxide nitrogen. Generally, pyrrolic nitrogen results primarily from conversion of amides in peats due to thermal stress [5]. In addition, ZJ-1 has a lower intensity of the N-6 peak and a greater intensity of the N-Q peak. The similar distribution of the N-6 and N-Q peaks also occurs in ZJ-UA unaltered coal.

The intensity of the N-5 peak is also the highest in ZJ-2, which is almost equivalent to ZJ-1 (Fig. 5). In contrast to the distribution of ZJ-1, the N-Q peak has a significantly lower intensity than the N-6 peak (Fig. 5). It is interesting to remark that the sum of N-6 and N-Q has remained nearly constant between ZJ-1 and ZJ-2. It is implied that the N-Q peak observed in ZJ-1 and ZJ-2 represents “protonated” quaternary nitrogen, which is a structure of pyridinic nitrogen protonated by oxygen groups. The loss of oxygen groups can result in a decrease in the N-Q peak accompanied by an increase in the N-6 peak, which is in agreement with a considerable decrease of oxygen content from ZJ-1 to ZJ-2. Kelemen et al. [10] also observed the conversion of N-Q to N-6 upon pyrolysis in Argonne Premium coals, and the sum of N-6 and N-Q was preserved during pyrolysis. These behaviors were ascribed to mild heat-treatment pyrolysis conditions (673 K) proposed by Kelemen et al.

Table 1

Coal quality and elemental composition (wt.%) of the studied coals.

Sample	Coal quality ^a			Elemental composition ^a				N/C ratio	O/C ratio	Distance from dike (m)
	M_{ad}	A_{ad}	V_{daf}	C_{daf}	N_{daf}	O_{daf}	$S_{t,ad}$			
ZJ-UA	1.05	13.66	39.98	83.12	1.49	6.50	0.95	0.018	0.08	–
ZJ-1	1.21	13.19	37.37	85.41	1.44	6.28	0.97	0.017	0.07	2.3
ZJ-2	0.98	19.23	25.63	89.68	1.75	2.58	0.79	0.020	0.03	1.1
ZJ-3	0.91	23.71	15.42	91.32	0.98	1.93	0.64	0.011	0.02	0.5
ZJ-4	0.70	26.32	11.41	94.67	0.62	1.05	0.63	0.007	0.01	0.02

^a ± ca. 5%; daf: dry-ash-free basis; ad: air-dry basis; M_{ad} : moisture; A_{ad} : ash yield; V_{daf} : volatile matter; C_{daf} : carbon; N_{daf} : nitrogen; O_{daf} : oxygen; $S_{t,ad}$: total sulfur.

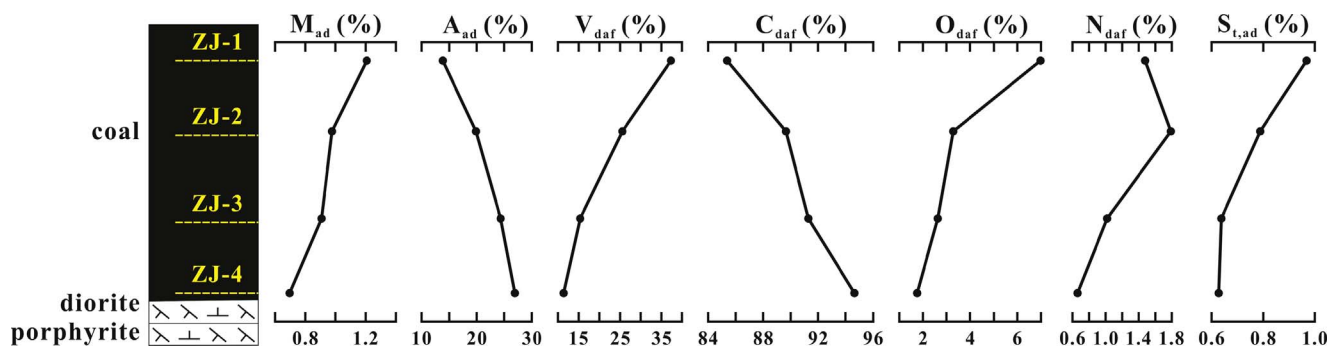


Fig. 3. Variations of moisture (M_{ad}), ash yield (A_{ad}), volatile matter (V_{daf}), carbon content (C_{daf}), oxygen content (O_{daf}), nitrogen content (N_{daf}) and total sulfur content ($S_{t,ad}$) in the four coals from the transect.

[10]. Therefore, we inferred that there is a relatively moderate impact on ZJ-2 from the magmatic intrusion. The total amounts of nitrogen from the surface and the bulk are slightly enriched in ZJ-2, which suggests that the intrusion may hardly induce the elimination of nitrogen according to the above discussion (Section 3.1). It is suggested that the elimination of nitrogen probably depends on the nitrogen structure in coal [38]. Some nitrogen cannot be eliminated easily, but can be transformed to other thermally stable structures. Similar results were observed in the case of chars prepared under mild and moderate thermal treatment (773 K), where the transformation of pyrrolic to pyridinic forms was initiated and the release of NO_x and N_2O was delayed [38].

In ZJ-3, with a C_{daf} value of 91.32 wt%, the N-5 peak has disappeared completely and only the N-6 and N-Q peaks are observed with the N-Q peak as the major peak (Fig. 5). Boudou et al. [4] reported that in coals with C_{daf} above 90 wt%, the relative abundance of the N-5 and N-6 peaks strongly decrease, and the N-Q peak has a strong increase and becomes the predominant form. According to the pyrolysis experiments

Table 2
Results from XPS N 1s spectra of the studied coals.

Sample	Nitrogen forms (% of total nitrogen)			C(1s)	N(1s)	O(1s)
	N-5	N-6	N-Q			
ZJ-UA	53.5	13.92	32.58	60.01	1.58	38.41
ZJ-1	49.15	15.31	35.54	60.59	1.54	37.87
ZJ-2	53.82	26.45	19.73	72.16	1.95	25.89
ZJ-3	0.00	22.01	77.99	79.55	1.15	19.3
ZJ-4	0.00	0.00	100.00	85.48	0.95	13.57

of Pels et al. [8], the N-5 peak is stable until 873 K; above that temperature the N-5 peak disappears gradually and is converted to the N-6 and N-Q peaks; at 1173 K the N-5 peak has disappeared entirely. Based on those conditions, we suggest that the thermal energy caused by the magmatic intrusion reaches enough high temperature to destroy all nitrogen forms of the N-5 peak in ZJ-3. Strong N-Q peak is observed in

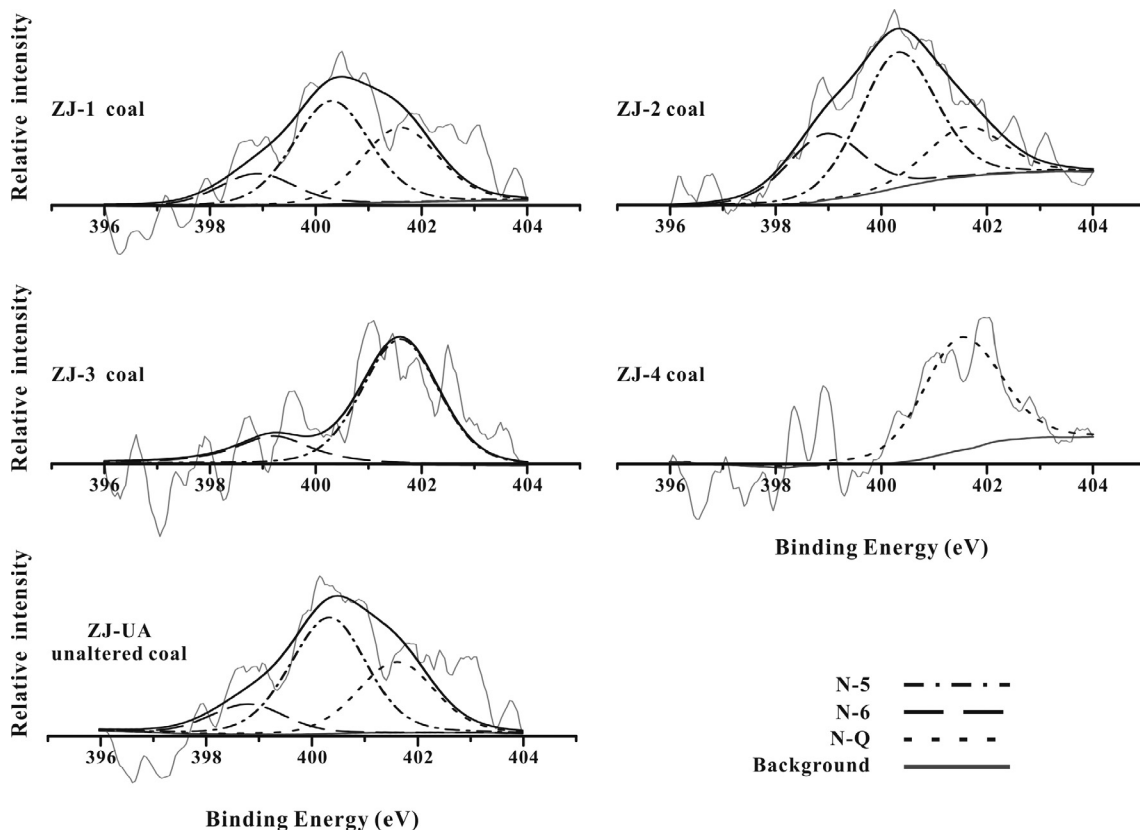


Fig. 4. XPS N 1s spectra of the studied coals and curve resolution into different components.

Table 3
Comparison between XPS and elemental analysis results for total nitrogen.

Sample	Total Nitrogen (per 100 Carbons)		(XPS-EA)/XPS*100%
	Elemental analysis (EA)	XPS	
ZJ-UA	1.79	2.62	33%
ZJ-1	1.68	2.54	33%
ZJ-2	1.95	2.70	27%
ZJ-3	1.07	1.45	26%
ZJ-4	0.65	1.11	40%

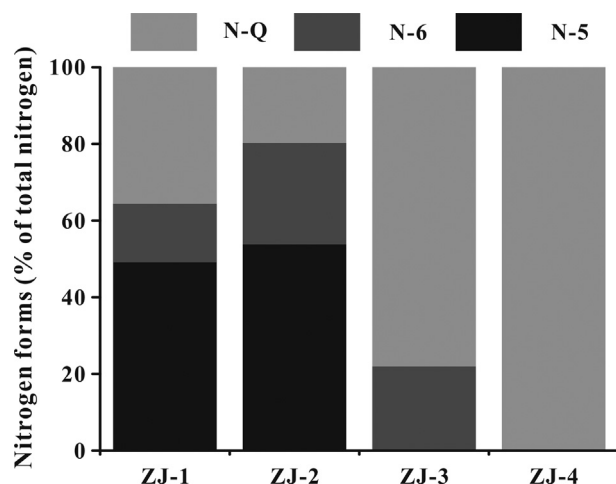


Fig. 5. Relative amounts of nitrogen forms in the studied coals.

the spectra of ZJ-3, as is seen in the spectra of severely heat-treated coal chars prepared at 1173 K [8]. The remarkable amounts of N-Q may not be assigned to “protonated” quaternary nitrogen observed in ZJ-1 and ZJ-2. Kelemen et al. [10] demonstrated that “protonated” quaternary nitrogen decreased with the loss of oxygen groups and showed a positive correlation of the occurrence of “protonated” quaternary nitrogen with oxygen content in coals. The quite low oxygen content and O/C ratios in ZJ-3 may suggest the appreciable depletion of oxygen groups. Hence, the presence of large amount of “protonated” quaternary nitrogen is hardly expected in ZJ-3. Meanwhile, Boudou et al. [4] indicated that in coals with C_{daf} above 90 wt%, the N-Q peak represents a structure of N-C₃. ZJ-3 has a C_{daf} value of 91.32 wt%. Therefore, a more valid explanation for the high intensity of the N-Q peak is that nitrogen atoms are incorporated into a graphene layer as “graphitic” quaternary nitrogen, at the expense of edge-located nitrogen, such as pyrrolic and pyridinic nitrogen. In addition, the decrease in the N-6 peak relative to ZJ-2, could be ascribed to pyridinic nitrogen transformation to “graphitic” quaternary nitrogen [4,8,36]. In this case, we can conclude that nitrogen in ZJ-3 has already fully located at more stable six-membered rings, as part of larger graphitic structures, which is attributed to rapid heating caused by the magmatic intrusion.

The N 1s spectra of ZJ-4 shows only a single N-Q peak (Fig. 5), and this coal has the lowest levels of nitrogen relative to other studied coals. Compared with ZJ-3, pyridinic nitrogen has disappeared entirely. ZJ-4, closest to the magmatic intrusion, underwent intense and instantaneous heating. Almost all nitrogen atoms in ZJ-4 incorporated into the graphene layers, replaced carbon atoms and formed “graphitic” quaternary nitrogen as organic nitrogen N-C₃ atoms.

4. Conclusions

Variations in the coals approaching the magmatic intrusion in the Huainan coalfield were investigated with respect to changes in coal quality parameters, elemental composition and organic nitrogen forms.

Data show a continuous increase in ash yield and carbon content, accompanied with a decrease in moisture, volatile matter, oxygen, nitrogen and total sulfur due to heating associated with the magmatic intrusion.

The XPS analysis of the N 1s spectra shows that the N-5 peak decreases in the coal towards the magmatic intrusion, but the N-6 and N-Q peaks reveal different trends. The N-5 peak is the highest and stable in unaltered and moderately altered coals, whereas all organic nitrogen forms of the N-5 peak decompose completely in the coals under the stronger influence of the magmatic intrusion. The N-Q peak in unaltered and moderately altered coals mainly represents “protonated” quaternary nitrogen. However, in the coals (ZJ-3 and ZJ-4) closer to the magmatic intrusion, the N-Q peak is assigned to “graphitic” quaternary nitrogen, as a nitrogen atom incorporated into the condensed aromatic system, and becomes dominant. The N-6 peak in ZJ-2 considerably increases due to the loss of oxygen groups and deprotonation of “protonated” quaternary nitrogen, but pyridinic nitrogen disappears entirely at severe heating conditions caused by the magmatic intrusion. In conclusion, with the decrease in distance to the magmatic intrusion, less stable nitrogen forms are transformed to more stable forms in coal.

Acknowledgments

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