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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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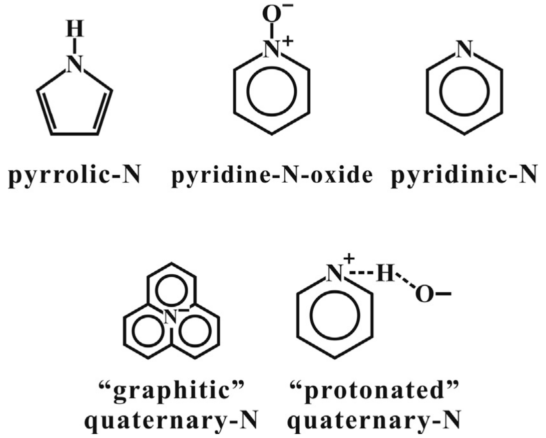

**Fig. 1.** Structures of major nitrogen forms presenting in coal. Modified from the literature reported by (Boudou et al. [4]; Pels et al. [8]).

coals with $C_{daf}$ above ~90 wt%, the N-Q peak represents a structure of $N\text{-}C_3$ 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 $N\text{-}C_3$ 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 $km^2$. 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 $km^2$.

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 μm 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 Kα 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,