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RESEARCH ARTICLE

Geochemical characteristics of *n*-alkanes and isoprenoids in coal seams from Zhuji coal mine, Huainan coalfield, China, and their relationship with coal-forming environment

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Abstract

Ten coal seams in Upper Shihezi Formation, Lower Shihezi Formation, and Shanxi Formation from the Zhuji mine, Huainan coalfield, China, were analyzed for *n*-alkanes and isoprenoids (pristine and phytane) using gas chromatography-mass spectrometry (GC-MS), with an aim of reconstructing the coal-forming plants and depositional environments along with organic carbon isotope analyses. The total *n*-alkane concentrations ranged from 34.1 to 481 mg/kg. Values of organic carbon isotope ($\delta^{13}C_{org}$) ranged from − 24.6 to − 23.7‰. The calorific value ($Q_{b,d}$), maximum vitrinite reflectance (Ro_{max}), proximate, and ultimate analysis were also determined but showed no correlation with *n*-alkane concentrations. Carbon Preference Index (CPI) values ranged from 0.945 to 1.30, suggesting no obvious odd/even predominance of *n*-alkane. The predominance of C_{11} and C_{17} *n*-alkanes implied that the coal may be deposited in the fresh and mildly brackish environment. According to the contrary changing trend of pristine/phytane (Pr/Ph) ratio and boron concentrations, Pr/Ph can be used as an indicator to reconstruct the marine transgression-regression in sedimentary environment of coal formation. The influence of marine transgression may lead to the enrichment of pyrite sulfur in the coal seam 4-2. C3 plants (− 32 to − 21‰) and marine algae (− 23 to − 16‰) were probably the main coal-forming plants in the studied coal seams. No correlation of the *n*-alkane concentration and redox condition of the depositional environment with organic carbon isotope composition were found.

Keywords *n*-Alkane · Coals · Organic carbon isotope · Depositional environments · Zhuji coal mine

Introduction

n-Alkane, widespread in coal, is a class of organic compounds composed of straight-chain saturated hydrocarbons (Wang et al. 47; Sojinu et al. 41). Exploring the geochemical characteristic of *n*-alkane has significant implication in recognizing their forming paths and mechanisms in coal, and consequently, tracing their geochemical behaviors in supergene environment.

n-Alkane has the ability to record the special information of original matrix due to its high resistance to microbial degradation (Fernandes and Sicre 14; Meyers 31). It has been regarded as a tracer to determine the potential sources and maturity of organic matter (Sojinu et al. 41; Choi et al. 9) and reconstruct paleoclimatic and paleodepositional conditions (Fu and Sheng 16; Bai et al. 3; Li et al. 25). Previous researches (Fu and Sheng 16; Fu et al. 17) have shown that *n*-alkane can be successfully applied to distinguish the depositional paleoenvironment (including fresh, mildly brackish, and marine environments).

Pristane and phytane are derived from the phytol side chain of chlorophyll (Naeher and Grice 32). Phytol is converted to pristane under oxidation condition, while phytane is formed from phytol via reductive pathway (Rontani et al. 38; Rahman* et al. 36). Hence, the ratio of pristane to phytane (Pr/Ph) can be applied successfully to reconstruct the paleo-

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redox depositional conditions in coal (Escobar et al. 13; Wang et al. 48).

However, most previous researches reconstructed the coal-forming plants and environment using traditional indicators, such as the Sr/Ba ratio and boron and organic carbon isotope. The Sr/Ba ratio and boron are good paleosalinity indicators of coal-forming environment (Li et al. 24; Sun et al. 42). Organic carbon isotope in coal provides reliable evidences for the reconstruction of paleoenvironmental changes and paleovegetation (Bechtel et al. 4; Schwarzbauer et al. 39). It is considered to be related to climatic evolution (e.g., temperature, dry-humidity) and atmospheric CO_2 levels (Hayes et al. 20; Lücke et al. 28; Bechtel et al. 4). Organic carbon isotope in coal can be used to distinguish C_3 and C_4 plants, which have the different carbon isotope composition due to their different photosynthetic pathways (Deines 11; Ehleringer and Pearcy 12; Schwarzbauer et al. 39).

Zhuji coal mine is located in northwestern of Huainan Coalfield, Anhui province (Sun et al. 43; Sun et al. 44). It is an active and important coal-producing base in China. Boron element contents have been detected in coal-bearing strata of Upper Shihezi, Lower Shihezi, and Shanxi Formation in Zhuji mine in our previous study (Sun et al. 42). Hence, the Permian coal deposit in Zhuji coal mine is chosen to reconstruct the coal-forming plants and depositional environment from the perspective of organic tracers (*n*-alkane, phytane, and pristine) combined with organic carbon isotope analyses. Moreover, statistical correlations between these indicators (including boron) were conducted to further explore the relevance and reliability of organic tracers.

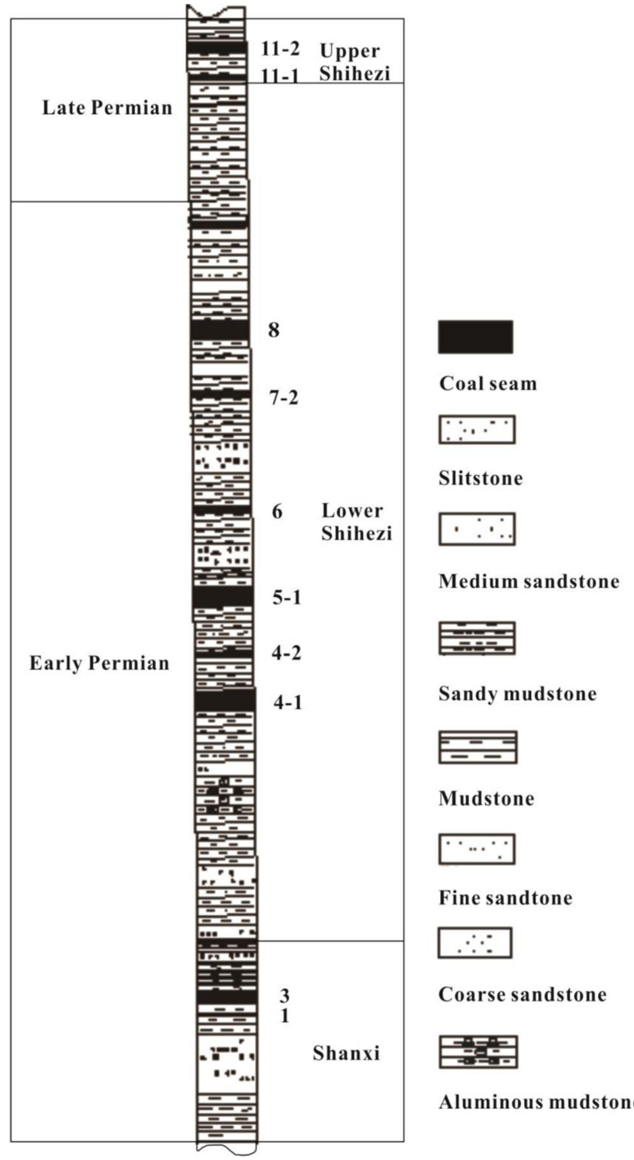

Fig. 1 Lithologic characteristics of the sedimentary strata and selected coal seams from stratigraphic column in Zhuji exploration area

Material and methods

Study area and sample collection

The Zhuji mine, situated in the northwestern of Huainan Coalfield, covers an area of 45.13 km^2. The whole coalfield is covered by Tertiary and Quaternary unconsolidated strata. More details of local geology and coal-bearing strata have been described in our previous study (Sun et al. 42). Ten coal seams from Permian strata were selected for use in this study, including Upper Shihezi Formation (i.e., 11-2 and 11-1), Lower Shihezi Formation (i.e., 8, 7-2, 6, 5-2, 4-2, and 4-1), and Shanxi Formation (i.e., 3 and 1). The stratigraphic and lithologic characteristics of the coal-bearing strata are illustrated in Fig. 1.

Sample extraction and separation

Coal samples were dried and ground to pass through a 100-mesh sieve. Powdered coal aliquot samples (5 g dry wt.) were extracted with dichloromethane (250 ml) for 48 h by following Soxhlet extraction method. Activated copper pieces were added to the extracts for desulfurization. Each extract was concentrated with a vacuum rotary evaporator and then redissolved in hexane. They were purified by a glass column filled with alumina (6 cm), silica gel (12 cm), and anhydrous Na_2SO_4 (2 cm) from bottom to top. The *n*-alkane fraction (including isoprenoids) was eluted with 15 ml of hexane.

Eluted solutions were concentrated to 1 ml using a vacuum rotary evaporator. All the reagents were chromatographically grade.

Gas chromatography-mass spectrometry

Identification and quantification of *n*-alkanes and isoprenoids were carried out using an Agilent 6890 gas chromatograph (GC) in conjunction with an Agilent 5972 mass selective detector (MSD). The GC was equipped with a DB-5 column (30 m × 0.25 mm × 0.25 μm). High-purity helium was used as carrier gas at a flow rate of 1.5 ml/min. The oven program was kept at 60 °C for 3 min and heated to 200 °C at 8 °C/min, then heated to 300 °C at 3 °C/min (held 10 min). The quantification of *n*-alkanes and isoprenoids was conducted by external standard method. The concentrations were calculated by comparing the peak areas between samples and standards.

Proximate and ultimate analysis

The proximate analysis, including moisture (M_{ad}), volatile matter (V_{daf}), and ash yield (A_d), were determined according to Chinese Standard GB/T-212-2008, and calorific value ($Q_{b,d}$) was determined according to Chinese Standard GB/T-213-2008 (Chen et al. 6; Tang et al. 45). The ultimate analysis was conducted by elementar vario EL.

Stable organic carbon isotopes ($\delta^{13}C_{org}$)

Coal samples were treated with 2 M HCl for 24 h to exclude the inorganic carbon. Then, they were washed with (double-distilled) DDI water until neutral and dried at 40 °C. Thirty milligrams of coal sample was loaded into the evacuated sealed quartz tube in the presence of Ag foil, cupric oxide, and Cu foil, then combusted at 850 °C for 4 h. The purified carbon oxide was then analyzed for carbon isotopes using a MAT-251 gas mass spectrometer with dual inlet system. Isotopic ratios in samples are expressed as per mil deviations relative to V-PDB (Vienna Peedee Belemnite standard), with an uncertainty below 0.4: $\delta^{13}C$ (‰) = (Rsa/Rst-1) × 1000. Rsa and Rst is the $^{13}C/^{12}C$ ratio for sample and standard, respectively. The analyses of all the samples were finished by Institute of Earth Environment, State Key Laboratory of Loess and Quaternary Geology, The Chinese Academy of Sciences, Xi'an.

Results and discussion

n-Alkane distribution in coal seams

n-Alkane in the range C_9 to C_{31} was detected in this study. The distributions of *n*-alkane in all the studied coal seams (Upper Shihezi Formation, Lower Shihezi Formation, and Shanxi Formation) are depicted in Fig. 2. Several *n*-alkanes (C_9, C_{10}, and C_{25}-C_{31}) were only detected in a few coal seams. Furthermore, as shown in Fig. 2, C_{17} was the main species in coal seams 11-2 and 8, while C_{11} was apparent in other coal seams (11-1, 7-2, 6, 5-1, 4-2, 3, and 1). The total *n*-alkane concentrations of all the coal seams are listed in Table 1. The lowest concentration (34.1 mg/kg, dry wt.) was identified in coal seam 7-2, and the highest concentration (481 mg/kg, dry wt.) was detected in coal seam 4-2.

Although *n*-alkane has strong structural stability, they may undergo physical degradation or biodegradation during the long-term coal formation process. The degree of *n*-alkane degradation can be expressed by the ratio of pristine/C_{17} (Pr/C_{17}) and phytane/C_{18} (Ph/C_{18}) (Peters and Moldowan 34; Wang et al. 46). The Pr/C_{17} and Ph/C_{18} values were relatively low in the present study (Table 1), with averages of 0.55 and 0.27, respectively, indicating a minor degradation of *n*-alkane.

In this study, Carbon Preference Index (CPI) values ranged from 0.945 to 1.30, with an average of 1.07, indicating no obvious odd/even predominance of *n*-alkane. In general, the abundance of even *n*-alkanes gradually closes to that of the odd *n*-alkanes in the process of coal formation. The longer the time of coal formation, the closer the CPI value is to 1. Similar CPI values to this study have also been reported in other studies (Norgate et al. 33; Adedosu et al. 1). The CPI value in the early Cretaceous coal (middle Benue trough, Nigerian) was close to 1, without any odd over even predominance (Adedosu et al. 1). In contrast, *n*-alkanes in the middle Eocene bituminous coals, which were deposited relatively late, showed an odd over even predominance (Norgate et al. 33).

CPI is widely used as a proxy to identify the potential sources of *n*-alkane (Marzi et al. 30; Lyu et al. 29). CPI for *n*-alkane stemmed from terrestrial higher plants is greater than 5 (Wang et al. 49). Moreover, *n*-alkanes originated from higher plant leaf wax usually present significant odd over even predominance (Ficken et al. 15; Liu and Huang 26). Therefore, the low CPI values in the studied coal cannot prove the terrestrial higher plant input during the process of coal formation.

As shown in Fig. 2, low-molecular-weight (LMW; $\leq C_{17}$) *n*-alkanes were dominated in the three formations, which were probably derived from algae and/or bacteria (Ficken et al. 15). The LMW *n*-alkanes were most abundant in Shanxi

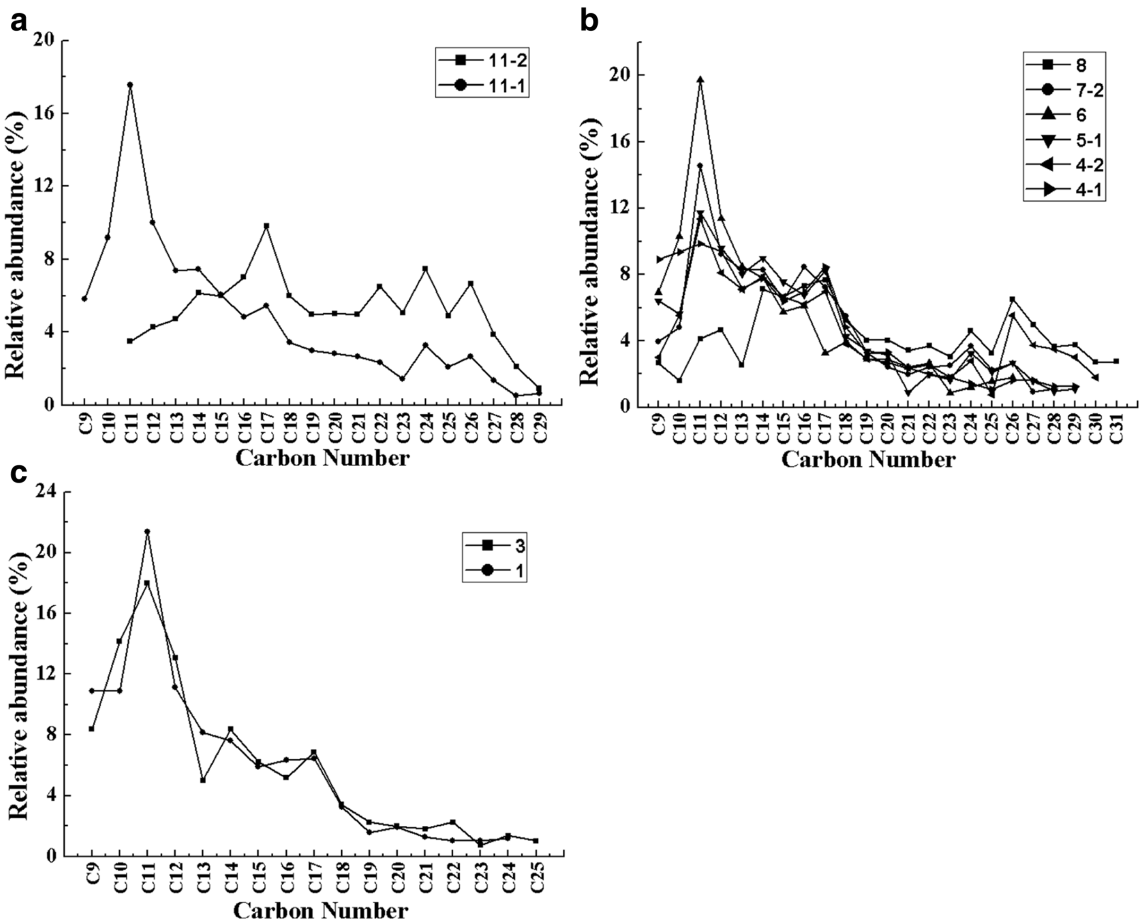

Fig. 2 Distributions of *n*-alkane in different coal seams. **a** Upper Shihezi formation. **b** Lower Shihezi formation. **c** Shanxi formation from Zhuji mine, Huainan coalfield, China

Formation, accounting for 88.7 and 85.2% of total *n*-alkanes in the coal seam 1 and 3, respectively. Moreover, Shanxi Formation strata were deposited on a lower-deltaic plain (Shao et al. 40). Hence, it can be inferred that coals in the Shanxi Formation may suffer from seawater intrusion.

Table 1 *n*-Alkane concentration (mg/kg dry wt.) and related proxies in coal seams from Zhuji coal mine, Huainan coalfield, China

Coal seams	T-ALK	MH	CPI	Pr/Ph	Pr/C_{17}	Ph/C_{18}
11-2	164	C_{17}	0.945	4.32	0.689	0.262
11-1	153	C_{11}	1.15	5.58	1.19	0.339
8	78.7	C_{17}	0.947	2.67	0.568	0.315
7-2	34.1	C_{11}	1.06	3.48	0.614	0.230
6	66.6	C_{11}	1.09	2.93	0.816	0.230
5-1	188	C_{11}	1.12	3.84	0.550	0.277
4-2	481	C_{11}	0.987	3.20	0.283	0.160
4-1	46.2	C_{11}	1.09	1.25	0.201	0.281
3	63.6	C_{11}	1.01	2.48	0.365	0.301
1	83.8	C_{11}	1.30	1.43	0.224	0.304

T-ALK total *n*-alkane concentration, *MH* major hydrocarbons, *CPI* Carbon Preference Index, *Pr/Ph* pristane/phytane, Pr/C_{17} pristane/n-heptadecane, Ph/C_{18} phytane/n-octadecane

Proximate and ultimate analysis

The results of proximate and ultimate analysis are listed in Table 2. The moisture (M_{ad}), volatile matter (V_{daf}), ash yield (A_d), and calorific value ($Q_{b,d}$) are basic parameters to evaluate the economic value of coal (Table 2). The M_{ad} values varied from 1.14 (coal seam 4-2) to 1.65% (coal seam 11-1) on an air-dried basis. The V_{daf} values ranged from 13.9 (coal seam 4-2) to 37.6% (coal seam 11-1) on a dried-ash-free basis. The A_d values ranged from 21.4 (coal seam 4-2) to 38.6% (coal seam 1) on a dry basis. The $Q_{b,d}$ values ranged from 20.5 (coal seam 1) to 27.9 MJ/kg (coal seam 4-2) on a dry basis. The minimum values of M_{ad}, V_{daf}, and A_d and maximum value of $Q_{b,d}$ were observed in coal seam 4-2. As mentioned before, coal seam 4-2 also had the highest *n*-alkane concentration. The spearman correlation analyses between *n*-alkane concentrations and these coal quality parameters were performed, indicating no statistical correlation.

Table 2 The proximate and ultimate analysis of all selected coal seams from Zhuji coal mine

	11-2	11-1	8	7-2	6	5-1	4-2	4-1	3	1
Ultimate analysis (wt.%)										
C	53.3	45.3	69.5	53.7	68.3	60.2	70.1	72.1	77.3	77.3
H	3.55	3.35	4.67	3.76	4.59	4.12	3.43	4.40	4.82	4.62
O	12.4	9.95	9.99	9.89	8.24	10.6	7.64	9.86	9.28	7.96
N	0.928	0.848	1.32	3.22	1.16	0.893	1.38	1.27	1.50	1.39
S	0.415	0.0790	0.649	0.343	0.530	0.874	0.937	0.635	0.313	0.624
H/C	0.0666	0.0740	0.0672	0.0700	0.0672	0.0684	0.0489	0.0610	0.0624	0.0598
O/C	0.233	0.220	0.144	0.184	0.121	0.176	0.109	0.137	0.120	0.103
Proximate analysis (wt.%)										
M_{ad}	1.38	1.65	1.46	1.47	1.30	1.39	1.14	1.44	1.64	1.58
A_d	26.4	28.5	25.8	28.5	26.4	24.7	21.4	25.9	29.4	38.6
V_{daf}	27.4	37.6	30.5	35.4	29.6	33.8	13.9	34.8	36.2	20.3
Ro_{max} (wt.%)	0.796	0.944	0.900	0.904	0.902	0.899	0.955	0.862	0.800	0.868
$Q_{b,d}$ (MJ/kg)	26.4	25.5	26.8	25.5	26.3	26.9	27.9	26.6	25.9	20.5

M_{ad} moisture, on an air-dried basis, A_d ash yield, on a dry basis, V_{daf} volatile matter, on a dried-ash-free basis, $Q_{b,d}$ calorific value, on a dry basis

The H/C and O/C ratios are important indicators of coal rank (Bae et al. 2). Their values decrease with the increase of coal rank (Yu et al. 51; Liu et al. 27). H/C values fluctuated within a narrow range in this study, from 0.0489 to 0.0740, indicating the small differences of coal rank between these coal seams. O/C ratio values varied from 0.103 to 0.233, with a mean value of 0.155, suggesting the predominance of aromatic hydrocarbon in coal (Zhao et al. 52; Bae et al. 2). The maximum vitrinite reflectance (Ro_{max}) can also reflect the coal rank and maturity (Robbins et al. 37), ranging from 0.796 to 0.955% in this study. According to Petersen (Petersen 35), the start of the effective oil window had vitrinite reflectance values that ranged from 0.85 to 1.05%, indicating good oil generation potential of the studied coal.

The total sulfur content varied from 0.0790 (coal seam 11-1) to 0.937% (coal seam 4-2), with an average value of 0.540%. Pyritic sulfur ($S_{p,d}$) is one of the main forms of sulfur in coals. The relative high proportion of $S_{p,d}$ occurred in coal seams 4-2 and 5-1, accounting for 48.2 and 46.5% of the total sulfur content, respectively. The $S_{p,d}$ percentage of the coal was most abundant in the coal seams 4-2, which can be calculated as 0.453%. Previous studies have shown that sulfate-reducing bacteria were involved in the formation of pyrite (Berner and Raiswell 5). The growth of algae could cause the rising of pH in the environment, and the alkalescent condition is conducive to the growth and reproduction of bacteria (Kostova et al. 23; Chou 10). Therefore, it was inferred that coal seam 4-2 may be influenced by marine transgression and the large influx of algae promoted the formation and enrichment of pyrite.

Coal-forming depositional environment

Previous researches (Fu and Sheng 16; Fu et al. 17) have pointed out that geochemical characteristics of *n*-alkane can be successfully applied to reconstruct the depositional paleoenvironment. Firstly, fresh water environment: it is characterized by a dominance of long-chain *n*-alkanes (such as C_{27} and C_{29}) with significant odd/even predominance, representing the input of terrestrial higher plants. Secondly, fresh and mildly brackish environment: it is dominated by short chain *n*-alkanes (such as C_{17}), representing the abundant input of algae. Thirdly, brackish or marine environment: it is dominated by *n*-alkanes in the range of C_{18} to C_{28} (peaking at C_{22}, C_{24}, and C_{28}) with obvious even over odd predominance. As discussed in the "*n*-Alkane distribution in coal seams" section, the most abundant *n*-alkane in the studied coal seams were C_{11} and C_{17}, corresponding to the second depositional environment. It can be inferred that coals from the Upper Shihezi Formation, Lower Shihezi Formation, and Shanxi Formation were deposited in the fresh and mildly brackish environment.

The ratio of pristane to phytane (Pr/Ph) is a sensitive indicator of redox conditions in the depositional environment (Naeher and Grice 32). The variation of Pr/Ph ratio in the studied coal seams is illustrated in Fig. 3a. All values of Pr/Ph ratio were greater than one, indicating suboxic conditions, even oxidizing conditions (Groune et al. 18; Hakimi et al. 19). Furthermore, the observed trend of Pr/Ph ratio is contrary to that of the boron contents in the same coal seams (Fig. 3b) reported in our previous study (Sun et al. 42). The spearman correlation analysis between Pr/Ph ratio and boron content was performed. A statistically significant negative correlation was observed (Spearman correlation coefficient,

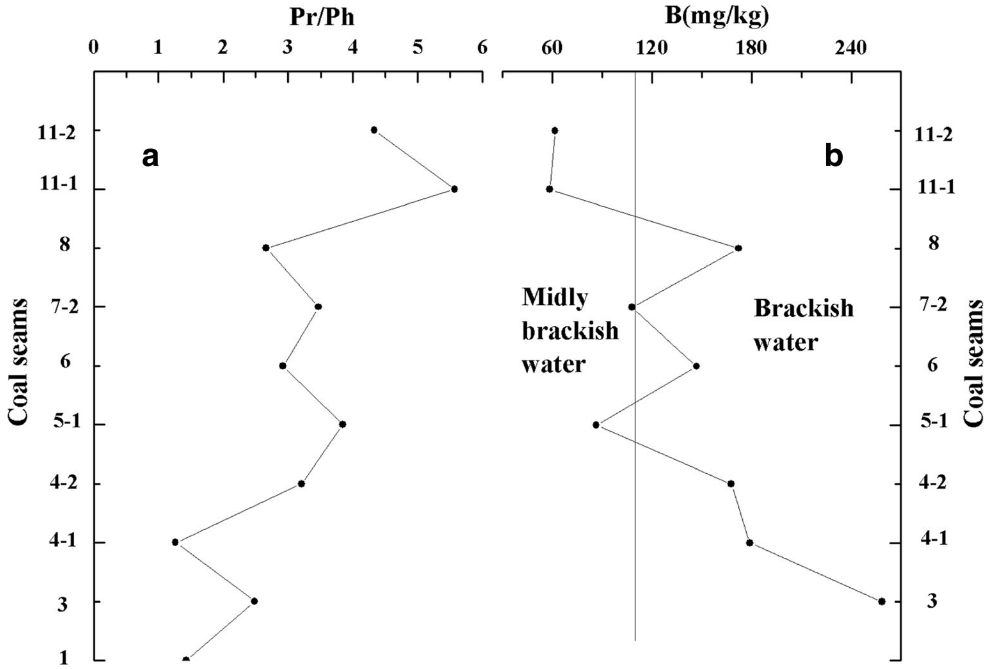

Fig. 3 **a** The variation of Pr/Ph ratio in the studied coal seams. **b** Vertical variation of B contents in 9 coal seams (Sun et al., 2010); the dot line is at 110 mg/kg

− 0.967; $P < 0.01$). Boron is an important indicator to reconstruct the paleosalinity in sedimentary environment of coal formation (Sun et al. 42; Wang et al. 50). Thus, it was inferred that the Pr/Ph ratio can be utilized to indentify marine transgression-regression in coal-forming environment. The low Pr/Ph ratio representing reduction condition may be subject to marine transgression, whereas the high Pr/Ph ratio indicating oxidation condition may be related to marine regression.

Organic carbon isotope composition of coal seam

Organic carbon isotope ($\delta^{13}C_{org}$) has been applied for source identification of organic matter and reconstruction of coal-forming environments (Cheung et al. 7). Plant photosynthesis is an important factor affecting organic carbon isotope fractionation. According to the photosynthetic pathway, terrestrial plants are divided into C_3 and C_4 plants (Khan et al. 22). $\delta^{13}C$ values for C_3 plants vary from − 32 to −21‰, while the values for C_4 plants range from − 17 to − 9‰ (Deines 11; Chmura and Aharon 8; Khan et al. 22).

Figure 4 illustrated the fluctuation variation of $\delta^{13}C_{org}$ values in the selected coal seams, ranging from − 24.6 to − 23.7‰, with a mean value of − 24.0‰. These values were well within the range of − 32 to − 21‰, indicating that C_3 plants were probably the main coal-forming plants in the studied coal seams. Moreover, marine algae have $\delta^{13}C$ values ranging from − 23 to − 16‰ and freshwater algae range in $\delta^{13}C$ from − 30 to − 26‰ (Hemminga and Mateo 21; Khan et al. 22), which probably indicate the contribution of marine algae.

Organic carbon isotope composition in coals is also related to regional climatic conditions (such as temperature) and atmospheric pCO_2 fluctuations (Lücke et al. 28; Bechtel et al. 4). The increasing trend of $\delta^{13}C_{org}$ values from coal seam 3 to coal seam 5-1 may correspond to the increase of temperature and atmospheric pCO_2. In contrast, the decrease of $\delta^{13}C_{org}$ values from coal seam 7-2 to coal seam 11-2 may

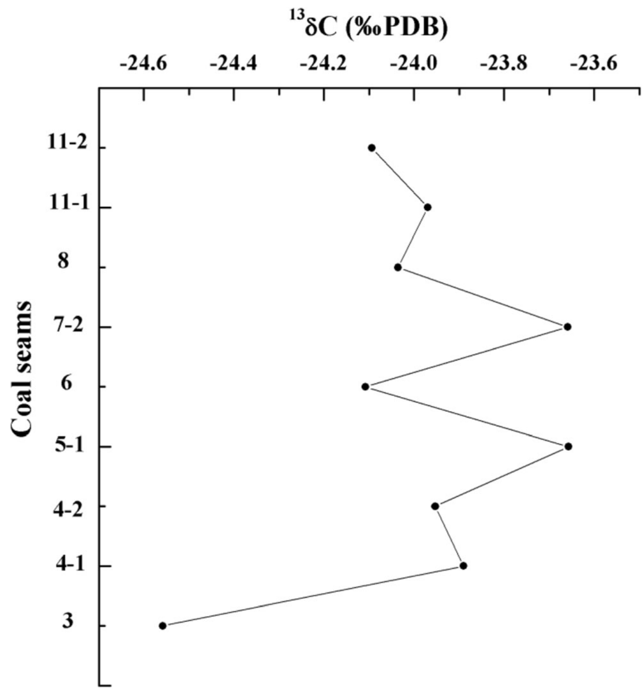

Fig. 4 Organic carbon isotope composition of coal seams from Zhuji mine, Huainan coalfield, China

correspond to the decrease of temperature and atmospheric pCO_2.

Furthermore, there was no statistical correlation between $\delta^{13}C_{org}$ values and *n*-alkane concentrations, Pr/Ph ratio values, indicating that redox condition of the depositional environment and *n*-alkane concentrations may be not correlated with carbon isotope composition in the studied coals.

Conclusion

The geochemical characteristics of *n*-alkanes and isoprenoids (pristine and phytane) in the ten coal seams have been investigated. *n*-Alkanes in the range C_9 to C_{31} were detected without odd/even predominance. The low values of Pr/C_{17} and Ph/C_{18} ratios indicated a minor degradation of *n*-alkane in coals. The most abundant *n*-alkanes (C_{11} and C_{17}) in the studied coal seams reflected the coal may be deposited in fresh and mildly brackish environment. Moreover, the influence of marine transgression may lead to the enrichment of pyrite sulfur in the coal seam 4-2. It was inferred that the Pr/Ph ratio can be used as an indicator to reconstruct the marine transgression-regression in sedimentary environment of coal formation. C_3 plants and marine algae were probably the main coal-forming plants. Furthermore, redox condition of the depositional environment and *n*-alkane concentrations were probably not correlated with carbon isotope composition in coal.

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