

Origin and genetic family of Huhehu oil in the Hailar Basin, northeast China

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Received: 25 January 2018 / Revised: 20 May 2018 / Accepted: 6 July 2018 / Published online: 17 July 2018
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Abstract The Huhehu Sag is one of the most important oil and gas depressions in the Hailar Basin. However, the origin of Huhehu oil is still controversial. Previous studies on source rocks have mainly focused on the Nantun Formation (K_1n); a few studies have investigated the Damoguaihe Formation (K_1d). Based on the Rock–Eval pyrolysis parameters, 172 drill cutting samples from the Huhehu Sag were analyzed to evaluate their geochemical characteristics. Based on the Rock–Eval data, the mudstones from the first member of the Damoguaihe Formation (K_1d_1) and the second member of the Nantun Formation (K_1n_2) have moderate to high hydrocarbon generation potential, while mudstones from the first member of the Nantun Formation (K_1n_1) have poor to good hydrocarbon generation potential. Additionally, both the K_1n_1 and K_1n_2 coal members have poor to fair hydrocarbon generation potential, but the K_1n_2 coal member has a better generative potential. Fifteen Huhehu oils were collected for molecular geochemical analyses to classify the oils into genetic families and to identify the source rock for each oil using chemometric methods. The Huhehu oils were classified into three groups with different maturity levels using hierarchical cluster analysis and principal component analysis. Group A oils

(high maturity) are characterized by relatively moderate ratios of Pr/Ph, Pr/ n - C_{17} , and Ph/ n - C_{18} , as well as an abundance of C_{29} steranes, mainly derived from the K_1n_2 and K_1n_1 mudstone members. In comparison, group B oils (moderate maturity) have relatively low Pr/Ph ratios, moderate Pr/ n - C_{17} and Ph/ n - C_{18} ratios, and low concentrations of C_{29} steranes. Group C oils (low maturity) show relatively high ratios of Pr/Ph, Pr/ n - C_{17} , and Ph/ n - C_{18} , as well as high concentrations of C_{29} steranes. Furthermore, group B oils derived from the K_1d_1 mudstone member and group C oils derived from the K_1n_2 coal member were also identified by principal component analysis score plots. Correlation studies suggest a major contribution from the K_1n mudstone Formation and the K_1d_1 mudstone member to the oils of the Huhehu Sag. So, the Nantun Formation and relatively shallow strata of the Damoguaihe Formation (e.g., the K_1d_1 member) represent important targets for future oil-reservoir exploration in the Huhehu Sag.

Keywords Hailar Basin · Huhehu Sag · Biomarkers · Chemometrics · Oil–oil and oil–source rock correlations

1 Introduction

The Hailar Basin is the second largest continental petroliferous basin in the Daqing oil area in China and forms within a Paleozoic fold basement (Wang et al. 2009; Fig. 1a). By the end of 2014, the Huhehu Sag, located in the southeastern part of the Hailar Basin (Fig. 1b), had three low-yield oil wells (Chen 2014). In addition, the Huhehu Sag has received a great deal of attention due to its high quality of source rocks and the large potential of coalbed gases (Cui et al. 2007; Yang et al. 2008; Zhang 2014).

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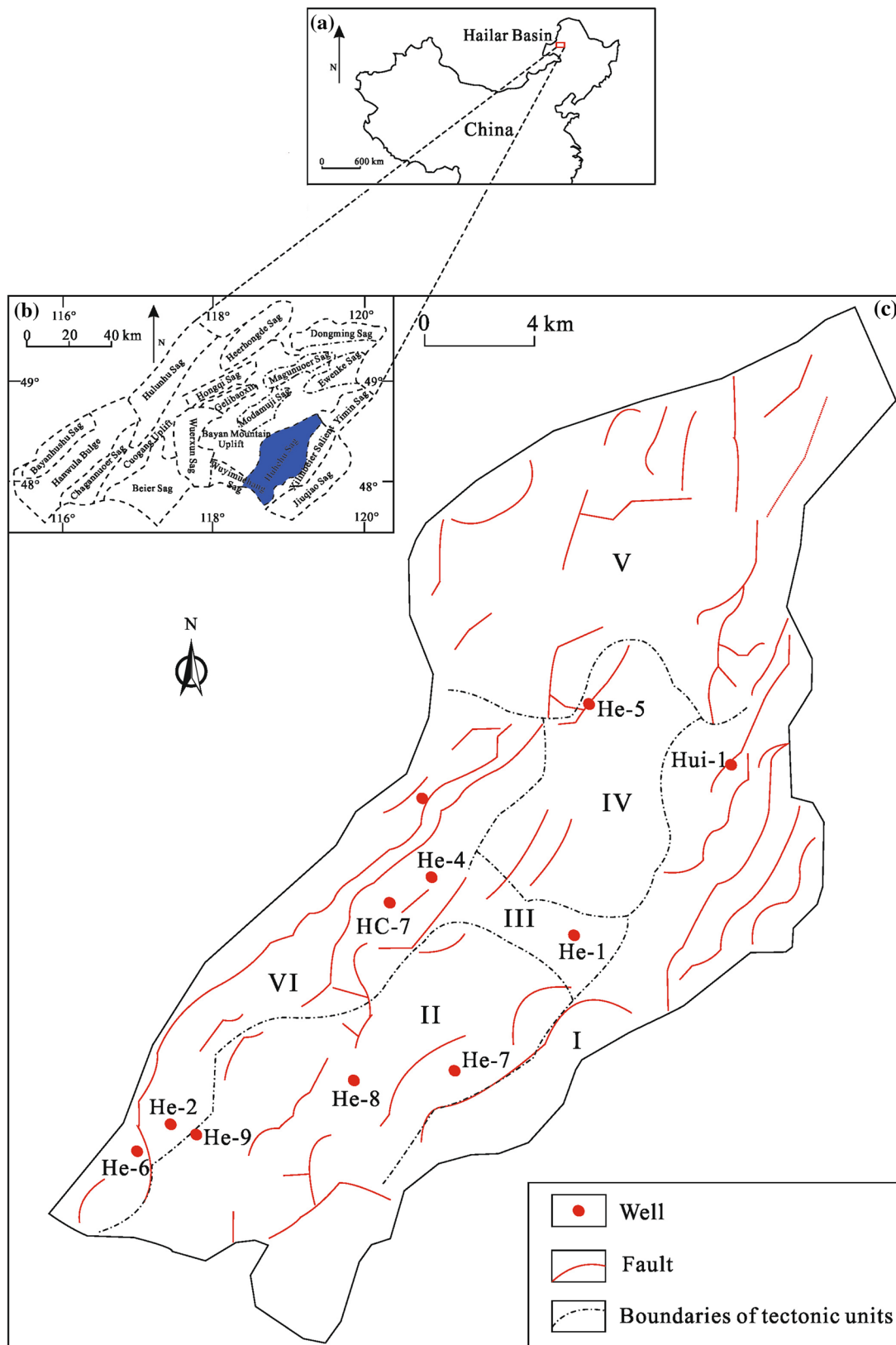


Fig. 1 Maps of **a** the Hailar Basin, and **b** Huhehu Sag, and **c** well distribution in the study area (Chen et al. 2011). I: southeast steep slope zone, II: south depression zone, III: central salient zone, IV: north depression zone, V: north slope zone, and VI: northwest gentle slope zone

Previous studies have confirmed that the study area has three sets of source rocks: the K_{1d_1} member (the first member of the Damoguaihe Formation), the K_{1n_2} member (the second member of the Nantun Formation), and the K_{1n_1} member (the first member of the Nantun Formation) (Li et al. 2009; Lu et al. 2010; Wu and Li 2012). These source rocks are all Cretaceous (Fig. 2). Only limited oil–source rock correlation studies have been conducted in the Huhehu Sag, and the origin of Huhehu oil remains controversial (Lu et al. 2010; Chen 2014). Lu et al. (2010) found that the Huhehu oils have a good correlation with the K_{1n_2} member (both mudstone and coal), while H Chen (2014) suggested that the Huhehu oils are mainly derived from the K_{1n_2} coal member and the K_{1n_1} mudstone member. Many publications have documented the Nantun Formation in detail in terms of molecular characteristics (Cao et al. 2010; Lu et al. 2010), organic matter enrichment, and kerogen type (Dong et al. 2011; Wu and Li 2012), but little is known about the quality of the Damoguaihe Formation. Accordingly, the present study aimed to comprehensively evaluate the source rocks of the Huhehu Sag (including the K_{1d_1} , K_{1n_2} , and K_{1n_1} members) in terms of organic matter enrichment, kerogen type, depositional environment, and thermal maturity. In addition, chemometric methods were applied to determine detailed oil–oil and oil–source rock correlations. The methods used [mainly hierarchical cluster analysis (HCA) and principal component analysis (PCA)] have been widely employed in the field of environmental science for analyzing water chemistry data (Amiri et al. 2017; Ding et al. 2017) and have proven reliable in analyzing oil–oil and oil–source rock correlations (Telnæs and Cooper 1991; Chakhmakhchev et al. 1996; Zumberge et al. 2005; Peters et al. 2007, 2008, 2013, 2016; Hao et al. 2009, 2010, 2011; He et al. 2012; Wang et al. 2016, 2018; Brito et al. 2017).

2 Geological setting

The Huhehu Sag, a secondary tectonic unit of the Hailar Basin (Cao et al. 2010; Chen et al. 2011), extends northeast and has a large potential for hydrocarbon exploration (Wu and Li 2012). The Huhehu Sag is bounded by the Xilinbeier Salient, Bayan Mountain Uplift, Yimin Sag, and Tamtsag Basin of Mongolia, which lie to the east, west, south, and north, respectively (Li et al. 2010). The Huhehu Sag can be further divided into: the southeast steep slope zone (I), south depression zone (II), central salient zone (III), north depression zone (IV), north slope zone (V), and northwest gentle slope zone (VI) (Chen et al. 2011; Fig. 1c).

The Huhehu Sag covers an area of 2500 km² at a maximum burial depth as high as 4600 m (Li et al. 2010).

The Huhehu Sag has undergone three stages in tectonic evolution (Fig. 2): the extensional faulted-depression stage, the thermal subsidence fault-depression stage, and the late depression stage (Chen et al. 2007). The Huhehu Sag is mainly filled with a Cretaceous sediment sequence, which from bottom to top is as follows: the Tongbomiao Formation (K_{1t}), Nantun Formation (K_{1n}), Damoguaihe Formation (K_{1d}), Yimin Formation (K_{1y}), and Qingyuangang Formation (K_{2q}). A detailed lithology of these different formations is shown in Fig. 2. The Qingyuangang Formation is composed of mudstone interbedded with sandy conglomerate. This sequence unconformably overlies the Yimin Formation. The Yimin Formation is characterized by sandstone and coal interbedded with mudstone in the lower part, and sandy conglomerate interbedded with sandstone and mudstone in the upper part (including the K_{1y_3} and K_{1y_2} members). The Yimin Formation conformably overlies the Damoguaihe Formation. The Damoguaihe Formation is composed of coal, sandstone, and sandy conglomerate in the upper part, and dominated by mudstone in the lower part. The Damoguaihe Formation displays an unconformable contact with the underlying Nantun Formation. An argillite-dominated lithology comprising mudstone, sandstone, coal, and sandy conglomerate constitutes the Nantun Formation. The Nantun Formation conformably overlies the Tongbomiao Formation. The Tongbomiao Formation consists of sandstone, sandy conglomerate, and mudstone.

3 Samples and methods

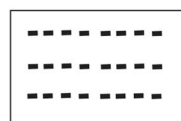
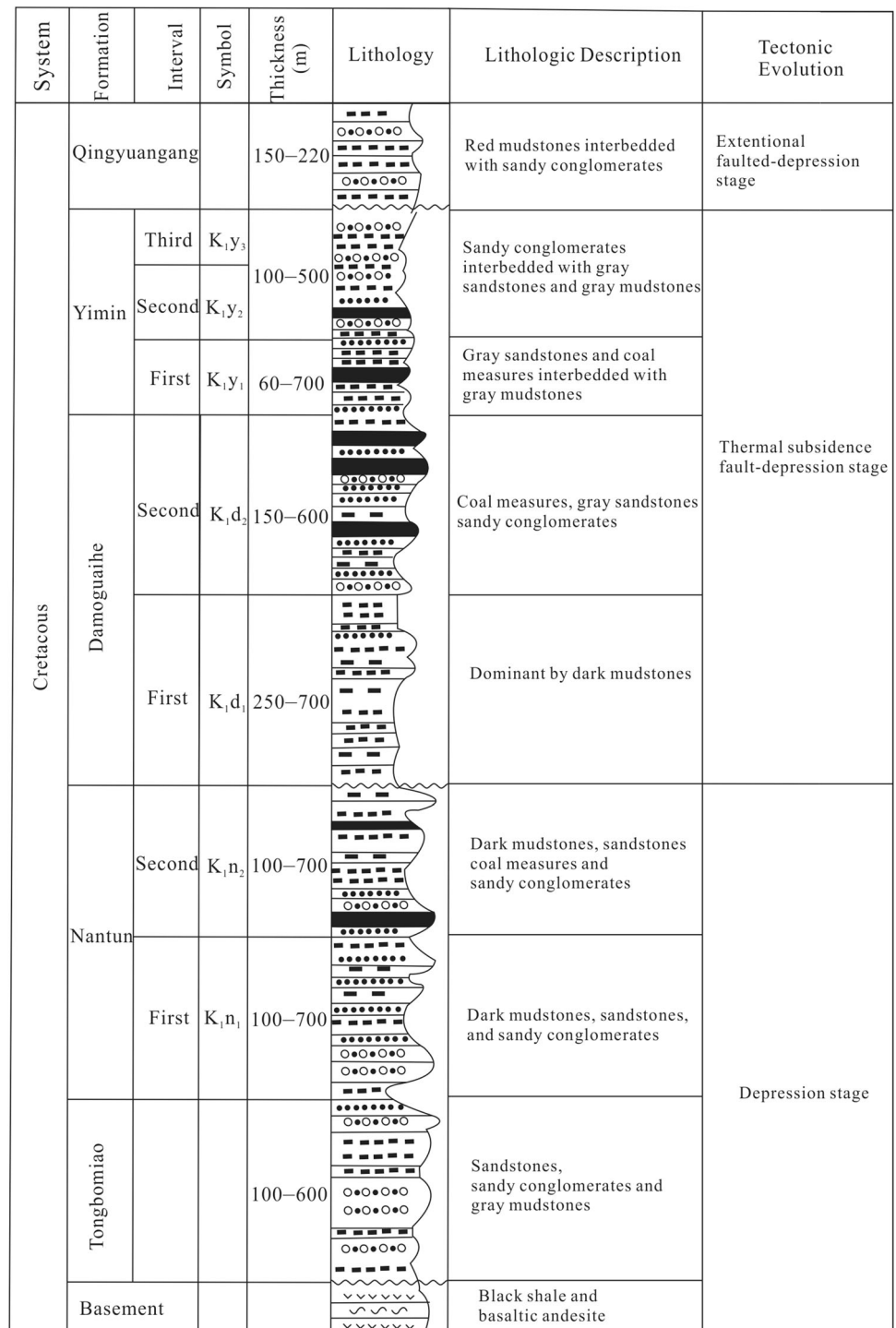
3.1 Samples

We collected 155 mudstone and 17 coal samples for Rock–Eval pyrolysis. The samples were from the K_{1d_1} (45 samples), K_{1n_2} (62 samples), and K_{1n_1} (65 samples) members exposed in nine wells distributed throughout the sag. Additionally, 15 oil samples, collected from the He-2, He-6, and He-9 wells, were analyzed using gas chromatography–mass spectrometry (GC–MS) to assess their molecular characteristics.

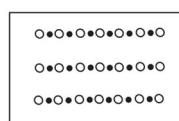
3.2 Rock–Eval pyrolysis and bitumen extraction of source rocks

Before the Rock–Eval analysis and bitumen extraction, all drill cutting samples were cleaned using redistilled water. The samples were subsequently dried at 60 °C and crushed into powder. The powder samples were analyzed (using IFP Rock–Eval 6) for total organic carbon (TOC), hydrogen index (HI), and hydrocarbon generation potential ($S_1 + S_2$). The powder samples were initially heated to

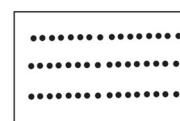
Fig. 2 Generalized stratigraphic column for the Huhehu Sag (Wu and Li 2012)



Mudstone



Sandy conglomerate



Sandstone



Coal measures

300 °C for 3 min to yield the Rock–Eval S_1 peak that represents the amount of free hydrocarbons, and then heated to 650 °C at a rate of increase of 25 °C/min to produce the Rock–Eval S_2 peak that represents the hydrocarbons generated from kerogen cracking. The temperature (°C) at which the maximum hydrocarbon yield generated from kerogen cracking occurred is T_{max} . Following pyrolysis, the pyrolyzed samples were heated from 300 to 850 °C at a rate of 20 °C/min in an oxidation furnace of the Rock–Eval 6 instrument to obtain the residual organic and inorganic carbon content. Bitumen was extracted from source rocks using a Soxhlet apparatus for 72 h with dichloromethane (DCM) mixed with methanol (93:7). All extracts and oils were separated into saturated, aromatic, and resin fractions using column chromatography.

3.3 Gas chromatography–mass spectrometry

GC–MS analyses were performed for the saturated fraction in the oils and source-rock extracts using a Thermo Fisher Trace GC Ultra gas chromatography coupled to a DSQ II mass spectrometer, equipped with a capillary column (60 m × 0.25 mm × 0.25 μm). The carrier gas was helium. The GC oven was initially kept at 60 °C for 1 min, then increased to 220 °C at a rate of 8 °C/min, then to 300 °C at a rate of 2 °C/min, and finally held at 300 °C for 25 min.

The mass spectrometer was operated at an ion source temperature of 230 °C and ionization energy of 70 eV. The analysis was conducted using mode-combining selective ion monitoring (SIM) with full-scan detection with a scan range of 50–550 Da.

3.4 Chemometric analysis

In this study, chemometric methods including HCA and PCA were applied to oil–oil and oil–source rock correlations in the Huhehu Sag. HCA and PCA are two common techniques used for chemometric exploratory data (Peters et al. 2005). Additionally, biomarker parameters, such as tricyclic terpanes, pentacyclic terpanes, and regular steranes (Peters et al. 2007, 2013), are commonly used in HCA and PCA. This study used nine source-related biomarker parameters for HCA and PCA, mainly including pentacyclic terpanes and regular steranes such as Pr/Ph, Ts/(Ts + Tm), H29/H30, C₃₅/C₃₄, Ga/C₃₁R, S/H, %C₂₇, %C₂₈, and %C₂₉, owing to the low abundance of tricyclic terpanes. These selected parameters are less likely to be affected by biodegradation, thermal maturity, and migration (Seifert and Moldowan 1978), similar to previous studies (Peters et al. 2007, 2013; Wang et al. 2016, 2018). Both HCA and PCA were completed using a commercial

chemometrics program (Pirouette 4.5, Infometrix Inc., Woodinville, WA, USA). HCA was performed by range scale preprocessing, Euclidean metric distance, and incremental linkage. The PCA simplified multiple variables into a few new independent variables. Before PCA, the data were also range scaled as for HCA. The selected biomarker parameters for PCA were the same as those for HCA.

4 Results and discussion

4.1 Hydrocarbon potential and kerogen type of source rocks

The TOC contents of the mudstone samples for the K_{1d1}, K_{1n1}, and K_{1n2} members ranged from 1.46 to 4.27 wt% (45 samples, mean = 2.22 wt% and standard deviation = 0.66), 0.16 to 9.80 wt% (61 samples, mean = 1.71 wt% and standard deviation = 1.79), and 0.65 to 9.08 wt% (49 samples, mean = 2.82 wt% and standard deviation = 1.74), respectively (Tables 1, 2, 3). The TOC contents of the K_{1n1} and K_{1n2} coal members are in the range of 12.11–40.57 wt% (4 samples, mean = 28.72 wt% and standard deviation = 11.70) and 23.00–73.30 wt% (13 samples, mean = 49.99 wt% and standard deviation = 16.37), respectively (Tables 1, 2 and 3). The TOC contents of most K_{1d1} and K_{1n2} mudstone samples are > 2 wt%, while those of the K_{1n1} mudstone samples are generally between 1 and 2 wt%. The genetic potential ($S_1 + S_2$) is mostly between 2 and 6 mg HC/g rock for the K_{1d1} and K_{1n2} mudstone members, but is generally < 2 mg HC/g rock for the K_{1n1} mudstone member. It is noteworthy that the Huhehu Sag is a coal-rich basin, and the source rocks of the K_{1d} and K_{1n} Formations belong to typical coal-bearing strata (Chen 2014; Zhang 2014). Some criteria have been established for evaluating hydrocarbon generation potential of organic matter in coal measures in China (Huang and Xiong 1996; Chen et al. 1997; Wang 1998). The criteria from Huang and Xiong (1996) and Wang (1998) for the assessment of hydrocarbon-generating potential of coal-bearing strata are based mainly on two Rock–Eval parameters: TOC and hydrocarbon generative potential ($S_1 + S_2$). However, Chen et al. (1997) found that a plot of HI versus hydrocarbon generative potential ($S_1 + S_2$) is more effective for describing coal-bearing source rock. The criteria from Huang and Xiong (1996) and Wang (1998) are based only on a small number of samples and study areas, while the criteria from Chen et al. (1997) are based on over 23,000 rock samples from coal measure strata in northwestern China. Therefore, the standard established by Chen et al. (1997), which is probably more accurate for evaluating hydrocarbon-generating potential in coal-bearing strata and has been widely accepted (Jiang

Table 1 Rock–Eval data for the K₁d₁ member

Well	Depth (m)	Formation	Lithology	TOC	S ₁	S ₁ /TOC	S ₂	S ₁ + S ₂	HI	OI	T _{max}
He-1	1258	K ₁ d ₁	Mudstone	3.90	0.10	0.03	3.68	3.78	94.29	23.32	434
He-1	1261.3	K ₁ d ₁	Mudstone	3.81	0.08	0.02	2.81	2.89	73.79	29.41	436
He-1	1263.5	K ₁ d ₁	Mudstone	3.63	0.11	0.03	3.42	3.53	94.24	31.41	435
He-1	1265.6	K ₁ d ₁	Mudstone	4.27	0.10	0.02	4.13	4.23	96.65	36.51	430
He-1	1635.3	K ₁ d ₁	Mudstone	2.67	0.31	0.12	7.20	7.51	269.87	10.49	431
He-1	1637.7	K ₁ d ₁	Mudstone	2.43	0.47	0.19	11.47	11.94	472.99	11.55	434
He-1	1640.3	K ₁ d ₁	Mudstone	2.88	0.29	0.10	10.16	10.45	352.78	10.42	435
He-1	1736	K ₁ d ₁	Mudstone	1.96	0.21	0.11	5.95	6.16	303.57	87.24	440
He-1	1739.8	K ₁ d ₁	Mudstone	2.36	0.28	0.12	7.04	7.33	298.05	46.99	439
He-6	1357.4	K ₁ d ₁	Mudstone	2.88	0.17	0.06	3.06	3.23	106.15	1520.67	442
He-6	1349.1	K ₁ d ₁	Mudstone	1.79	0.07	0.04	1.84	1.91	102.91	827.42	439
He-6	1350.1	K ₁ d ₁	Mudstone	1.53	0.05	0.03	1.49	1.54	97.20	118.36	440
He-6	1352.4	K ₁ d ₁	Mudstone	1.67	0.06	0.04	1.22	1.28	72.97	225.99	448
He-6	1353.1	K ₁ d ₁	Mudstone	1.91	0.07	0.04	1.90	1.97	99.69	8.69	436
He-6	1354.3	K ₁ d ₁	Mudstone	1.48	0.08	0.05	1.84	1.92	123.99	8.20	441
He-6	1355.1	K ₁ d ₁	Mudstone	1.77	0.06	0.03	1.54	1.60	86.91	2193.58	442
He-X1	2083.8	K ₁ d ₁	Mudstone	1.89	0.28	0.15	4.21	4.49	222.56	1092.27	447
He-X1	2084.3	K ₁ d ₁	Mudstone	2.18	0.33	0.15	5.58	5.91	255.55	602.94	446
He-X1	2084.8	K ₁ d ₁	Mudstone	1.81	0.26	0.14	4.86	5.12	268.28	613.99	446
He-X1	2085.3	K ₁ d ₁	Mudstone	1.73	0.26	0.15	3.55	3.81	204.73	1200.78	442
He-X1	2085.7	K ₁ d ₁	Mudstone	1.61	0.23	0.14	3.37	3.60	209.36	1262.23	445
He-X1	2086.2	K ₁ d ₁	Mudstone	2.18	0.34	0.16	5.70	6.04	261.54	2331.94	445
He-X1	2086.7	K ₁ d ₁	Mudstone	2.29	0.36	0.16	7.02	7.38	305.90	289.09	447
He-X1	2087.2	K ₁ d ₁	Mudstone	1.46	0.18	0.12	2.59	2.77	176.91	2842.32	439
He-X1	2087.6	K ₁ d ₁	Mudstone	1.69	0.24	0.14	3.74	3.98	221.26	2296.84	446
He-X1	2088	K ₁ d ₁	Mudstone	2.26	0.35	0.15	6.80	7.14	301.09	531.84	446
He-X1	2088.4	K ₁ d ₁	Mudstone	1.69	0.23	0.14	4.19	4.41	246.96	209.90	446
He-X1	2089.2	K ₁ d ₁	Mudstone	1.99	0.28	0.14	5.62	5.90	281.89	11.97	447
He-X1	2090.2	K ₁ d ₁	Mudstone	2.20	0.33	0.15	6.56	6.89	298.44	779.19	446
He-X1	2090.4	K ₁ d ₁	Mudstone	1.61	0.21	0.13	4.07	4.28	252.11	842.11	447
He-X1	2090.9	K ₁ d ₁	Mudstone	1.81	0.22	0.12	4.78	5.00	264.16	281.72	448
He-X1	2091.2	K ₁ d ₁	Mudstone	1.88	0.22	0.12	4.75	4.97	252.00	12.38	447
He-X1	2091.5	K ₁ d ₁	Mudstone	1.82	0.21	0.12	4.72	4.93	259.42	126.98	447
Hui-1	1170	K ₁ d ₁	Mudstone	2.11	0.09	0.04	1.37	1.46	64.93	433.63	418
Hui-1	1230	K ₁ d ₁	Mudstone	2.61	0.11	0.04	1.85	1.96	70.77	15.91	420
Hui-1	1340	K ₁ d ₁	Mudstone	1.73	0.11	0.06	2.53	2.64	146.50	144.58	416
He-10	1752	K ₁ d ₁	Mudstone	1.96	0.08	0.04	3.02	3.09	154.16	10.99	438
He-10	1816	K ₁ d ₁	Mudstone	2.62	0.11	0.04	3.27	3.38	124.86	8.33	439
He-12	1868.5	K ₁ d ₁	Mudstone	2.01	0.24	0.12	5.07	5.31	252.14	201.82	440
He-12	1871.4	K ₁ d ₁	Mudstone	2.03	0.23	0.11	4.59	4.82	226.49	11.95	440
He-12	1872.8	K ₁ d ₁	Mudstone	2.53	0.42	0.17	8.13	8.55	321.23	8.60	440
He-12	1875.2	K ₁ d ₁	Mudstone	3.17	0.36	0.11	10.19	10.56	321.20	7.97	441
He-15	1920	K ₁ d ₁	Mudstone	1.73	0.10	0.06	2.60	2.71	150.72	158.29	445
He-15	1940	K ₁ d ₁	Mudstone	1.84	0.01	0.01	2.52	2.52	136.91	624.33	442
He-15	1960	K ₁ d ₁	Mudstone	2.44	0.08	0.03	3.34	3.42	136.80	211.35	437

The units of the Rock–Eval pyrolysis parameters and indices: TOC: wt%; T_{max}: °C; S₁: mg HC/g rock; S₁/TOC: mg HC/g TOC; S₂: mg HC/g rock; S₃: mg CO₂/g rock; HI: mg HC/g TOC; OI: mg CO₂/g TOC

Table 2 Rock–Eval data for the K_{1n2} member

Well	Depth (m)	Formation	Lithology	TOC	S ₁	S ₁ /TOC	S ₂	S ₁ + S ₂	HI	OI	T _{max}
He-1	1785.7	K _{1n2}	Mudstone	2.46	0.28	0.11	4.30	4.58	174.65	0.00	432
He-1	1827.3	K _{1n2}	Mudstone	2.69	0.41	0.15	8.37	8.78	310.92	7.80	435
He-1	1829.3	K _{1n2}	Mudstone	2.39	0.30	0.13	5.55	5.85	232.70	17.19	436
He-1	1831.4	K _{1n2}	Mudstone	2.45	0.36	0.15	6.57	6.93	268.16	1.22	440
He-1	1938	K _{1n2}	Mudstone	3.27	0.51	0.16	5.99	6.50	183.29	0.00	442
He-1	2024	K _{1n2}	Mudstone	6.95	3.15	0.45	18.82	21.97	270.99	0.00	437
He-9	1895	K _{1n2}	Mudstone	2.16	0.03	0.01	0.18	0.21	8.34	1058.38	472
He-9	1900	K _{1n2}	Mudstone	3.97	0.10	0.03	2.46	2.56	62.04	1642.40	437
He-9	1905	K _{1n2}	Mudstone	2.69	0.11	0.04	2.08	2.19	77.27	337.30	440
He-9	1910	K _{1n2}	Mudstone	2.51	0.33	0.13	3.35	3.67	133.57	1151.28	444
He-9	1915	K _{1n2}	Mudstone	1.43	0.25	0.17	2.18	2.43	152.45	967.99	446
He-9	1920	K _{1n2}	Mudstone	1.19	0.02	0.02	0.23	0.26	19.38	1539.65	450
He-9	1925	K _{1n2}	Mudstone	1.08	0.07	0.06	1.13	1.20	104.63	19.16	442
He-9	1930	K _{1n2}	Mudstone	1.71	0.04	0.02	0.66	0.69	38.60	409.36	439
He-9	1935	K _{1n2}	Mudstone	7.29	0.25	0.03	10.02	10.27	137.39	6.39	442
He-9	1940	K _{1n2}	Mudstone	1.35	0.19	0.14	1.78	1.98	131.95	24.12	446
He-9	1945	K _{1n2}	Mudstone	0.65	0.07	0.11	0.72	0.79	110.68	4.16	448
He-9	1950	K _{1n2}	Mudstone	1.71	0.12	0.07	2.31	2.42	135.01	0.50	449
He-9	1955	K _{1n2}	Mudstone	1.48	0.17	0.11	2.20	2.37	149.15	4.19	449
He-9	1965	K _{1n2}	Mudstone	2.31	0.33	0.14	4.10	4.43	177.41	1279.30	449
He-9	1970	K _{1n2}	Mudstone	2.22	0.10	0.05	2.05	2.15	92.51	1032.03	444
He-9	1975	K _{1n2}	Mudstone	0.78	0.05	0.06	0.67	0.72	86.34	1342.87	449
He-9	1980	K _{1n2}	Mudstone	1.61	0.23	0.14	2.75	2.98	170.60	110.05	449
He-9	1985	K _{1n2}	Mudstone	1.49	0.20	0.13	1.89	2.09	126.51	96.50	443
He-9	1990	K _{1n2}	Mudstone	1.69	0.23	0.14	2.42	2.65	143.20	146.59	449
He-10	1857	K _{1n2}	Mudstone	2.00	0.08	0.04	2.38	2.45	118.76	144.44	436
He-10	1873	K _{1n2}	Mudstone	2.05	0.06	0.03	2.52	2.58	123.11	122.81	439
He-10	1889	K _{1n2}	Mudstone	5.88	1.02	0.17	11.50	12.51	195.51	26.88	436
He-10	1905	K _{1n2}	Mudstone	2.27	0.14	0.06	2.27	2.41	99.82	1871.76	439
He-10	2050	K _{1n2}	Mudstone	2.84	0.36	0.13	4.07	4.43	143.16	1631.05	441
He-10	2065	K _{1n2}	Mudstone	2.60	0.42	0.16	4.18	4.60	160.89	688.49	447
He-10	2109	K _{1n2}	Mudstone	4.18	0.68	0.16	6.89	7.57	164.99	543.73	447
He-10	2308	K _{1n2}	Mudstone	3.21	0.42	0.13	4.58	5.00	142.90	3.31	451
He-10	2328	K _{1n2}	Mudstone	9.08	1.94	0.21	18.45	20.39	203.24	325.40	461
He-10	2348	K _{1n2}	Mudstone	5.47	0.48	0.09	7.59	8.07	138.71	685.92	443
He-15	2312	K _{1n2}	Mudstone	4.11	0.90	0.22	4.39	5.29	106.65	1122.42	463
He-15	2312.2	K _{1n2}	Mudstone	6.03	1.73	0.29	8.60	10.33	142.67	1163.77	464
He-15	2312.6	K _{1n2}	Mudstone	0.83	0.05	0.06	0.37	0.42	44.58	1532.13	479
He-15	2416	K _{1n2}	Mudstone	4.42	2.05	0.46	5.47	7.52	123.59	1837.28	468
He-X1	2295.2	K _{1n2}	Mudstone	2.45	0.44	0.18	4.05	4.49	165.01	11.99	449
He-X1	2295.7	K _{1n2}	Mudstone	2.32	0.39	0.17	3.86	4.25	166.11	18.44	450
He-X1	2296.2	K _{1n2}	Mudstone	2.64	0.48	0.18	4.56	5.04	172.75	14.46	450
He-X1	2296.6	K _{1n2}	Mudstone	2.37	0.45	0.19	3.58	4.03	151.33	27.60	450
He-X1	2297	K _{1n2}	Mudstone	2.26	0.46	0.20	3.18	3.64	140.56	51.96	448
He-X1	2297.6	K _{1n2}	Mudstone	2.18	0.39	0.18	3.99	4.38	182.74	28.97	450
He-X1	2298	K _{1n2}	Mudstone	2.18	0.38	0.17	4.20	4.58	192.51	19.42	449
He-X1	2298.5	K _{1n2}	Mudstone	2.28	0.41	0.18	3.69	4.10	161.84	259.04	450
He-X1	2299	K _{1n2}	Mudstone	2.25	0.46	0.20	3.03	3.49	135.14	59.20	445

Table 2 continued

Well	Depth (m)	Formation	Lithology	TOC	S ₁	S ₁ /TOC	S ₂	S ₁ + S ₂	HI	OI	T _{max}
He-X1	2299.9	K _{1n2}	Mudstone	2.55	0.50	0.20	4.06	4.56	159.47	37.00	450
He-1	1833.7	K _{1n2}	Coal	64.15	31.92	0.50	239.46	271.38	373.28	3.97	430
He-1	1835.3	K _{1n2}	Coal	55.06	8.07	0.15	92.85	100.92	168.63	2.86	435
He-6	1485.9	K _{1n2}	Coal	34.69	4.05	0.12	89.63	93.68	258.37	2.35	417
He-6	1489.3	K _{1n2}	Coal	72.57	9.58	0.13	141.41	150.99	194.86	8.79	420
He-6	1491.6	K _{1n2}	Coal	60.61	7.00	0.12	97.80	104.80	161.36	9.40	440
He-6	1492.4	K _{1n2}	Coal	53.70	5.32	0.10	127.02	132.34	236.54	11.47	431
He-6	1492.7	K _{1n2}	Coal	32.72	4.76	0.15	98.12	102.88	299.84	9.39	427
He-6	1492.7	K _{1n2}	Coal	32.72	4.76	0.15	98.12	102.88	299.84	10.11	427
He-8	2524.8	K _{1n2}	Coal	32.82	7.55	0.23	60.75	68.30	185.10	10.11	460
He-9	1632.9	K _{1n2}	Coal	49.54	21.72	0.44	186.09	207.81	375.64	4.91	427
He-9	1635.8	K _{1n2}	Coal	23.00	2.98	0.13	54.35	57.33	236.30	4.43	426
He-X1	2275	K _{1n2}	Coal	64.98	13.07	0.20	152.42	165.49	234.57	2.10	437
He-X1	2283	K _{1n2}	Coal	73.30	16.53	0.23	228.49	245.02	311.71	9.93	440

The units of the Rock-Eval pyrolysis parameters and indices: TOC: wt%; T_{max}: °C; S₁: mg HC/g rock; S₁/TOC: mg HC/g TOC; S₂: mg HC/g rock; S₃: mg CO₂/g rock; HI: mg HC/g TOC; OI: mg CO₂/g TOC

et al. 2014; Meng et al. 2014; Song et al. 2015; Zhang et al. 2016), was used in this study. These data indicate that the mudstone samples from the K_{1d1} and K_{1n2} members are fair to good source rocks, while the mudstone samples from the K_{1n1} member have poor source rock characteristics (Figs. 3a–c; Chen et al. 1997).

Based on the analysis of a large number of coal samples in China, Chen et al. (1997) found that a combination of HI and S₁ + S₂ can better estimate the hydrocarbon-generating potential of coal. The hydrocarbon generative potential of the coal samples from the K_{1n1} and K_{1n2} members ranged from 12.90 to 81.08 mg HC/g TOC (mean = 43.45 mg HC/g TOC) and from 57.33 to 271.38 mg HC/g TOC (mean = 138.76 mg HC/g TOC), respectively; HI values are in the range of 50.83 to 186.91 mg HC/g TOC (mean = 136.61 mg HC/g TOC) and 161.36 to 375.64 mg HC/g TOC (mean = 256.62 mg HC/g TOC), respectively (Tables 2 and 3). These data indicate that the K_{1n1} coal members have poor hydrocarbon potential, and the K_{1n2} coal member has poor to good hydrocarbon potential (Fig. 3d). The cross plot of HI versus T_{max} (Fig. 4) indicates that the Huhehu source rocks are primarily type II₂ kerogen, with some samples falling in the zone of type II₁ and III kerogen. The Rock–Eval parameters S₁ and TOC are useful in distinguishing between the indigenous and nonindigenous organic matter present in the studied source rock samples (Hunt 1996). A migration index (S₁/TOC) < 1.5 indicates that samples have not been affected by migrated hydrocarbon (e.g., Mashhadi et al. 2015). All the studied source rocks exhibit S₁/TOC ratios < 1.5, indicating that the studied samples were not contaminated by migrated hydrocarbon.

4.2 Molecular characteristics of source rocks

The gas chromatogram shows front-end biased distribution and enrichment of low molecular compounds, typically at *n*-C₁₇ to *n*-C₂₃ (Figs. 5 and 6). No apparent odd-over-even predominance was observed other than in coal. A low Pr/Ph ratio (< 1) indicates an anoxic depositional environment, whereas a higher Pr/Ph ratio (> 1) indicates oxic depositional conditions (Didyk et al. 1978). Additionally, extremely high values of the Pr/Ph ratio (> 3) are believed to be associated with terrigenous organic matter inputs under oxic depositional settings (Peters et al. 2005). The Pr/Ph ratios for the source rock from the K_{1d1}, K_{1n1}, and K_{1n2} members are in the range of 1.25 to 2.39 (mean = 1.77, 16 samples), 2.24 to 3.24 (mean = 2.74, 2 samples), and 1.43 to 4.07 (mean = 2.52, 13 samples) (Table 4), respectively, suggesting oxic depositional conditions for these source rock members. Furthermore, the mean values of Pr/Ph increase as follows: K_{1d1} < K_{1n2} < K_{1n1} members, probably indicating relatively oxic depositional conditions.

Sterane mass chromatograms (m/z 217) of the representative source rocks are shown in Figs. 5 and 6. The relative abundances of C₂₇, C₂₈, and C₂₉ steranes for the source rocks are in the range of 12.27%–41.51%, 8.16%–24.56%, and 41.98%–74.11%, respectively (Table 4). Previous work observed that C₂₇ sterols (steranes) dominate in marine organic matter, while C₂₉ sterols (steranes) dominate in terrigenous organic matter (Huang and Meinschein 1979). Our data suggest a dominant contribution of terrigenous organic matter input (Fig. 7). In addition, sterane/hopane ratios for the source rocks range from 0.07

Table 3 Rock-Eval data for the K_{1n1} member

Well	Depth (m)	Formation	Lithology	TOC	S ₁	S ₁ /TOC	S ₂	S ₁ + S ₂	HI	OI	T _{max}
He-10	2368	K _{1n1}	Mudstone	2.99	0.32	0.11	3.24	3.56	108.43	41.83	450
He-10	2388	K _{1n1}	Mudstone	1.09	0.10	0.09	1.32	1.42	120.77	46.66	456
He-10	2409	K _{1n1}	Mudstone	1.39	0.18	0.13	1.52	1.69	109.35	620.14	461
He-10	2428	K _{1n1}	Mudstone	5.20	0.67	0.13	8.16	8.84	156.92	16.54	452
He-10	2448	K _{1n1}	Mudstone	2.81	0.33	0.12	3.98	4.30	141.74	18.16	456
He-10	2472	K _{1n1}	Mudstone	3.92	0.68	0.17	6.16	6.83	156.98	16.06	453
He-10	2492	K _{1n1}	Mudstone	1.12	0.06	0.05	0.94	1.00	84.15	49.24	456
He-10	2512	K _{1n1}	Mudstone	1.94	0.34	0.18	2.52	2.85	130.10	81.05	441
He-10	2553	K _{1n1}	Mudstone	3.58	0.70	0.20	6.26	6.96	175.01	14.54	454
He-10	2572	K _{1n1}	Mudstone	1.43	0.34	0.24	2.04	2.38	142.56	29.35	458
He-8	3353	K _{1n1}	Mudstone	0.62	0.01	0.02	0.16	0.17	25.88	82.48	498
He-8	3373	K _{1n1}	Mudstone	9.33	0.31	0.03	4.07	4.38	43.62	14.36	502
He-8	3391	K _{1n1}	Mudstone	9.80	0.90	0.09	8.03	8.93	81.92	7.35	486
He-8	3414	K _{1n1}	Mudstone	1.08	0.04	0.04	0.35	0.39	32.32	93.26	480
He-8	3425	K _{1n1}	Mudstone	0.45	0.01	0.02	0.19	0.20	42.44	808.58	461
He-8	3445	K _{1n1}	Mudstone	4.53	0.35	0.08	4.48	4.83	99.01	303.87	447
He-8	3458	K _{1n1}	Mudstone	1.42	0.09	0.06	1.09	1.18	76.76	452.82	449
He-9	2047	K _{1n1}	Mudstone	3.02	0.16	0.05	2.58	2.73	85.37	65.52	447
He-9	2048	K _{1n1}	Mudstone	0.98	0.06	0.06	0.83	0.89	84.55	113.07	445
He-9	2050	K _{1n1}	Mudstone	2.22	0.20	0.09	2.88	3.09	129.91	56.38	448
He-9	2052	K _{1n1}	Mudstone	1.89	0.21	0.11	2.37	2.58	125.33	615.55	449
He-9	2054	K _{1n1}	Mudstone	1.19	0.13	0.11	1.16	1.28	97.73	131.42	450
He-9	2056	K _{1n1}	Mudstone	2.41	0.18	0.07	2.23	2.40	92.61	696.43	447
He-9	2058	K _{1n1}	Mudstone	1.14	0.11	0.10	1.34	1.45	117.13	86.54	449
He-9	2060	K _{1n1}	Mudstone	0.53	0.06	0.11	0.59	0.66	110.69	724.20	446
He-9	2062	K _{1n1}	Mudstone	2.79	0.29	0.10	3.23	3.52	115.90	76.43	448
He-9	2064	K _{1n1}	Mudstone	1.29	0.13	0.10	1.73	1.86	134.42	102.56	449
He-9	2066	K _{1n1}	Mudstone	1.35	0.13	0.10	1.72	1.86	127.50	3575.98	444
He-9	2068	K _{1n1}	Mudstone	2.73	0.30	0.11	3.37	3.67	123.44	1369.96	443
He-9	2070	K _{1n1}	Mudstone	1.45	0.19	0.13	2.20	2.39	151.31	756.53	451
He-9	2072	K _{1n1}	Mudstone	1.52	0.08	0.05	1.67	1.75	109.65	1192.38	441
He-9	2074	K _{1n1}	Mudstone	0.73	0.04	0.05	0.71	0.75	97.80	154.27	448
He-9	2076	K _{1n1}	Mudstone	1.43	0.19	0.13	1.97	2.16	137.86	548.64	447
He-9	2078	K _{1n1}	Mudstone	0.50	0.06	0.12	0.53	0.60	105.01	828.21	450
He-9	2080	K _{1n1}	Mudstone	1.27	0.12	0.09	1.42	1.54	111.72	567.27	446
He-9	2082	K _{1n1}	Mudstone	0.64	0.10	0.16	0.60	0.70	93.72	745.08	450
He-9	2084	K _{1n1}	Mudstone	1.57	0.38	0.24	2.62	3.00	167.09	47.83	449
He-9	2086	K _{1n1}	Mudstone	1.33	0.22	0.17	1.72	1.94	129.23	174.31	448
He-9	2088	K _{1n1}	Mudstone	1.24	0.31	0.25	2.44	2.75	196.30	67.58	450
He-9	2090	K _{1n1}	Mudstone	0.81	0.12	0.15	1.03	1.15	126.72	182.09	451
He-9	2092	K _{1n1}	Mudstone	1.60	0.18	0.11	1.91	2.09	119.67	904.76	447
He-9	2094	K _{1n1}	Mudstone	0.73	0.12	0.16	0.71	0.83	97.72	8867.33	452
He-9	2096	K _{1n1}	Mudstone	2.14	0.33	0.15	2.39	2.73	111.94	705.39	449
He-9	2098	K _{1n1}	Mudstone	1.51	0.26	0.17	2.24	2.50	148.05	1308.00	449
He-9	2100	K _{1n1}	Mudstone	0.82	0.08	0.10	0.90	0.98	110.06	2151.16	448
He-9	2102	K _{1n1}	Mudstone	1.04	0.08	0.08	1.16	1.24	111.11	2192.53	444
He-9	2104	K _{1n1}	Mudstone	1.82	0.21	0.12	2.22	2.43	121.78	414.70	440
He-X1	3063.8	K _{1n1}	Mudstone	0.57	0.02	0.04	0.14	0.16	25.12	26.88	502

Table 3 continued

Well	Depth (m)	Formation	Lithology	TOC	S ₁	S ₁ /TOC	S ₂	S ₁ + S ₂	HI	OI	T _{max}
He-X1	3064.4	K _{1n1}	Mudstone	0.43	0.01	0.02	0.11	0.12	26.28	26.97	499
He-X1	3065	K _{1n1}	Mudstone	0.85	0.04	0.05	0.25	0.28	29.10	17.32	501
He-X1	3065.4	K _{1n1}	Mudstone	0.30	0.00	0.00	0.06	0.06	18.64	57.24	498
He-X1	3065.9	K _{1n1}	Mudstone	0.17	0.00	0.00	0.02	0.02	12.08	130.43	495
He-X1	3066.4	K _{1n1}	Mudstone	0.16	0.00	0.00	0.02	0.02	10.32	130.46	495
He-X1	3067.3	K _{1n1}	Mudstone	0.81	0.03	0.04	0.22	0.25	26.88	23.55	500
He-X1	3128.2	K _{1n1}	Mudstone	0.39	0.01	0.03	0.07	0.07	16.81	53.54	500
He-X1	3129.1	K _{1n1}	Mudstone	0.58	0.03	0.05	0.13	0.16	21.98	30.28	504
He-X1	3129.5	K _{1n1}	Mudstone	0.19	0.00	0.00	0.03	0.03	14.56	95.68	502
He-X1	3130.4	K _{1n1}	Mudstone	0.28	0.01	0.04	0.04	0.04	13.78	67.11	502
He-X1	3130.8	K _{1n1}	Mudstone	0.78	0.05	0.06	0.14	0.19	17.74	23.48	500
He-X1	3131.1	K _{1n1}	Mudstone	0.86	0.04	0.05	0.15	0.19	17.64	20.31	501
He-X1	3131.6	K _{1n1}	Mudstone	1.32	0.13	0.10	0.39	0.52	29.29	11.02	500
He-10	2532	K _{1n1}	Coal	12.11	1.60	0.13	21.96	23.56	181.34	4.74	457
He-X1	3070	K _{1n1}	Coal	40.57	4.59	0.11	51.67	56.26	127.37	5.62	442
He-X1	3080	K _{1n1}	Coal	23.36	1.02	0.04	11.88	12.90	50.83	0.00	445
He-X1	3160	K _{1n1}	Coal	38.83	8.50	0.22	72.58	81.08	186.91	9.54	455

The units of the Rock-Eval pyrolysis parameters and indices: TOC: wt%; T_{max}: °C; S₁: mg HC/g rock; S₁/TOC: mg HC/g TOC; S₂: mg HC/g rock; S₃: mg CO₂/g rock; HI: mg HC/g TOC; OI: mg CO₂/g TOC

to 0.54, indicative of terrigenous or microbially reworked organic matter (Tissot and Welte 1984).

Terpane mass chromatograms (m/z 191) of the representative source rocks are characterized by a high abundance of pentacyclic terpanes relative to tricyclic terpanes (Figs. 5 and 6), consistent with coal-bearing source rocks in northwestern China (J Chen et al. 1998). The C₃₅/C₃₄ ratios for the source rocks range from 0.19 to 0.39, indicating oxic depositional conditions (Peters and Moldowan 1991). The gammacerane/C₃₁R ratios in the source rocks are in the range of 0.01 to 0.23, indicating a lack of stratification because a high gammacerane/C₃₁R ratio is usually expected both with stratification and with reducing depositional conditions (Fu et al. 1986; Sinninghe Damsté et al. 1995).

4.3 Maturity of source rocks

To evaluate the thermal maturity of the source rocks, several maturity indicators, including Rock–Eval pyrolysis and biomarker parameters were used. The Rock–Eval pyrolysis parameter, T_{max}, preferred by type II/III organic matter (Tissot et al. 1987), is a reliable index for evaluating thermal maturity of source rocks (Tissot and Welte 1984). Based on T_{max} values in the source rock members (Peters 1986), the K_{1d1} mudstone member is at immature to peak stage, ranging from 416 to 448 °C, and the K_{1n2} mudstone member is at early to late stage, ranging from 432 to

479 °C. It is noteworthy that the K_{1n1} mudstone member has the highest maturity level, while coals from the K_{1n1} and K_{1n2} members are mostly at an immature or early mature stage (Peters 1986). In general, the thermal maturity of the source rock members increase as follows: K_{1d1} < K_{1n2} < K_{1n1} members (Tables 1, 2, 3).

With increasing maturity, three biomarker ratios—C₃₂ homohopanes 22S/(22S + 22R), C₂₉ steranes 20S/(20R + 20S), and C₂₉ ββ/(αα + ββ)—increase from 0 to approximately 0.6, 0–0.5, and 0–0.7, respectively (Seifert and Moldowan 1980, 1986). The values of C₃₂ homohopane 22S/(22S + 22R) ratios for the Huhehu source rocks are in the range of 0.57–0.61 (Table 4), indicating that most of the source rocks have reached or even surpassed the oil window. The ratios of C₂₉ steranes 20S/(20R + 20S) and C₂₉ ββ/(αα + ββ) in the Huhehu source rocks are in the range of 0.20–0.55 and 0.30–0.53 (K_{1d1} member), 0.29–0.62 and 0.41–0.50 (K_{1n2} member), and 0.40 to 0.55 and 0.44 to 0.49 (K_{1n1} member) (Table 4). These data suggest that most of the studied samples are mature, which is consistent with the T_{max} values.

4.4 Oil-oil correlation

When the similarity line was placed at a similarity coefficient value of slightly greater than 0.6, the Huhehu oils were divided into three groups: A, B, and C (Fig. 8). This is consistent with PCA results (Fig. 9).

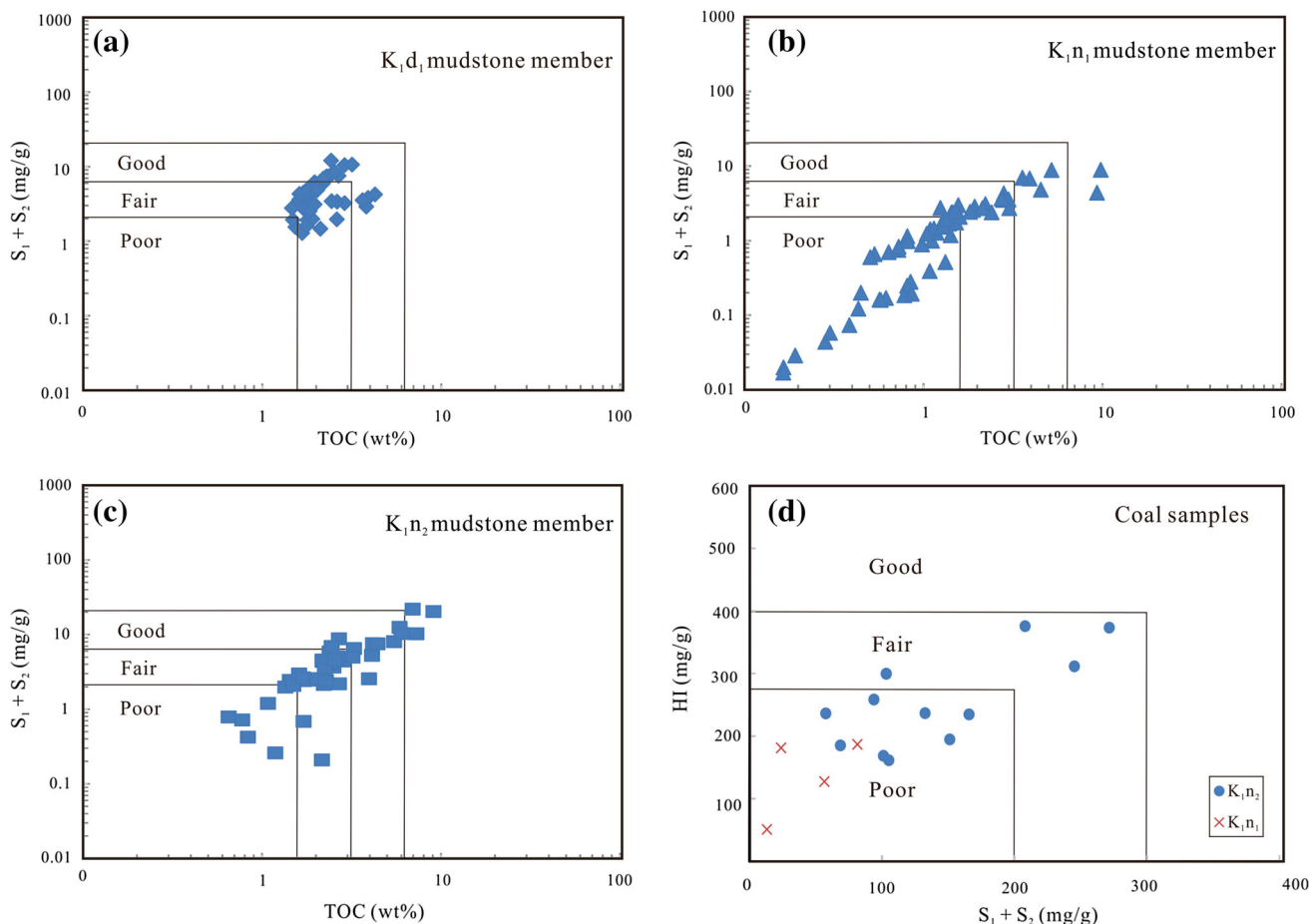


Fig. 3 Plots of the Rock–Eval parameters total organic carbon (TOC) versus $S_1 + S_2$ for source rocks from the K_{1d_1} , K_{1n_2} , and K_{1n_1} mudstone members (a–c), and $S_1 + S_2$ versus hydrogen index (HI) for source rocks from the K_{1n_2} and K_{1n_1} coal members (d)

4.4.1 Bulk physical properties of crude oils

The physical characteristics of the Huhehu oils have been reported by Lu et al. (2010), and include low density (0.80 g/cm^3), viscosity (1.93 mPa s), freezing point ($19 \text{ }^\circ\text{C}$), and wax content. These physical properties suggest that the Huhehu oils belong to light crude oil with a low wax content and freezing point (Lu et al. 2010).

4.4.2 Molecular characteristics of crude oil

Gas chromatograms of the representative Huhehu oils are shown in Fig. 10, and the related parameters are listed in Table 4. The n -paraffin distribution of the oil has a wide distribution ($n\text{-C}_{14}\text{--}n\text{-C}_{35}$) with a maximum at about $n\text{-C}_{19}$ to $n\text{-C}_{21}$. The high abundance of low-weight molecular n -alkanes in the oil suggests a lack of significant biodegradation. Low values of $\text{Pr}/n\text{-C}_{17}$ and $\text{Ph}/n\text{-C}_{18}$ ratios also support that the oils are non-biodegraded (Table 4). The plot of $\text{Pr}/n\text{-C}_{17}$ and $\text{Ph}/n\text{-C}_{18}$ indicates that the oils can be divided into three families (Fig. 11). The Pr/Ph ratios for

the oils are in the range of 1.57–4.53, with an average of 2.94, probably indicating a dominant contribution of terrigenous organic matter input deposited under oxic depositional conditions. The group A oils have moderate values of Pr/Ph , ranging from 2.04 to 3.13. The group B oils display relatively low values of Pr/Ph , ranging from 1.57 to 2.02. The group C oils are characterized by high values of Pr/Ph , ranging from 3.24 to 4.53. These data may indicate that group C oils were deposited under more oxic depositional conditions in comparison with group A and B oils.

Figure 12 shows mass chromatograms of the steranes (m/z 217) of saturated hydrocarbon fractions from the representative Huhehu oils. Although the oils from different categories varied in the distribution of regular steranes ($\text{C}_{27}\text{--}\text{C}_{29}$), all the oils show high concentrations of C_{29} steranes, which is indicative of a dominant contribution of terrigenous organic matter (Fig. 13). This is consistent with low hopane/sterane ratios, which often infer terrigenous or microbially reworked organic matter input (Tissot and Welte 1984). In comparison with the oils from the two other groups, the group C oils have relatively high

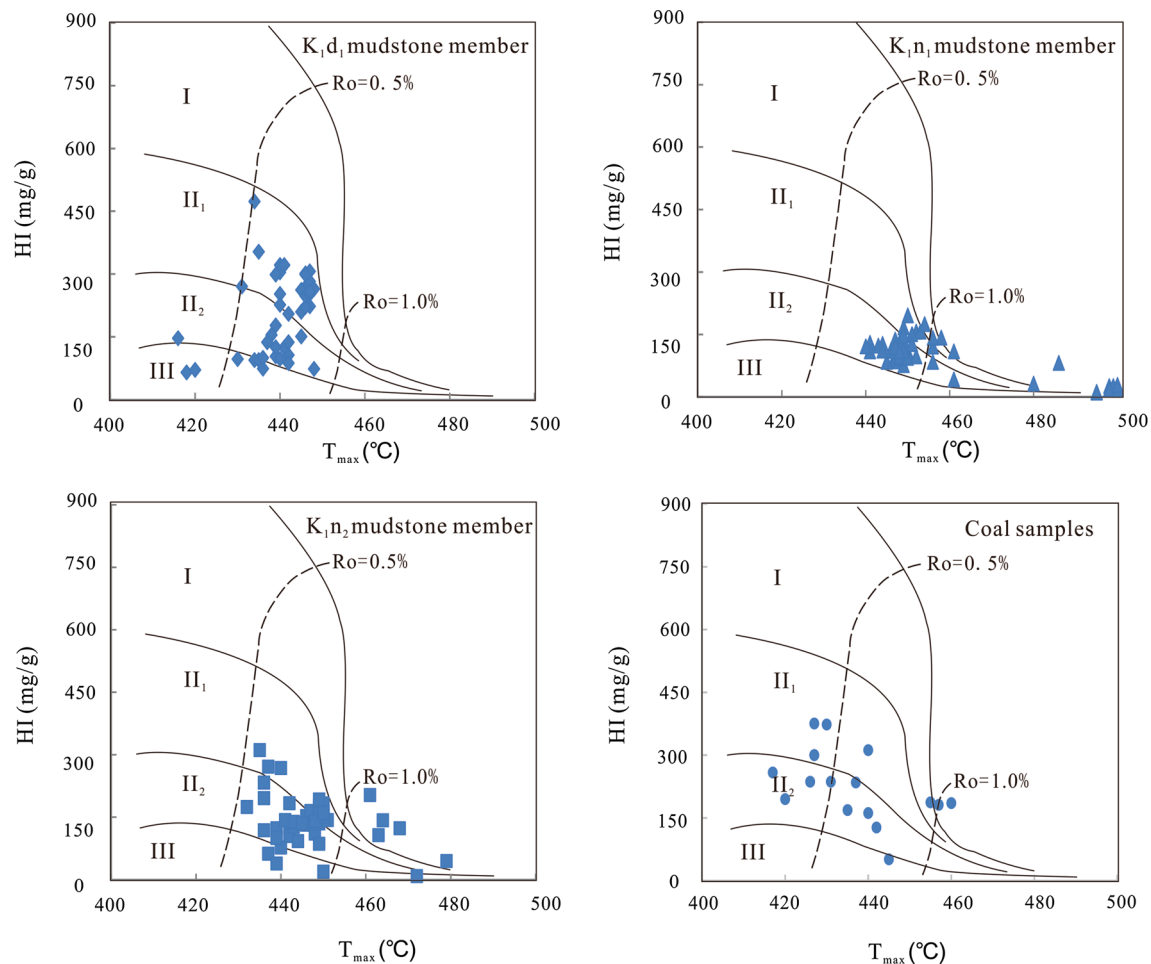


Fig. 4 Plot of hydrogen index (HI) versus T_{max} for the Huhehu source rock showing hydrocarbon generative types

concentrations of C_{29} steranes, probably indicating more terrigenous organic matter input.

Figure 12 displays m/z 191 mass chromatograms of saturated hydrocarbon fractions from the representative Huhehu oils, which clearly display a dominant abundance of pentacyclic terpanes relative to tricyclic terpanes. The low values of C_{35}/C_{34} ratios for the studied crude oils, ranging from 0.05 to 0.45 (Table 4), indicate oxic depositional conditions (Peters and Moldowan 1991). The gammacerane/ $C_{31}R$ ratios of the oils indicate a lack of stratification during source rock deposition.

4.4.3 Thermal maturity of crude oil

The C_{32} homohopane $22S/(22S + 22R)$ ratios for the oils are in the range of 0.50–0.60, indicating that the oils have reached equilibrium (Seifert and Moldowan 1980). Group A oils have high ratios of C_{29} steranes $20S/(20R + 20S)$ and $C_{29} \beta\beta/(\alpha\alpha + \beta\beta)$ (ranging from 0.44 to 0.47 and from 0.45 to 0.53, respectively), indicating that they are mature (Seifert and Moldowan 1986). In comparison, the group C

oils have relatively low values of C_{29} steranes $20S/(20R + 20S)$ and $C_{29} \beta\beta/(\alpha\alpha + \beta\beta)$ (ranging from 0.32 to 0.40 and from 0.32 to 0.42, respectively); and the group B oils have moderate values of C_{29} steranes $20S/(20R + 20S)$ and $C_{29} \beta\beta/(\alpha\alpha + \beta\beta)$ (0.35–0.43 and 0.43–0.49, respectively). Thermal maturity of the crude oils in all the groups decreases overall in the following order: A > B > C (Fig. 14).

4.5 Oil–source rock correlation

The three-dimensional view of PCA was used to identify the relationship between the oils and the candidate source rocks using range scale preprocessing, Euclidean metric distance, and incremental linkage in Pirouette® (Infometrix, Inc.). The first three components of the PCA (PC1, PC2, and PC3) account for 90% of the total variance in the original dataset. As shown in Fig. 15a, three genetic oil families were determined. Group A oils show strong affinity to the K_{1n2} and K_{1n1} mudstones members. The K_{1d1} mudstone member is related to the group B oils, and

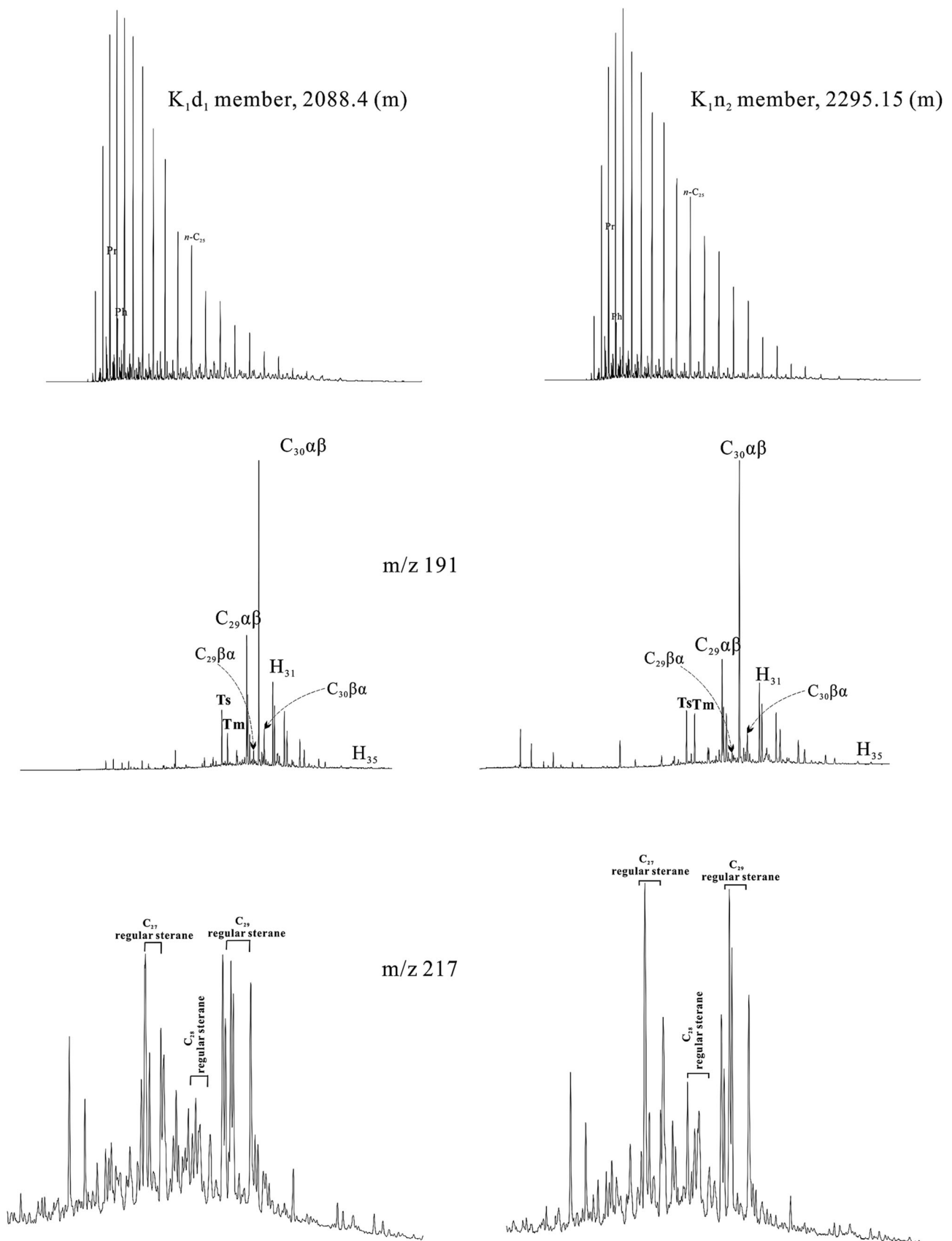


Fig. 5 Representative TIC, hopane (m/z 191), and sterane (m/z 217) mass chromatograms for the source rocks from the K_1d_1 and K_1n_2 members

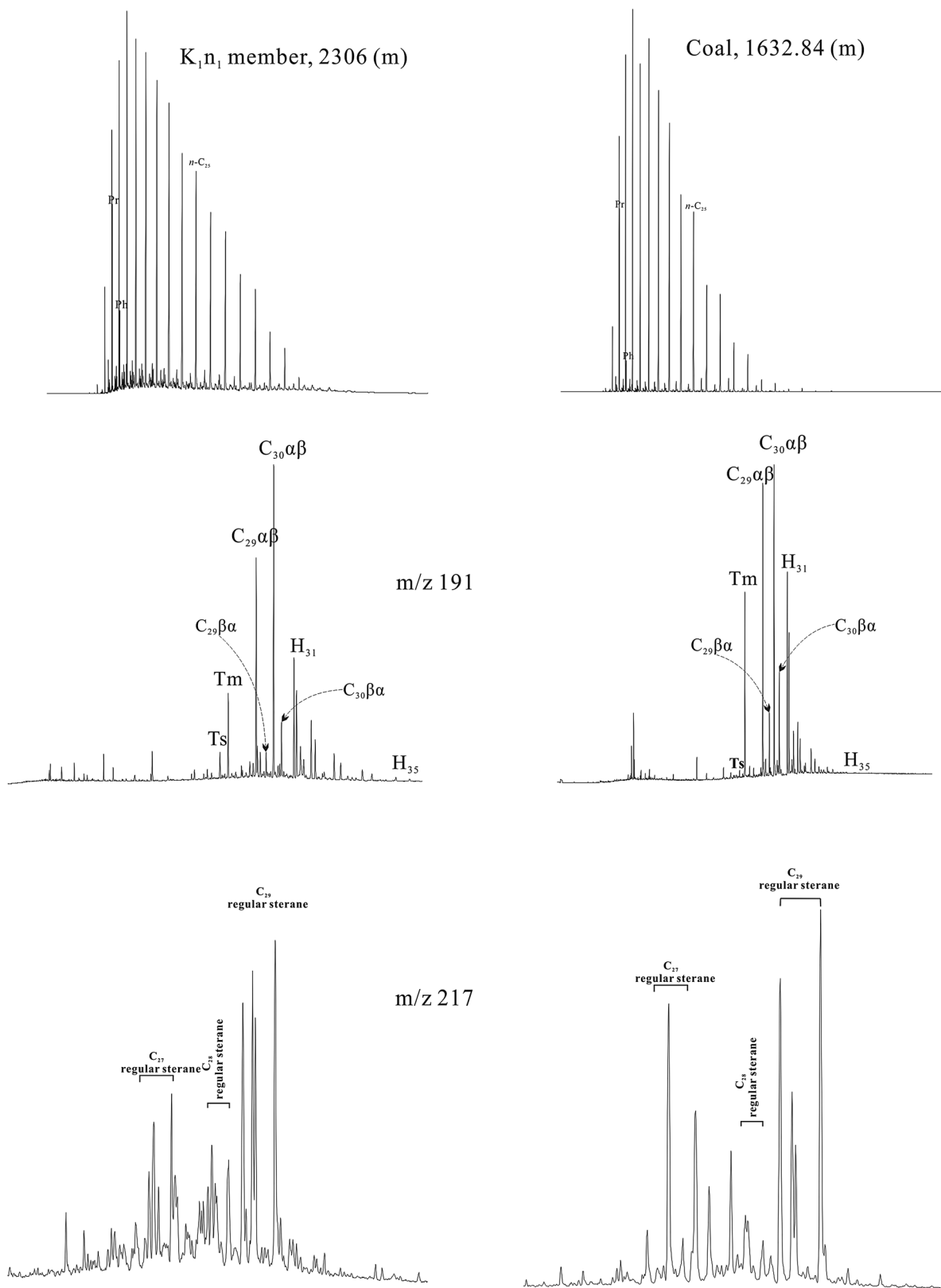


Fig. 6 Representative TIC, hopane (m/z 191), and sterane (m/z 217) mass chromatograms for the source rocks from the K_1n_1 member and coal samples

Table 4 Selected biomarker parameters for the source rock extracts and oils in the Huhuhu Sag

Lab no.	Strata	Lithology	well	Depth (m)	R1#	R2	R3	R4#	R5#	R6	R7#	R8#	R9#	R10#	R11#	R12#	R13#	R14	R15
1	K ₁ d ₁	Mudstone	He-1	1736	1.38	0.52	0.22	0.25	0.8	0.59	0.27	0.21	0.04	0.18	39.55	12.54	47.91	0.22	0.35
2	K ₁ d ₁	Mudstone	X1	2083	1.91	0.29	0.11	0.64	0.41	0.58	0.19	0.32	0.15	0.07	33.77	12.1	54.14	0.54	0.53
3	K ₁ d ₁	Mudstone	X1	2084.3	1.99	0.31	0.13	0.63	0.4	0.58	0.18	0.32	0.09	0.07	34.9	11.56	53.54	0.53	0.52
4	K ₁ d ₁	Mudstone	X1	2086.2	2.12	0.35	0.13	0.66	0.41	0.58	0.18	0.33	0.09	0.08	31.64	12.58	55.78	0.52	0.51
5	K ₁ d ₁	Mudstone	X1	2088.4	1.92	0.31	0.12	0.61	0.42	0.58	0.2	0.25	0.06	0.12	32.58	13.35	54.07	0.53	0.5
6	K ₁ d ₁	Mudstone	X1	2090.4	2.18	0.32	0.11	0.62	0.44	0.58	0.19	0.3	0.1	0.08	35.28	11.76	52.96	0.54	0.51
7	K ₁ d ₁	Mudstone	X1	2091.5	2.04	0.31	0.12	0.61	0.44	0.58	0.21	0.28	0.07	0.08	35.25	11.31	53.44	0.53	0.52
8	K ₁ d ₁	Mudstone	He-5	1707.1	1.75	0.54	0.17	0.9	0.78	0.57	0.47	0.22	0.01	0.17	26.09	14.42	59.49	0.2	0.3
9	K ₁ d ₁	Mudstone	He-5	1708.7	1.83	0.59	0.18	0.89	0.79	0.57	0.45	0.2	0.04	0.16	27.19	14.36	58.45	0.2	0.31
10	K ₁ d ₁	Mudstone	He-5	1894	2.39	0.7	0.18	0.25	0.58	0.58	0.26	0.37	0.01	0.22	33.46	24.56	41.98	0.35	0.39
11	K ₁ d ₁	Mudstone	He-5	1920	1.73	0.33	0.12	0.11	0.79	0.58	0.37	0.33	0.05	0.2	31.17	13.97	54.86	0.29	0.45
12	K ₁ d ₁	Mudstone	He-5	1966	1.68	0.46	0.16	0.35	0.64	0.6	0.27	0.33	0.04	0.14	33.46	12.93	53.61	0.37	0.46
13	K ₁ d ₁	Mudstone	He-8	2126.7	1.35	0.34	0.15	0.16	0.62	0.61	0.28	0.26	0.04	0.19	35.18	13.36	51.46	0.55	0.48
14	K ₁ d ₁	Mudstone	He-8	2127.6	1.43	0.32	0.09	0.25	0.59	0.6	0.27	0.31	0.06	0.21	38.03	14.1	47.87	0.53	0.5
15	K ₁ d ₁	Mudstone	He-8	2131.1	1.41	0.29	0.14	0.38	0.5	0.6	0.24	0.33	0.06	0.2	39.4	14.08	46.52	0.53	0.49
16	K ₁ d ₁	Mudstone	He-8	2135.2	1.25	0.23	0.11	0.42	0.47	0.6	0.23	0.32	0.05	0.2	41.51	13.67	44.82	0.55	0.5
17	K ₁ n ₂	Mudstone	X1	2295.2	2.82	0.42	0.11	0.51	0.35	0.58	0.2	0.29	0.09	0.19	33.02	14.37	52.61	0.51	0.46
18	K ₁ n ₂	Mudstone	X1	2297	2.81	0.41	0.11	0.48	0.35	0.58	0.19	0.26	0.07	0.17	29.74	15.07	55.19	0.55	0.49
19	K ₁ n ₂	Mudstone	X1	2299	2.74	0.47	0.12	0.42	0.36	0.59	0.21	0.28	0.1	0.19	30.99	15.29	53.72	0.54	0.48
20	K ₁ n ₂	Mudstone	X1	2309.4	2.08	0.79	0.26	0.39	0.46	0.59	0.18	0.3	0.05	0.3	28.95	13.32	57.73	0.56	0.48
21	K ₁ n ₂	Mudstone	X1	2319.5	2.88	0.47	0.12	0.44	0.39	0.59	0.21	0.28	0.08	0.22	25.45	16.97	57.58	0.53	0.49
22	K ₁ n ₂	Mudstone	He-5	2104	1.53	0.87	0.4	0.22	0.88	0.59	0.29	0.27	0.12	0.3	25.49	15.4	59.1	0.49	0.47
23	K ₁ n ₂	Mudstone	He-5	2016	1.81	1.55	0.32	0.07	1.22	0.6	0.38	0.28	0.08	0.16	21.41	13.02	65.57	0.44	0.46
24	K ₁ n ₂	Mudstone	He-7	2040.9	2.65	0.45	0.13	0.12	0.99	0.59	0.3	0.29	0.11	0.09	24.75	15.09	60.15	0.39	0.48
25	K ₁ n ₂	Mudstone	He-7	2042.1	2.86	0.87	0.16	0.05	1.01	0.6	0.32	0.29	0.04	0.13	25.51	11.54	62.95	0.38	0.49
26	K ₁ n ₂	Mudstone	He-9	1589.4	2.6	0.98	0.22	0.08	1.22	0.57	0.41	0.32	0.02	0.14	24.45	12.94	62.61	0.29	0.41
27	K ₁ n ₂	Mudstone	He-9	2014.1	4.07	0.44	0.07	0.28	0.45	0.59	0.3	0.39	0.05	0.21	22.78	13.76	63.46	0.55	0.5
28	K ₁ n ₂	Mudstone	He-9	2017.1	1.43	0.58	0.14	0.35	0.43	0.58	0.25	0.33	0.1	0.27	29.24	16.04	54.72	0.62	0.5
29	K ₁ n ₂	Mudstone	He-9	2017.6	2.07	1.14	0.17	0.37	0.41	0.59	0.22	0.26	0.07	0.34	23.65	15.53	60.82	0.61	0.5
30	K ₁ n ₁	Mudstone	He-2	1679.5	3.24	0.99	0.2	0.35	0.5	0.6	0.17	0.26	0.08	0.14	33.95	16.22	49.83	0.55	0.49
31	K ₁ n ₁	Mudstone	He-5	2306	2.24	0.82	0.2	0.24	0.62	0.59	0.28	0.33	0.23	0.24	24.38	18.18	57.45	0.4	0.44
32	K ₁ n ₂	coal	He-5	2240.7	3.93	2.52	0.3	0.3	0.46	0.6	0.28	0.29	0.08	0.34	15.08	14.11	70.82	0.35	0.34
33	K ₁ n ₂	coal	He-5	2243.7	3.45	1.96	0.26	0.86	0.47	0.6	0.25	0.28	0.07	0.3	16.07	15.93	68	0.34	0.34
34	K ₁ n ₂	coal	He-9	1632.8	5.17	0.66	0.1	0.95	0.88	0.61	0.45	0.19	0.08	0.25	28.19	13.72	58.09	0.29	0.27
35	K ₁ n ₁	coal	He-5	2237.5	2.46	3.47	0.3	0.26	0.56	0.6	0.3	0.29	0.13	0.45	12.27	13.63	74.11	0.44	0.37

Group A

Table 4 continued

Lab no.	Strata	Lithology	well	Depth (m)	R1#	R2	R3	R4#	R5#	R6	R7#	R8#	R9#	R10#	R11#	R12#	R13#	R14	R15
36	K _{1n1}	oil	He-2	1669.00-1649.80	2.04	0.31	0.14	0.56	0.45	0.57	0.17	0.44	0.1	0.34	22.07	16.2	61.73	0.46	0.49
37	K _{1n1}	oil	He-2	1669.00-1841.80	2.17	0.22	0.11	0.65	0.48	0.59	0.2	0.3	0.1	0.31	27.93	15.96	56.11	0.44	0.53
38	K _{1n2}	oil	He-9	1604.3	2.9	0.35	0.12	0.23	0.72	0.59	0.32	0.36	0.08	0.25	22.92	13.8	63.28	0.45	0.45
39	K _{1n1}	oil	He-2	1652.7	3.13	0.43	0.1	0.43	0.47	0.6	0.23	0.44	0.06	0.25	25.97	16.73	57.3	0.47	0.48
Group B																			
40	K _{1n2}	oil	He-2	1550.3	1.67	0.56	0.16	0.85	1.17	0.56	0.38	0.1	0.03	0.15	25.6	24.34	50.06	0.43	0.48
41	K _{1n2}	oil	He-2	1550.3	2.02	0.61	0.16	0.85	1.23	0.54	0.37	0.05	0.03	0.11	20.66	27.94	51.4	0.43	0.44
42	K _{1n2}	oil	He-2	1550.3	1.78	0.54	0.16	0.83	1.23	0.55	0.4	0.45	0.04	0.13	25.38	23.14	51.48	0.4	0.49
43	K _{1n2}	oil	He-2	1550.3	1.57	0.44	0.14	0.85	1.14	0.55	0.37	0.2	0.06	0.11	24.68	21.84	53.48	0.35	0.43
Group C																			
44	K _{1n2}	oil	He-6	1492.6	4.12	2.15	0.29	0.9	0.91	0.56	0.53	0.42	0.04	0.17	13.15	17.14	69.71	0.37	0.4
45	K _{1n2}	oil	He-6	1492.6	3.24	2.08	0.31	0.87	0.86	0.5	0.42	0.24	0.04	0.17	11	13.78	75.22	0.32	0.34
46	K _{1n2}	oil	He-6	1492.6	4.53	2.24	0.32	0.82	0.91	0.5	0.52	0.12	0.03	0.19	12.69	21.77	65.54	0.36	0.32
47	K _{1n2}	oil	He-6	1492.6	3.71	2.19	0.32	0.84	0.88	0.5	0.41	0.42	0.05	0.17	12.49	21.69	65.83	0.34	0.36
48	K _{1n2}	oil	He-6	1492.6	3.91	1.85	0.28	0.84	0.85	0.55	0.39	0.17	0.03	0.14	15.61	20.91	63.48	0.33	0.33
49	K _{1n2}	oil	He-6	1492.6	3.37	1.73	0.28	0.85	0.87	0.52	0.37	0.07	0.06	0.13	17	16.45	66.55	0.34	0.4
50	K _{1n2}	oil	He-6	1492.6	3.93	2.36	0.34	0.86	0.84	0.56	0.36	0.33	0.05	0.15	16.58	21	62.41	0.4	0.42

Those marked parameters with star are used in the cluster analysis, principal component analysis. R1 = pristane/phytane; R2 = pristane/n-C₁₇; R3 = phytane/n-C₁₈; R4 = Ts/(Ts + Tm); R5 = C₂₉ hopane/C₃₀ hopane; R6 = C₃₂ 22S/(22S + 22R) homohopane isomerization; R7 = C₃₁ 22R/C₃₀ hopane; R8 = C₃₅/C₃₄ homohopanes; R9 = gammacerane/C₃₁ 22R hopane; R10 = steranes/hopanes; R11 = %C₂₇ (e.g., %C₂₇/(%C₂₇+%C₂₉)); R12 = %C₂₈; R13 = %C₂₉; R14 = C₂₉ ββ/(αα + ββ); R15 = C₂₉ steranes 20S/(20R + 20S). These parameters can be referred to Peters et al. (2005) in detail

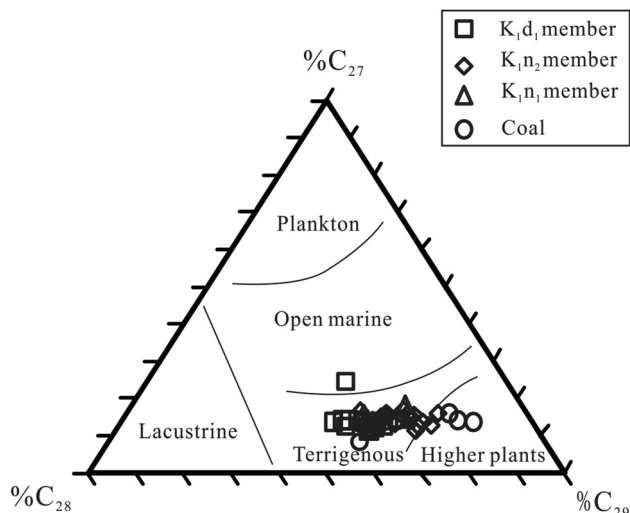


Fig. 7 Ternary diagram showing relative abundance of the C₂₇, C₂₈, and C₂₉ regular steranes in the saturated fraction of the Huhehu source rock extract

the group C oils is linked to the K₁n₂ coal member (Fig. 15a). Figure 15b shows the relative contribution from each of the 11 biomarker ratios to PC1, PC2, and PC3. The biomarker ratios of Ts/(Ts + Tm) and C₃₅/C₃₄ have large positive loadings on PC1. PC1 could be interpreted as an indicator of more reducing depositional conditions since the Ts/(Ts + Tm) ratio is a source-related parameter at lower maturity (Wang et al. 2018), and the C₃₅/C₃₄ ratio generally reflects anoxic depositional conditions (Peters and Moldowan 1991). The loadings on PC2 are dominated by a positive correlation with C₂₉ hopane/C₃₀ hopane and C₃₁ 22R/C₃₀ hopane ratios and a negative correlation with %C₂₇, which is indicative of more marine organic matter

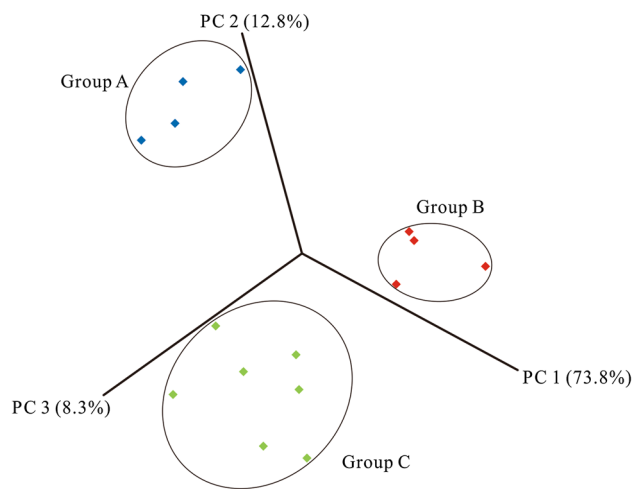
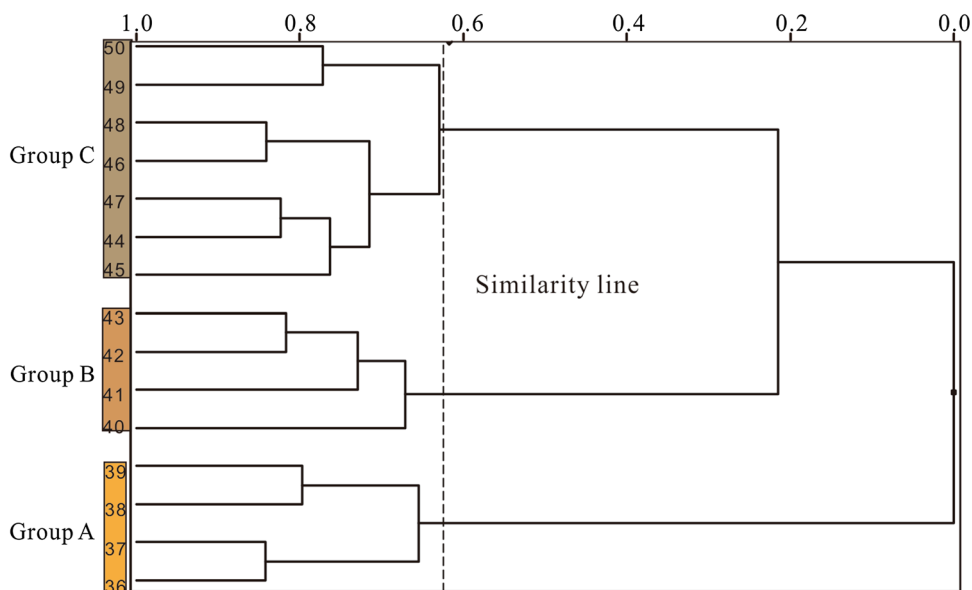


Fig. 9 Separation of the Huhehu oils into three different genetic oil families based on the principal component analysis (PCA) of nine source- and age-related biomarker ratios

input (Huang and Meinschein 1979; Peters et al. 2005). The loadings on PC3 mainly show a positive correlation with Pr/Ph and %C₂₉ and a negative correlation with %C₂₇. Thus, PC3 indicates more oxic depositional conditions (Didyk et al. 1978) and terrigenous organic matter input (W Huang and Meinschein 1979).

Geological evidence also provides support for geochemical oil-source correlations in the Huhehu Sag. For example, the discovered oils are mainly distributed in wells He-2 and He-6 (Table 4). The burial depths of the coal seams in He-2 and He-6 are in the range of 570 to 1600 m and 570 to 1550 m (Qu 2005), respectively. Such evidence indicates that group A oils are mainly derived from the K₁n mudstone Formation rather than from the coal formation

Fig. 8 Separation of the Huhehu oils into three different genetic oil families based on the hierarchical cluster analysis of nine source- and age-related biomarker ratios



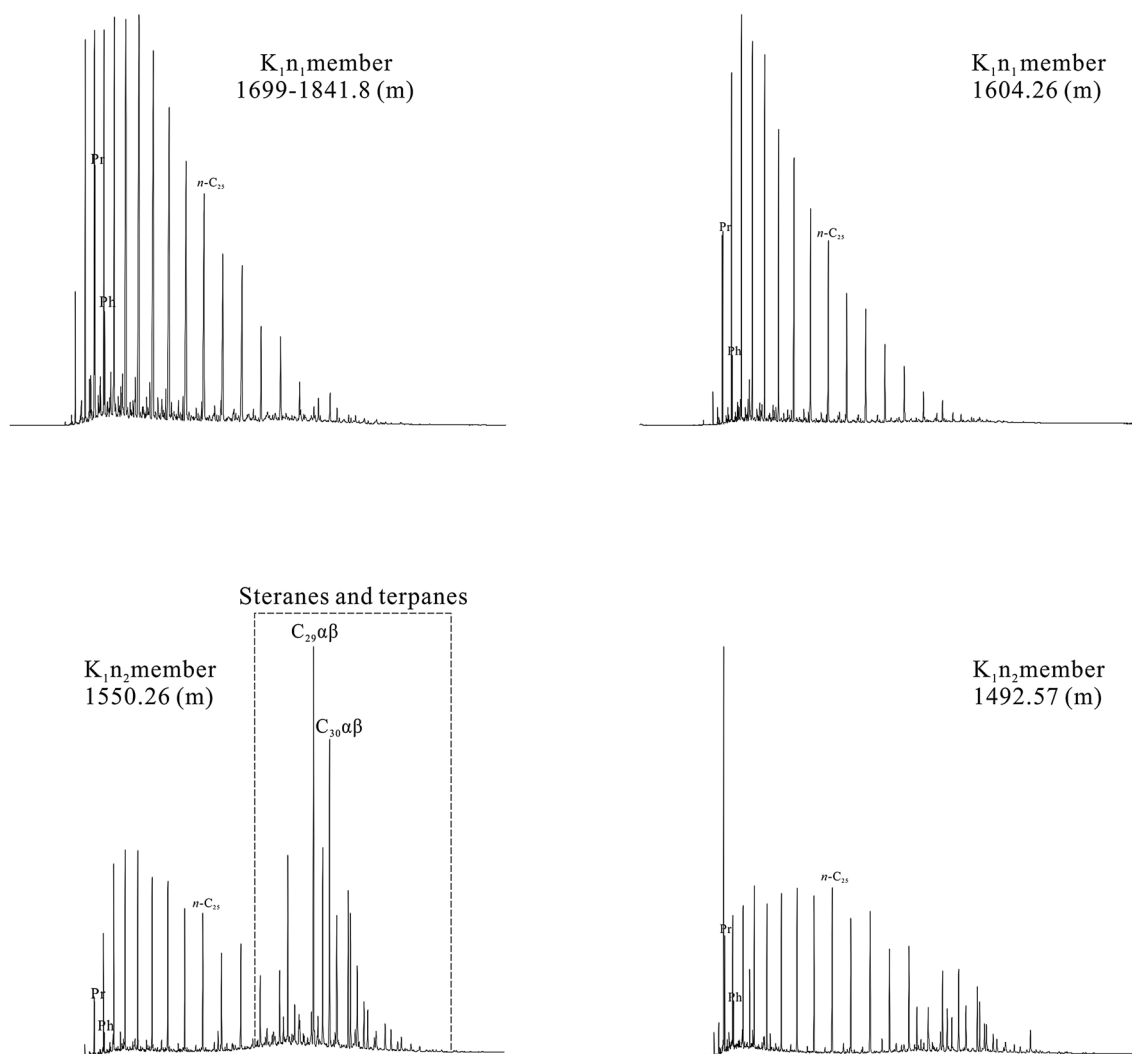


Fig. 10 Whole oil gas chromatograms of the Huhehu oils showing the relative distribution of *n*-paraffins

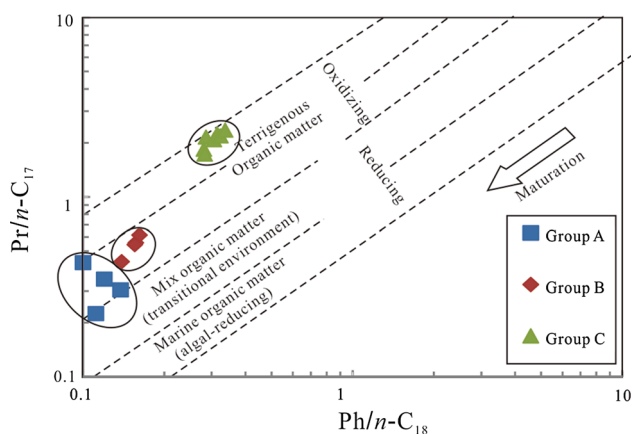


Fig. 11 Plot of $Pr/n-C_{18}$ versus $Ph/n-C_{17}$ for the Huhehu oils showing genetic oil categories and depositional conditions

because oils from group A have greater embedded depths (> 1600 m). In contrast, the depth of the group C oils is

within the coal seam distribution. Accordingly, the group C oils have good correlation with the coal extracts from the K_{1n2} member.

The oil–source rock correlation results are consistent with the thermal maturity of the Huhehu oils and source rocks (Fig. 11). For example, the group A oils have relatively high maturity and show a strong affinity to the relatively high maturity source rocks of the K_{1n2} and K_{1n1} mudstone members. Similar observations could be made for the group B and group C oils.

As discussed earlier, the K_{1d1} and K_{1n2} mudstone samples have moderate to high hydrocarbon generative potential, while the K_{1n1} mudstone member and K_{1n1} and K_{1n1} coal samples are relatively less promising and show poor-to-good and poor-to-fair hydrocarbon generation potential, respectively. The K_{1n2} coal member has a certain hydrocarbon-generating potential, but the K_{1n1} coal member is less promising, which is consistent with a

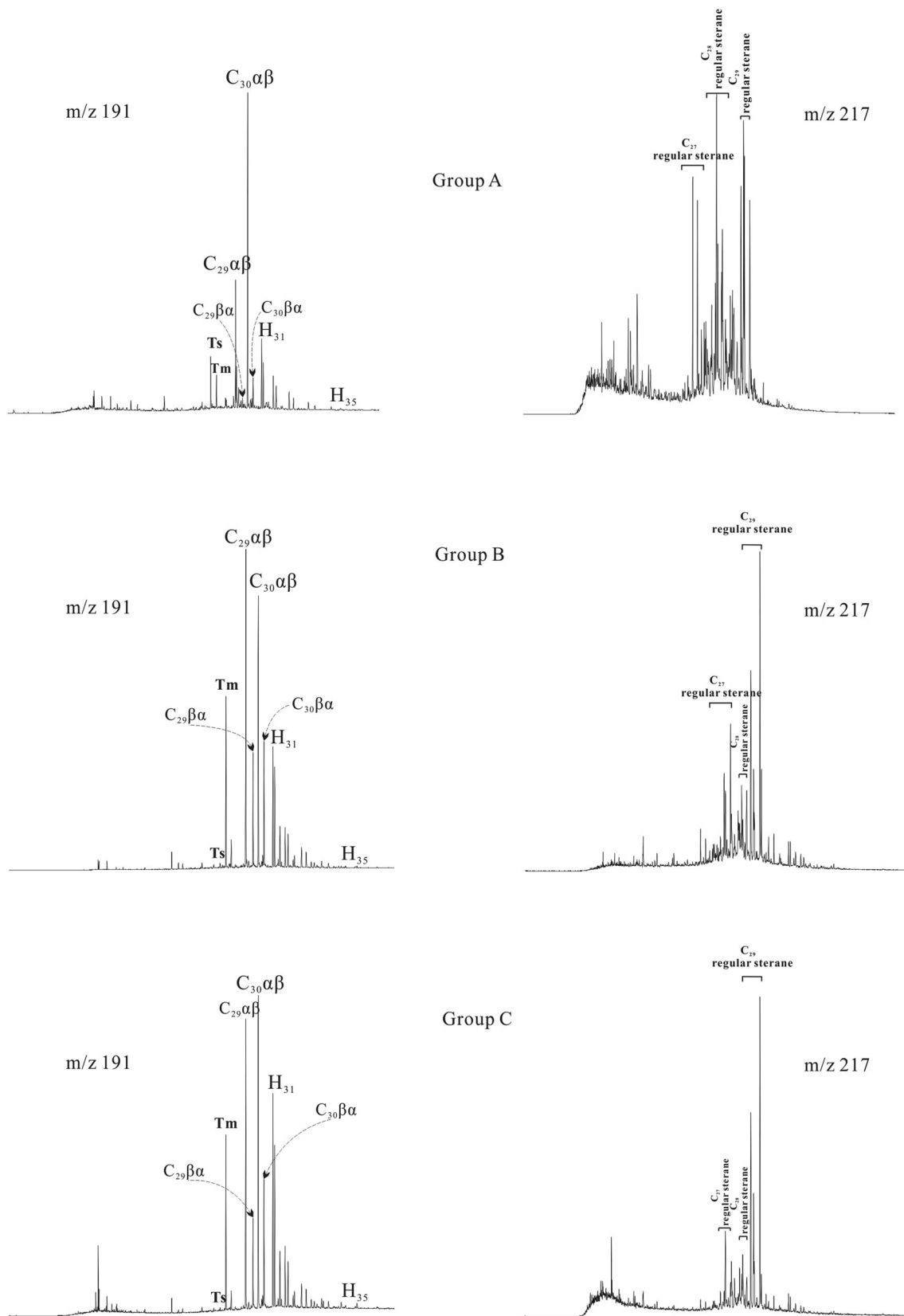


Fig. 12 Mass chromatograms (m/z 191 and 217) for the representative Huhehu oils

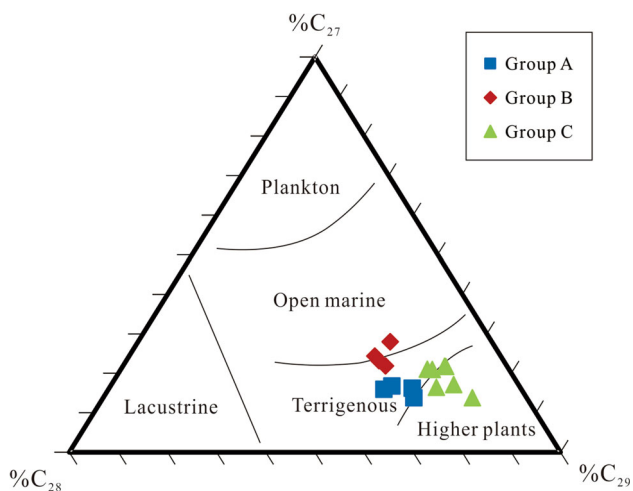


Fig. 13 Ternary diagram showing the relative abundance of the C₂₇, C₂₈, and C₂₉ regular steranes in the saturated fraction of the Huhehu oils

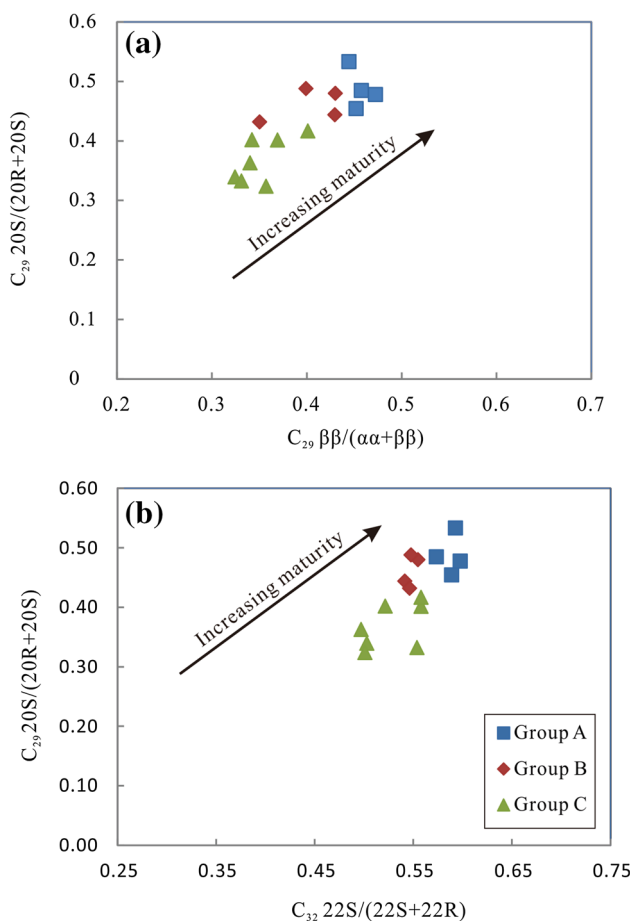


Fig. 14 Plots of C₂₉ steranes $\beta/(\alpha + \beta)$ versus C₂₉ steranes 20S/(20R + 20S) (a) and C₃₂ homohopane 22S/(22S + 22R) versus C₂₉ steranes 20S/(20R + 20S) (b) showing thermal maturity level of the Huhehu oils

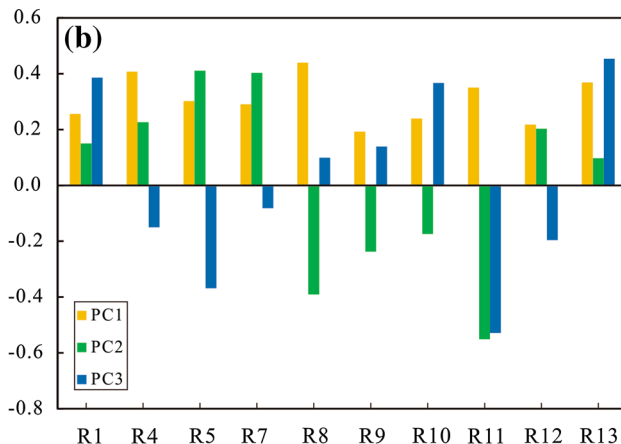
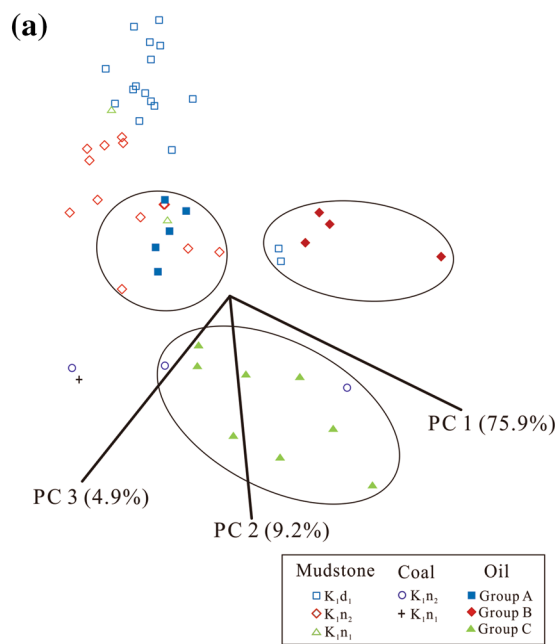


Fig. 15 The three Huhehu oil families (scores) and biomarker variables (loadings) employed in the principal component analysis. R1 = pristane/phytane; R4 = Ts/(Ts + Tm); R5 = C₂₉ hopane/C₃₀ hopane; R7 = C₃₁ 22R/C₃₀ hopane; R8 = C₃₅/C₃₄ homohopanes; R9 = gammacerane/C₃₁ 22R hopane; R10 = steranes/hopanes; R11 = %C₂₇ (e.g., %C₂₇/(%C₂₇–%C₂₉)); R12 = %C₂₈; R13 = %C₂₉

previous study (Liu 2010). Therefore, the hydrocarbon generation potential of the source rocks supports the results of the oil–oil and oil–source rock correlations in the present study. Future assessment of petroleum potential or exploration of the Huhehu Sag can be assisted by considering the proposed genetic relationship between the crude oils and source rocks. The results of oil–oil and oil–source rock correlation in the Huhehu Sag suggest that the K_{1n} Formation and K_{1d1} member are promising for future exploration.

5 Conclusions

Based on Rock–Eval pyrolysis data, mudstones from the K_{1d_1} and K_{1n_2} members have moderate to high hydrocarbon generating potential, while the K_{1n_1} mudstone member and coals from the K_{1n_2} and K_{1n_1} members in this region have relatively less potential.

Based on chemometric analysis and biomarker characteristics, we divided the Huhehu oils into three groups. Group A oils have relatively high maturity and are characterized by moderate values of Pr/Ph, low values of Pr/ n - C_{17} and Ph/ n - C_{18} , and moderate concentrations of C_{29} sterane, while group B oils have moderate maturity, low values of Pr/Ph, moderate values of Pr/ n - C_{17} and Ph/ n - C_{18} , and low concentrations of C_{29} sterane. Group C oils have low maturity; relatively high values of Pr/Ph, Pr/ n - C_{17} , and Ph/ n - C_{18} ; and low concentrations of C_{29} sterane. The oil–source rock correlation based on PCA analysis suggests group A oils are derived from the K_{1n_2} and K_{1n_1} mudstone members, while group B oils can be ascribed to the K_{1d_1} mudstone member, and group C oils to the K_{1n_2} coal member. These results suggest that not only the K_{1n} Formation, but also the K_{1d_1} member, are good prospects for hydrocarbon exploration.

Acknowledgements This study was funded by the Natural Science Funding Council of China (Grant Nos. 41273059), GIGCAS 135 project (Grant No. Y234021001) and Earmarked Fund of the State Key Laboratory of Organic Geochemistry (Grant No. sklog2016-A01). The authors are deeply indebted to two anonymous reviewers who provided constructive reviews in our original manuscript. We also wish to acknowledge managing editor Wang Binbin for the timely handling with the manuscript.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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