Four series of rearranged hopanes in the Mesoproterozoic sediments

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ARTICLE INFO

ABSTRACT

Analysis of the Mesoproterozoic molecular markers by gas chromatography–mass spectrometry (GC–MS) and GC–MS metastable reaction monitoring (MRM) revealed four series of rearranged hopanes in the solvent extractable hydrocarbons of the 1.45 billion-year-old Hongshuizhuang and 1.32 billion-year-old Xiamaling formations, the North China Craton. It includes $17\alpha(H)$-diahopane ($C_{27}D$ and C_{29}-$C_{35}D$), $18\alpha(H)$-neohopane ($C_{27}Ts$ and $C_{29}Ts$), early eluting rearranged hopane ($C_{27}E$, C_{29}-$C_{35}E$), and 28-nor-spergulane ($C_{29}Nsp$). The strong positive correlations between different parameters (e.g. $C_{29}D/C_{29}H$, $C_{30}D/C_{30}H$, $C_{30}E/C_{30}H$, $C_{29}Nsp/C_{29}H$ and $C_{29}Ts/C_{29}H$) indicate an identical genetic biological source and similar formation mechanism. The rearranged hopanes may not originate from widespread bacteria but from the bacterial communities living in a specific environment, which are probably restrained by high salinity water conditions. The variable concentration of rearranged hopanes in the Mesoproterozoic sediments, particularly the extremely low abundance in the sediment of the Gaoyuzhuang Formation (1.56 Ga), is mainly controlled by biological source and sedimentary environment rather than clay minerals. Moreover, the four series of rearranged hopanes could serve as the effective molecular fossils for recognizing the Proterozoic oils in the North China Craton.

1. Introduction

Regular hopanes namely $17\alpha(H),21\beta(H)$-hopanes are widely distributed in sediments and crude oils with a carbon number range of C_{27}-C_{35}, which are thought to be mainly derived from bacteriohopanetetrol in the cell wall of prokaryotic organisms (Ourisson et al., 1984). In addition to the ubiquitous regular hopanes, rearranged hopanes were also detected and identified in sediment extracts and/or crude oils from Phanerozoic basins, mainly including $18\alpha(H)$-neohopane (e.g. $C_{27}Ts$ and $C_{29}Ts$) (Smith, 1975; Killops and Howell, 1991; Moldowan et al., 1991; Farrimond and Telnæs, 1996), $17\alpha(H)$-diahopane ($C_{27}D$ and C_{29}-$C_{35}D$) (Philp and Gilbert, 1986; Killops and Howell, 1991; Moldowan et al., 1991), early eluting rearranged hopane ($C_{27}E$, C_{29}-$C_{35}E$) (Telnaes et al., 1992; Nytoft et al., 2007), and 28-nor-spergulane (e.g. $C_{29}Nsp$) (Nytoft et al., 2006). Moreover, a lot of discussion were carried out on their biological precursors, formation mechanisms, influencing factors and geochemical implications (Killops and Howell, 1991; Moldowan et al., 1991; Armanios et al., 1992;

Telnaes et al., 1992; Farrimond and Telnæs, 1996; Nytoft et al., 2006; Jiang and Zhang, 2015; Jin et al., 2019; Xiao et al., 2019). Most popularly, the rearranged hopanes and regular hopanes have similar molecular structure and carbon isotopic data, which are considered to be derived from the common precursors of bacteriohopanetetrol in prokaryotic organisms (mainly heterotrophic bacteria or cyanobacteria) (Moldowan et al., 1991). And their unsaturated precursors are easily formed by acidic catalysis rearrangement in the suboxic depositional conditions (Moldowan et al., 1991; Zhu et al., 2007a; Ruble et al., 2019; Xiao et al., 2019). Furthermore, because the rearranged hopanes have the characteristics of higher thermal stability than regular hopanes, they can be reliable maturity parameters in the stage of mature to high mature (Moldowan et al., 1991; Wang et al., 2000; Li et al., 2009; Chen and Zhang, 2016; Jiang et al., 2017; Ruble et al., 2019). To put it simply, high maturity is conducive to their enrichment in geological samples (Zhu et al., 2007a). Oppositely, Xiao et al. (2004) concluded that abundant occurrence of rearranged hopanes in the oils from the Tarim Basin is not related to maturity, but may be controlled by specific

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depositional environments. Especially, a moderate-salinity lacustrine depositional environment can promote the process of rearrangement reaction (Xiao et al., 2004). But Philp and Gilbert (1986) proposed that the high abundance of 17α(H)-diahopanes in the oils from the Korea Bay Basin is mainly controlled by biological sources, and possibly closely related to the inputs of terrigenous land plant material (Philp and Gilbert, 1986) and/or generated from bacterially reworked terrigenous organic matter (Killops and Howell, 1991; Xiao et al., 2019). In addition, the enrichment of rearranged hopanes in severely biodegraded crude oils relative to regular hopanes is sometimes also attributed to their stronger resistance to biodegradation (Armanios et al., 1992; Xiao et al., 2019).

In summary, the rearranged hopanes have been detected and studied for decades, but almost all of them were found in the Phanerozoic sediments (or related oils) deposited in various sedimentary environments. So far, four series of rearranged hopanes are rarely discovered simultaneously in the Precambrian geological samples, and even if they exist, only two series of 18α(H)-neohopane and 17α(H)-diahopane were reported (Summons et al., 1988a; Summons et al., 1988b; Zhang et al., 2007). Importantly, biomarkers have gradually become important in the study of the early environmental evolution and the origin of life on the earth (Bobrovskiy et al., 2018a; Bobrovskiy et al., 2018b; Zumberge et al., 2018). In the present paper, we focus on the presence of four series of rearranged hopanes in the sediments of the Mesoproterozoic Gaoyuzhuang Formation (1.56 Ga), Hongshuizhuang Formation (1.45 Ga), and Xiamaling Formation (1.32 Ga) in the North China Craton. Furthermore, we proposed that the distribution characteristics of rearranged hopanes in the Mesoproterozoic sediments mainly depend on the primitive biotic community and depositional conditions rather than clay minerals.

2. Geological setting

The Yanliao Faulted-Depression Zone (YFDZ) is an northern component of the North China Craton (NCC) (Fig. 1), which well develops the Meso- and Neoproterozoic sequences with a thickness of about 10 km (Luo et al., 2014; Wang and Gong, 2018). More than 200 Precambrian primary oil seepages have been discovered in the YFDZ till now and mainly distributed in the Xuanlong, Jibei and Liao depressions

(Liu et al., 2011). Although no commercial hydrocarbon accumulations has been discovered so far, a large number of oil seepages preserved in Precambrian strata indicate a good prospect for petroleum exploration in the study area (Sun and Wang, 2016). The NCC experienced a stable platform development period of nearly 1.0 billion years from the Mesoproterozoic to the Cambrian, during which a set of thick marine carbonate-clastic rocks sequence was deposited. Generally, the Meso- and Neoproterozoic strata in the NCC consists of five systems, namely the Changcheng System (1800– 1600 Ma), Jixian System (1600– 1400 Ma), Jinzhou System (1400– 1200 Ma), Unnamed System (1200– 1000 Ma) and Qingbaikou System (1000– 780 Ma) (Gao et al., 2010; Li et al., 2010b; Li et al., 2010a; Niu and Xin, 2013). They can be further divided into twelve formations, from bottom to top as the Changzhougou, Chuanlinggou, Tuanshanzi, Dahongyu, Gaoyuzhuang, Yangzhuang, Wumishan, Hongshuizhuang, Tieling, Xiamaling, Luotuoling and Jingeryu formations (Li et al., 2010a). Previous studies have revealed that the black argillaceous dolomite of the Gaoyuzhuang Formation, the black shale of the Hongshuizhuang Formation and the Xiamaling Formation contain high abundance of organic matter, which can be potential source rocks in the YFDZ (Luo et al., 2016; Sun and Wang, 2016; Zhao et al., 2019). However, except in the Xuanlong Depression, the source rock within the Xiamaling Formation in other depressions had prematurely lost their ability of hydrocarbon generation because of the influence of magma intrusion (Sun and Wang, 2016). In the study, we mainly pay attention to the distribution characteristics and geological implications of rearranged hopanes in typical black argillaceous dolomite of the Gaoyuzhuang Formation, the black shale of the Hongshuizhuang and the Xiamaling formations.

3. Samples and analytical methods

3.1. Samples

The locations of all sampling wells and sections are illustrated in Fig. 1. Four outcrop samples of the Xiamaling Formation from XHY section in the Xuanlong Depression (Fig. 2a). Their T_{max} and TOC values are in the range of 434– 442 °C and 6.43– 12.59%, respectively (Table 1). The samples are black oil shales with high abundance of organic matter and still in the low thermal maturity, which are excellent
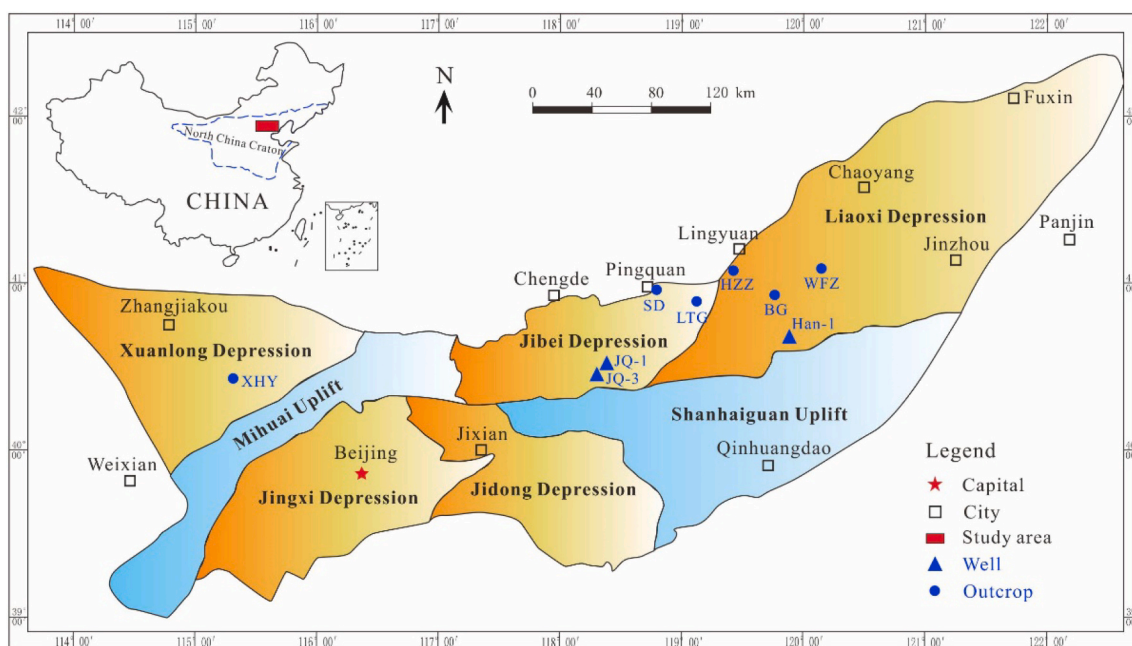

Fig. 1. Map of geographic location and tectonic units of the Yanliao Faulted-Depression Zone, and locations of the sampled wells and field sections.

Fig. 2. Representative rock samples photographs of the Xiamaling Formation from the XHY section (a), Hongshuizhuang Formation from the JQ-1 well (b), and Gaoyuzhuang Formation from the JQ-3 well (c).

Table 1
Analytical data for the Mesoproterozoic sediments.

No.	Wells/sections	Formation	TOC (%)	$S_1 + S_2$ (mg/g)	T_{max} (°C)
1	XHY	Xiamaling	6.43	25.67	434
2	XHY	Xiamaling	12.10	66.02	438
3	XHY	Xiamaling	7.36	36.20	442
4	XHY	Xiamaling	12.59	56.84	436
5	JQ-1	Hongshuizhuang	4.44	13.84	450
6	JQ-1	Hongshuizhuang	1.09	3.32	451
7	JQ-1	Hongshuizhuang	1.63	3.20	451
8	JQ-3	Gaoyuzhuang	0.41	0.21	509
9	JQ-3	Gaoyuzhuang	0.44	0.28	501

Note: TOC: total organic carbon; $S_1 + S_2$: genetic potential; T_{max}: temperature at maximum generation.

samples for studying Precambrian molecular fossils. Three core samples from JQ-1 well (Table 1 and Fig. 2b) were selected from the Hongshuizhuang Formation. These black mudstones of the Hongshuizhuang Formation contain moderate to high organic matter abundance with the TOC range value of 1.09–4.44%, and are still in mature stage with the T_{max} average value of 451 °C. In addition, two black argillaceous dolomite core samples of the Gaoyuzhuang Formation from JQ-3 well (Fig. 2c) also were geochemically analyzed.

In addition, six core samples in Han-1 well and eleven outcrop samples (WFZ, BG and HZZ sections) from the Hongshuizhuang Formation were analyzed to discuss the influence of depositional environment on the distribution of rearranged hopanes. Moreover, the solid bitumen from the Wumishan Formation in the Shuangdong section (SD), oil-seepages from the Tieling Formation in JQ-1 well and bituminous sandstones from the Xiamaling Formation in the Longtangou section (LTG) (Fig. 1) were also collected for the analysis of oil to source rock correlation.

3.2. Preparation for experiments

The sediments within the Xiamaling and Hongshuizhuang formations in the NCC are not only rich in organic matter, but also in a low and moderate degree of thermal maturity, respectively. In order to further ensure the syngeneity and indigeneity of soluble extractable hydrocarbons, we have carried out the following treatments: (1) Laboratory glassware cleaning: all glassware involved in the whole experiment were thoroughly washed with detergent, deionized water, the oxidizing mixture of potassium dichromate and concentrated sulfuric acid; (2) Reagents purification and laboratory material: all reagents (e.g. dichloromethane, petroleum ether and *n*-hexane) and materials (e.g. filter papers, silica gel, alumina) were redistilled and extracted, respectively; (3) Decontamination of core samples: a minor portion of rock surface was removed by abrasive paper, and further soaked and washed with dichloromethane (CH_2Cl_2); (4) Blank experiment analysis: a blank experiment analysis was conducted under the same conditions to exclude potential contamination in laboratory instruments.

3.3. GC–MS and GC–MS-MS analyses

The gas chromatography–mass spectrometry (GC–MS) analysis of saturated hydrocarbon were performed by an Agilent 6890 gas chromatograph and Agilent 5975i mass selective detector. The GC instrument was equipped with an HP-5 MS fused silica capillary column (60 m × 0.25 mm inner diameter with a 0.25 μm film coating). The initial temperature of the GC oven was 50 °C (hold 1 min), and increased to 120 °C at a rate of 20 °C/min, then finally raised to 310 °C at 3 °C/min (hold 25 min).

The gas chromatography–mass spectrometry-mass spectrometry (GC–MS-MS) analysis of saturated hydrocarbons was used to identify the four series of rearranged hopanes. GC–MS-MS analysis was conducted by Agilent 6890 Series gas chromatograph interfaced to a Quatro II mass spectrometer, and fitted with a DB-5 column (60 m × 0.25 mm inner diameter with a 0.25 μm film coating). The temperature conditions before 120 °C is same as GC–MS analysis, and then raised to 250 °C at 4 °C/min and 310 °C at 3 °C/min (hold 30 min). The carrier gas was He at a constant flow of 1 ml/min. The ionization energy was 70 eV, and Ar was used as collision gas at 2×10^{-4} mbar with a collision energy of 20 eV. The mass spectrometer was operated in the multiple reaction monitoring mode for the following transitions: m/z 370 + 14n ($n = 0$–8) → 191 for rearranged hopanes.

4. Results and discussions

4.1. Occurrence and identification

4.1.1. Detection of four series of rearranged hopanes

In the m/z 191 mass chromatograms of saturated hydrocarbon from the Mesoproterozoic sediments in the NCC, the abundant distribution of regular hopanes and four series of rearranged hopanes can be clearly identified (Fig. 3), including the 18α(H)-neohopanes (Ts series), 17α(H)-diahopanes (D series), early eluting rearranged hopanes (E series), and 28-nor-spergulanes (Nsp series). Generally, D series presents in a carbon number range of C_{29} to C_{34} with trace C_{35} in the m/z 191 mass chromatograms, which always elute earlier than regular hopanes with the equivalent carbon number (Fig. 3a). Moreover, D series shows a very similar distribution characteristics to regular hopanes, including C_{30}D as the predominant peak and C_{31}-C_{35}D as paired peaks of 22S and 22R isomers (Fig. 3a). Interestingly, E series is the most volatile pentacyclic triterpenoid with shorter and more compact molecular structure, which makes its elution time more than two carbon numbers earlier than the regular hopanes. Because of the relative low concentration of E series, only one homologue (C_{30}E) can be undoubtedly detected in the m/z 191 mass chromatograms. Its peak position is always between Ts and Tm, and usually closer to Tm, or even as a shoulder peak of Tm (Fig. 3a) (Nytoft et al., 2006; Jiang et al., 2018). However, C_{29}Nsp always elutes midway between C_{30}D and C_{29}M with a low abundance (Fig. 3b). In addition to C_{29}Nsp, C_{30}Nsp was preliminarily detected by comparing the peak position and retention time in the m/z 191 mass chromatograms with previous publication (Fig. 3b) (Nytoft et al., 2006). To the best of
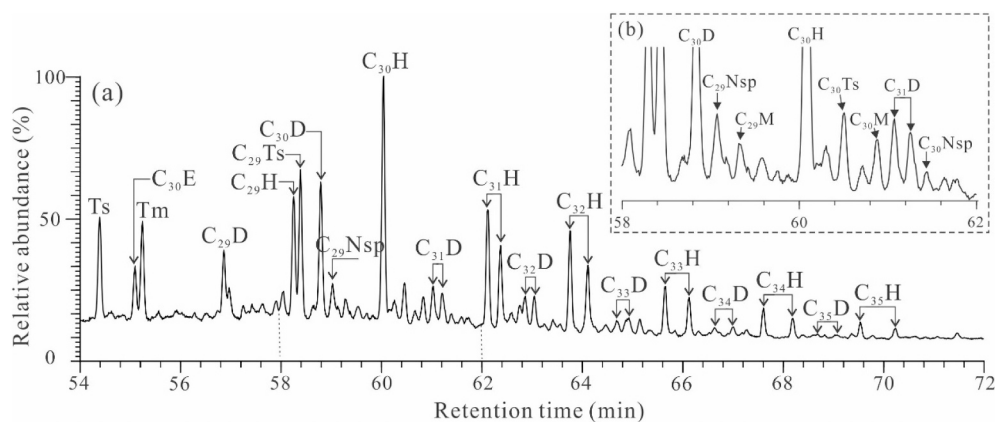
Fig. 3. Mass chromatograms of *m/z* 191 showing the hopanes distribution of saturated hydrocarbon from the Mesoproterozoic Xiamaling Formation sediment in the XHY section. Abbreviations: $C_{30}E = C_{30}$ early eluting rearranged hopane; C_{29}-C_{30}Nsp = C_{29}-C_{30} 21-methyl-28-norspergulane; C_{29}-C_{34}D = C_{29}-C_{34} 17α(H)-diahopane; Ts = 18α(H)-neohopane; C_{29}-C_{35}H = C_{29}-C_{35} 17α(H),21β(H)-hopane; C_{29}-C_{30}M = C_{29}-C_{30}17β(H),21α(H)-hopane or moretane.

our knowledge, the complete Nsp series from C_{29} to C_{35} has not yet been simultaneously detected in geological samples. Ts series usually contains C_{27}Ts and C_{29}Ts (Fig. 3a), which are widely and easily recognized in sediments and oils from different geological periods. On the basis of relative retention times and peak position (Farrimond and Telnæs, 1996), the uncommon C_{30}Ts was tentatively detected (Fig. 3b), while the more higher homologues (≥C_{31}Ts) were never detected unambiguously in any sediments and crude oils until now.

4.1.2. Identification of four series of rearranged hopanes

In order to further determine the four series of rearranged hopanes, it is necessary to analyze their diagnostic ions fragments and compare with published literature (Li et al., 2015; Xiao et al., 2019). In the paper, the

mass spectra of representative rearranged hopanes (C_{30}D, C_{30}E, C_{29}Ts and C_{29}Nsp) were comparatively analyzed after subtracting background mass spectra, which show same base peak ion at *m/z* 191 (Fig. 4). Both C_{30}D and C_{30}E have the molecular ions at M$^+$ 412 and an identical diagnostic ion fragment at *m/z* 397 (Fig. 4a-b), but the unique fragment ion at *m/z* 287 only appears in the mass spectra of C_{30}E (Fig. 4b) (Telnaes et al., 1992; Farrimond and Telnæs, 1996). C_{29}Ts and C_{29}Nsp contain the molecular ions at M$^+$ 398 with same diagnostic ion fragment at *m/z* 383, 369, 177 (Fig. 4c-d). Typically, C_{29}Nsp and uncommon C_{30}Nsp, as the latest reported series (Nytoft et al., 2006), usually present a relatively high abundance of ion fragment at *m/z* 369 (Fig. 4d and e), whilst C_{29}Ts has an abundant ion fragment at *m/z* 177 (Fig. 4c and e).
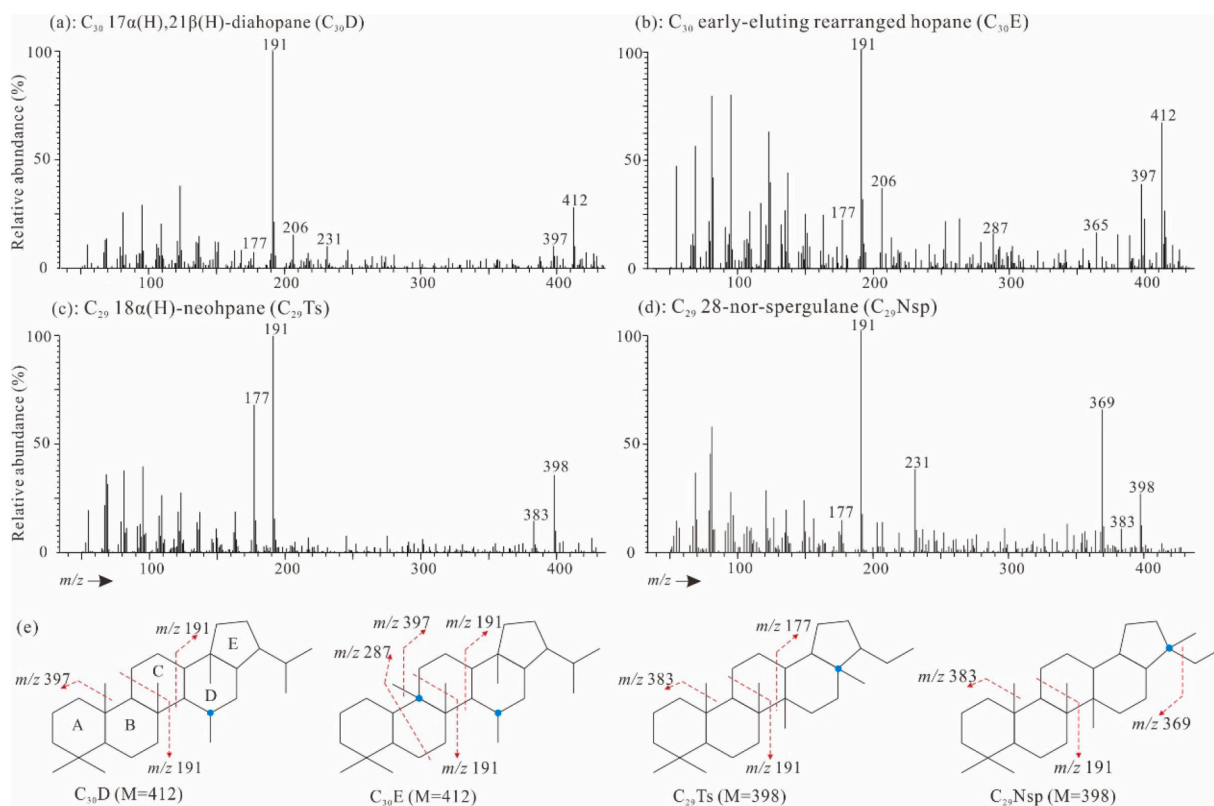
Fig. 4. Mass spectra and molecular structures of C_{30} 17α(H)-diahopane (a), C_{30} early eluting rearranged hopane (b), C_{29} 18α(H)-neohopane (c), and C_{29} 28-nor-spergulane series (d), all taken from the same full scan GC–MS analysis of sediment extracts.

4.2. Four series of rearranged hopanes

Based on the gas chromatography–mass spectrometry-mass spectrometry (GC–MS-MS) analysis, the four series of rearranged hopanes were simultaneously detected for the first time in the sediment extracts of the Mesoproterozoic Hongshuizhuang and Xiamaling formations, which contains high concentrations of $17\alpha(H)$-diahopane ($C_{27}D$ and C_{29}-$C_{35}D$), early eluting rearranged hopanes ($C_{27}E$ and C_{29}-$C_{35}E$), and $18\alpha(H)$-neohopanes ($C_{27}Ts$ and C_{29}-$C_{30}Ts$), as well as relative low amount of 28-nor-spergulanes (C_{29}-$C_{30}Nsp$) (Fig. 5). Usually, D and E series show extremely similar distribution features with regular hopanes, which have the characteristics of the carbon number range of C_{27}-C_{35} without C_{28} homologue, and two (22S and 22R) epimers of C_{31}-C_{35} homologues. Moreover, the exact retention time of the various series rearranged hopanes and regular hopanes in the m/z 191 mass chromatograms are determined, and the relationship between retention times and carbon numbers is shown in Fig. 6. According to the retention times and peak positions of all compounds, it is obvious that E series, D series, and regular hopanes elute in order for the same carbon number compounds, while Nsp series shows the last elution (Fig. 5). However, as the carbon number increase for the Ts series, the peak position of the three homologues ($C_{27}Ts$ and C_{29}-$C_{30}Ts$) have an evident delay, which shows that $C_{27}Ts$ peak elutes before $C_{27}H$, but $C_{29}Ts$ and $C_{30}Ts$ elute later than $C_{29}H$ and $C_{30}H$, respectively (Fig. 6). In addition, the distance of peak position or difference values of retention time between 22S and 22R isomers of C_{31}-$C_{35}E$ and C_{31}-$C_{35}D$ are distinctly smaller than that of C_{31}-$C_{35}H$ (Figs. 6 and 7).

4.3. Distribution of rearranged hopanes

In the Yanliao Faulted-Depression Zone, the black argillaceous dolomites from third to sixth members of the Gaoyuzhuang Formation, the black shale of the Hongshuizhuang Formation, and the black shale and oil shale of the third member of the Xiamaling Formation are considered to be three sets of potential source rocks (Fig. 7a) (Sun and Wang, 2016; Zhao et al., 2019). However, there is a striking difference in the biomarker compositions of three sets of source rock extracts. In the
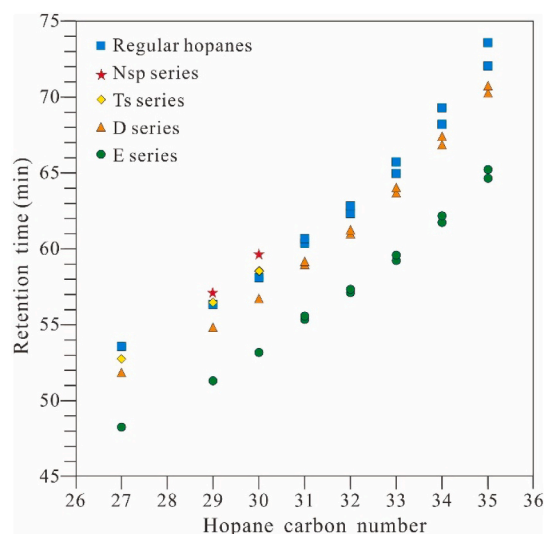

Fig. 6. Plot of retention times of different members of the hopane and rearranged hopane series vs. carbon number.

Fig. 7, the C_{27}-C_{35} regular hopanes abundantly occur in the sediment extracts of the Xiamaling and Gaoyuzhuang Formations, with $C_{30}H$ as the dominant peak. However, the total abundance of regular hopanes in the Hongshuizhuang Formation is low with a high baseline in the m/z 191 mass chromatograms, and the higher carbon hopanes ($>C_{32}$) are present only in trace amounts. In addition, four series of rearranged hopanes obviously present in the sediments of the Mesoproterozoic Hongshuizhuang (Fig. 7c) and Xiamaling formations (Fig. 7b), whereas the sediment of the Gaoyuzhuang Formation only contains the common C_{27}-$C_{29}Ts$ with trace concentration of C_{29}-$C_{30}D$, and E and Nsp are absent (Fig. 7d).

Lithologically, the selected rock samples of the Hongshuizhuang and Xiamaling Formations are mainly composed of shales with high content of clay minerals, the sediment of the Gaoyuzhuang Formation is
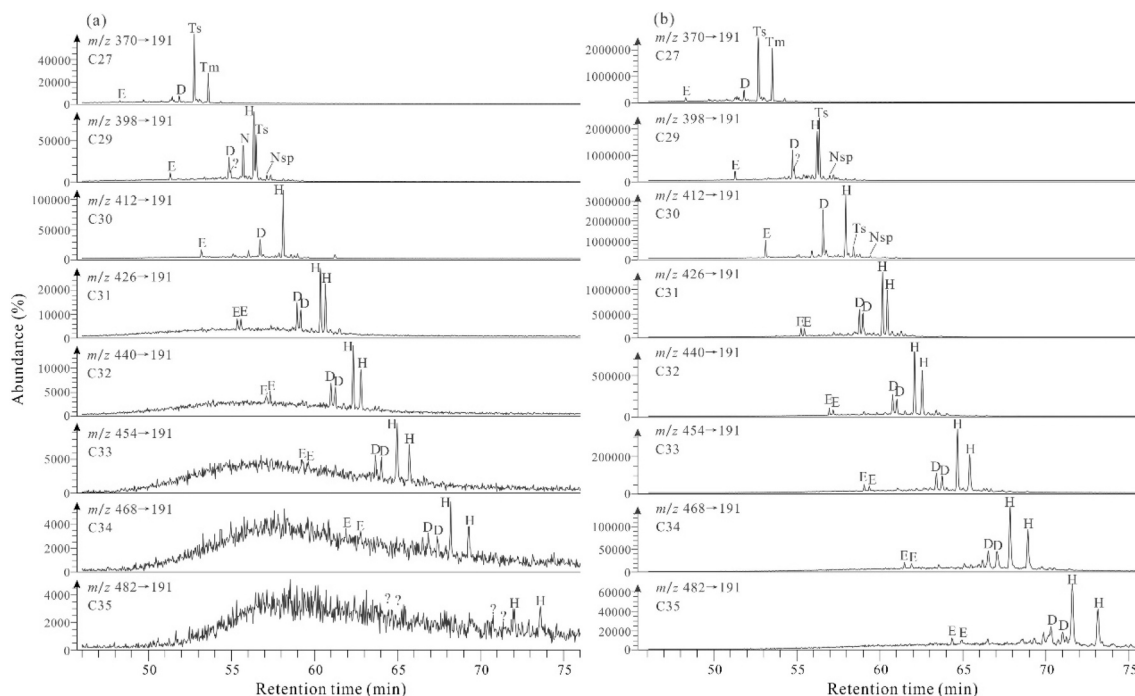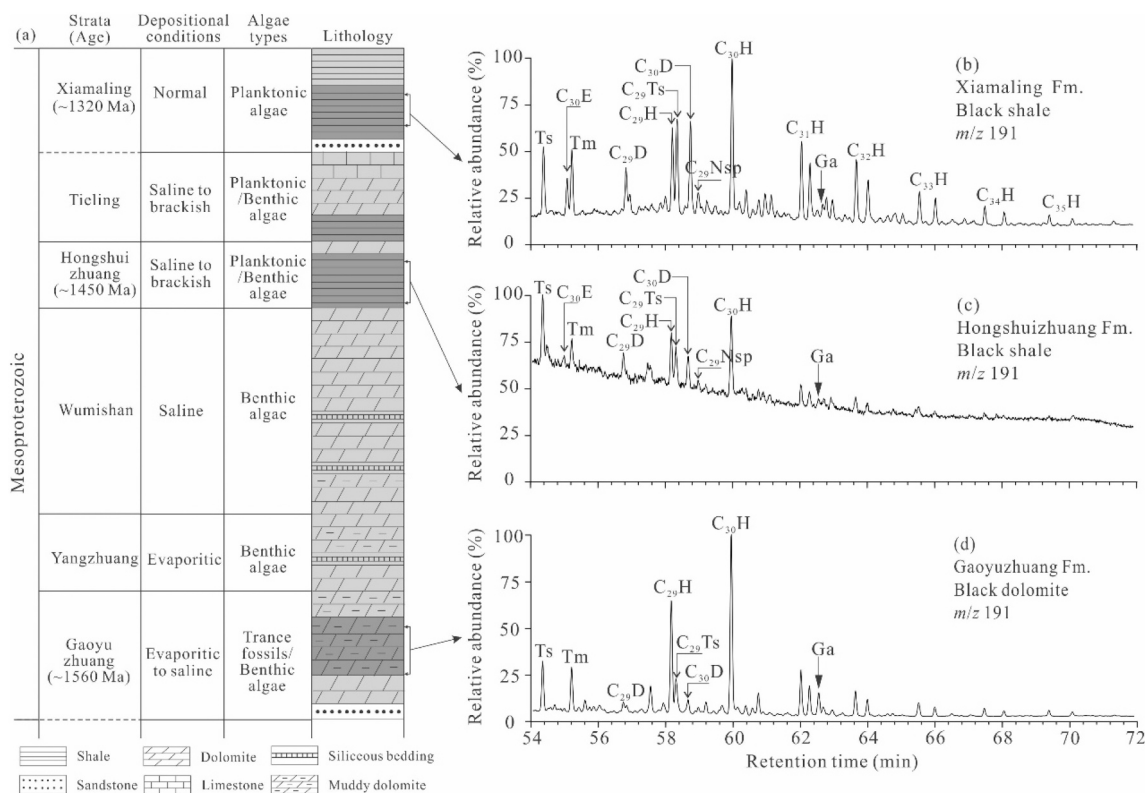

Fig. 5. Parent ion analysis of m/z 191 daughter ions by GC–MS-MS in the saturated hydrocarbons of the Mesoproterozoic Hongshuizhuang Formation sediment (a) and Xiamaling Formation sediment (b), showing the distribution of four series of rearranged hopanes.

Fig. 7. Lithologic column, depositional condition and biological community of the Mesoproterozoic Gaoyuzhuang Formation (1560 Ma) to Xiamaling Formation (1320 Ma) in study area (a), and mass chromatograms of *m/z* 191 showing the distribution of rearranged hopanes in saturated hydrocarbons of the Mesoproterozoic sediments (b-d).

argillaceous dolomites with a low content of clay minerals (Fig. 7a). Therefore, the influence of lithology on the presence of rearranged hopanes cannot be ruled out temporarily. However, according to a large number of previous publications, we can speculate that the clay minerals is not a key influencing factor in occurrence of rearranged hopanes. Firstly, sediments rich in clay minerals (shales and mudstones) can be observed in various sedimentary basins around the world, but the four series of rearranged hopanes do not extensively present in sediments and crude oils. Secondly, there are also significant variance in the contents of rearranged hopanes in same clay-rich sediment samples (Telnaes et al., 1992). More importantly, high abundance of rearranged hopanes have

also been detected in dolomite rocks (Summons et al., 1988a). Therefore, the authors putatively proposed that the active acidic sites on clay minerals may not be the prerequisite or necessary condition for the formation of rearranged hopanes, but cannot exclude its promotion effect on the rearrangement reaction.

4.4. Relationship between rearranged hopanes

Nine core samples (JQ-1 and Han-1 wells) and eleven outcrop samples (WFZ, BG and HZZ sections) were selected from the Hongshuizhuang Formation to analyzed the distribution relationships of

Table. 2
Selected parameters for saturated hydrocarbon of source rocks.

No.	Well/Section	Depth (m)	Formation	$Ga/C_{30}H$	$C_{29}Ts/C_{29}H$	$C_{30}E/C_{30}H$	$C_{30}D/C_{30}H$	$C_{29}D/C_{29}H$	$C_{29}Nsp/C_{29}H$
1	JQ-1	123.15	Hongshuizhuang	0.05	1.04	0.27	0.66	0.79	0.38
2	JQ-1	141.51	Hongshuizhuang	0.09	0.55	0.09	0.26	0.23	0.10
3	JQ-1	156.89	Hongshuizhuang	0.07	0.78	0.18	0.41	0.51	0.20
4	Han-1	2253.92	Hongshuizhuang	0.10	0.21	0.09	0.28	0.14	0.17
5	Han-1	2254.42	Hongshuizhuang	0.11	0.29	0.13	0.34	0.26	0.20
6	Han-1	2254.92	Hongshuizhuang	0.13	0.31	0.06	0.21	0.31	0.23
7	Han-1	2255.92	Hongshuizhuang	0.09	0.41	0.17	0.35	0.25	0.16
8	Han-1	2256.92	Hongshuizhuang	0.11	0.51	0.13	0.25	0.18	0.18
9	Han-1	2257.92	Hongshuizhuang	0.10	0.32	0.08	0.30	0.18	0.10
10	WFZ06	/	Hongshuizhuang	0.15	0.30	0.06	0.09	0.12	0.05
11	WFZ08	/	Hongshuizhuang	0.18	0.42	0.11	0.06	0.10	0.12
12	WFZ011	/	Hongshuizhuang	0.13	0.39	0.07	0.11	0.14	0.08
13	WFZ012	/	Hongshuizhuang	0.13	0.29	0.05	0.08	0.09	0.10
14	BG01	/	Hongshuizhuang	0.09	0.77	0.21	0.44	0.39	0.19
15	BG03	/	Hongshuizhuang	0.07	0.76	0.21	0.52	0.42	0.20
16	BG04	/	Hongshuizhuang	0.09	0.73	0.23	0.51	0.48	0.27
17	BG05	/	Hongshuizhuang	0.09	0.72	0.25	0.55	0.49	0.18
18	HZZ01	/	Hongshuizhuang	0.16	0.28	0.08	0.14	0.15	0.09
19	HZZ03	/	Hongshuizhuang	0.16	0.27	0.07	0.12	0.16	0.11
20	HZZ-4	/	Hongshuizhuang	0.16	0.28	0.04	0.12	0.11	0.09

rearranged hopanes. All values of calculated related parameters are listed in Table 2. As shown in Fig. 8a, there is a good linear relationship between the same series of rearranged hopanes ($C_{29}D/C_{29}H$ vs. $C_{30}D/C_{30}H$), and the value of coefficient of determination (R^2) can reach up to 0.8258. Similarly, the different series of rearranged hopanes, including $C_{30}D/C_{30}H$ vs. $C_{30}E/C_{30}H$ (Fig. 8b) and $C_{29}D/C_{29}H$ vs. $C_{29}Nsp/C_{29}H$ (Fig. 8c) also show strongly positive relationship, and their intercepts of linear equations are less than 0.06, suggesting a similar biological origins and formation conditions (Xiao et al., 2019). Differently, the linear equation in the plot of $C_{29}Ts/C_{29}H$ vs $C_{29}D/C_{29}H$ shows relatively high values of the slope (1.1626) and intercept (0.1624) (Fig. 8d), which suggests that Ts series has other partly different biohopanoid precursors (e.g. diplopterol and/or diploptene) compared to the other three rearranged hopane series (Farrimond and Telnæs, 1996; Sinninghe Damsté et al., 2014).

4.5. Influence factors

4.5.1. Potential biological origin

So far, the biological sources of rearranged hopanes is still controversial. The conventional view is that the rearranged hopanes have the same biological precursors as regular hopanes (Moldowan et al., 1991; Ruble et al., 2019), which are thought to be mainly derived from bacteriohopanetetrol of prokaryotic organisms (Ourisson et al., 1984). Some scholars have also detected abundant rearranged hopanes in sediments dominated by terrestrial organic matter inputs, indicating the source of high land plant material (Philp and Gilbert, 1986). According to biological evolution process, the primitive biological communities in the Mesoproterozoic ancient ocean were mainly prokaryotes, thus the rearranged hopanes in the Mesoproterozoic sediments are definitely not

derived from terrestrial higher plants, but may be derived from eukaryotic algae, such as benthic red algae (Zhang et al., 2007). However, fossils of benthic algae (Fig. 7a) (Yan and Liu, 1998), decimeter-scale multicellular macroscopic eukaryotes (Zhu et al., 2016), and striking steranes biomarkers (Li et al., 2003) were discovered in the sediments of Gaoyuzhuang Formation (1.56 Ga), but which only contain trace amounts of rearranged hopanes, even below the detection level. The above discussion provides a strong evidence that the rearranged steranes in the Mesoproterozoic sediments were not derived from eukaryotes (e.g. terrestrial higher plants and eukaryotic algae), but from prokaryotes (e.g. bacteria).

It is well known that bacteria are ubiquitous organisms living in almost any corner, but rearranged hopanes are not extensively found in all sediments deposited in various depositional environments of different ages. This phenomenon reveal that not all bacterial species are precursors to rearrangement of hopanes. Generally, prior to the "Cambrian substrate revolution" in the Late Neoproterozoic, benthic microbial mats were the dominant life forms in the oceans (Reid et al., 2000; Pawlowska et al., 2013), which pervasively present in the Proterozoic oceanic shelves (Blumenberg et al., 2015). Moreover, such mats would rework primitive organic matter, and cultivate a large number of heterotrophic bacteria communities in the lower layers of the mat (Pawlowska et al., 2013). The authors believe that the abundant rearranged hopanes in the sediments of the Hongshuizhuang Formation and the Xiamaling Formation may not originate from widespread prokaryotic bacteria but from bacterial communities (e.g. heterotrophic bacteria), which may reflect a particular set of sedimentological conditions (e.g. microbial mats) (Killops and Howell, 1991).
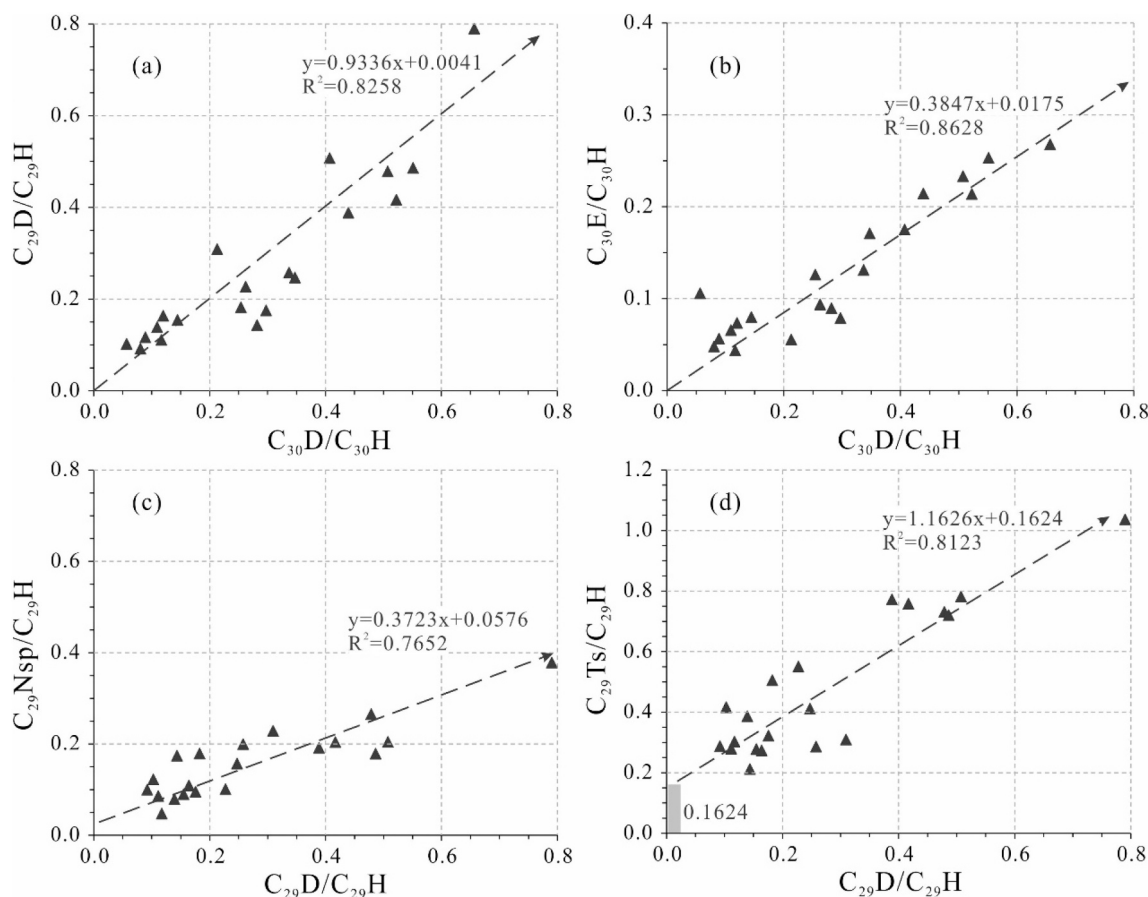
Fig. 8. Correlation between different rearranged hopane ratios: (a) $C_{29}D/C_{29}H$ vs. $C_{30}D/C_{30}H$; (b) $C_{30}E/C_{30}H$ vs. $C_{30}D/C_{30}H$; (c) $C_{29}Nsp/C_{29}H$ vs. $C_{29}D/C_{29}H$; (d) $C_{29}Ts/C_{29}H$ vs. $C_{29}D/C_{29}H$.

4.5.2. Depositional environment

In the study area, Yan and Liu (1998) have concluded that the black argillaceous dolomite of the Gaoyuzhuang Formation was mainly deposited in the evaporite to saline water environments, whereas the black shale of the Hongshuizhuang Formation were formed in saline to brackish water environments, and the salinity of depositional water during the period of the Xiamaling Formation was relatively lower, which belongs to a normal water environments (Fig. 7a) (Yan and Liu, 1998; Li et al., 2003). The Xiamaling Formation deposited in normal water typically shows low amounts of gammacerane and extremely high amounts of four series of rearranged hopanes (Fig. 5b and 7b). The black argillaceous dolomite of the Gaoyuzhuang Formation contains relatively high concentration of gammacerane, but shows low to trace amounts of Ts and D series and absent E and Nsp series (Fig. 7c), which is consistent with the crude oils generated from source rocks deposited in saline to hypersaline lacustrine depositional environments in the Uinta Basin and the South Atlantic rift basins (Telnaes et al., 1992). In addition, the water salinity of water conditions during the deposition period of the Hongshuizhuang Formation has a variation from saline to brackish indicating a fluctuation of the paleo-sedimentary environment (Fig. 5 and 7b-c). Interestingly, the values of $C_{30}D/C_{30}H$, $C_{30}E/C_{30}H$, $C_{29}Nsp/C_{29}H$ and $C_{29}Ts/C_{29}H$ ratios of twenty sediments from the Hongshuizhuang Formation display close covariance with gammacerane index (Fig. 9 and Table 2), which means that the distribution of rearranged hopanes is affected by the salinity of depositional environments. Therefore, the authors concluded that high-salinity water condition would inhibit the proliferation of rearranged hopane precursors.

4.5.3. Thermal maturity

Kolaczkowska et al. (1990) have calculated the thermodynamic stability of various isomeric hopanes, including alkylated, dealkylated, and rearranged hopanes, using molecular mechanics methods (Kolaczkowska et al., 1990), and the relative thermal stability of rearranged hopanes in the order 17α(H)-diahopane >18α(H)-neohopane > regular hopanes was proposed by Moldowan et al. (1991). Moreover, Zhu et al. (2007a, 2007b) proposed that the rearranged hopanes contain relatively greater thermal stability than regular hopanes, and high maturity of the Jurassic lacustrine oils in central Sichuan basin is conducive to the enrichment of rearranged hopanes (Zhu et al., 2007a; Zhu et al., 2007b).

Differently, the sediment of the Gaoyuzhuang Formation ($T_{max} \approx 500\,°C$) in the NCC is in high maturity level, but which only contains low amounts of Ts and D series and even absence of E and Nsp series (Fig. 7c). In contrast, the low-maturity sediment of the Xiamaling Formation ($T_{max} \approx 438\,°C$) is rich in four series of rearranged hopanes (Fig. 7a). It can be seen that the thermal maturity is not the key controlling factor for the observed variance in the rearranged hopanes distribution of the Mesoproterozoic sediments in the NCC.

4.6. Application in oil-source correlation analysis

In addition, several solid bitumen, oil-seepages and bituminous sandstones were collected to investigate the distribution of rearranged hopanes. In the Fig. 10, the four series of rearranged hopanes are unambiguously observed in the solid bitumen from the Wumishan Formation in the Shuangdong section (Fig. 10a) and the oil-seepages from the Tieling Formation in JQ-1 well (Fig. 10b), but absent in the bituminous sandstones of the Xiamaling Formation in the Longtangou section (Fig. 10c). Based on the comparison with the rearranged hopanes distribution of source rocks (Figs. 7 and 10), it can be preliminarily inferred that the discovered solid bitumen and oil-seepages in the in Wumishan and Tieling formations are possibly derived from the source rocks of the Hongshuizhuang and/or Xiamaling formations, whereas the oil origins of the bituminous sandstones of the Xiamaling Formation in the Longtangou section is possibly contributed by the Gaoyuzhuang Formation source rocks. Therefore, the rearranged hopanes can be used as an effective molecular fossils for oil to source correlation of Precambrian sediments in the NCC.

5. Conclusions

Based on the peak position, relative retention time, mass spectral diagnostic fragments, and comparison with published papers, four series of rearranged hopanes are simultaneously identified in the Mesoproterozoic sediments and related oil seepages in the NCC. It is the first time that four series of rearranged hopanes were simultaneously observed in the Mesoproterozoic Hongshuizhuang Formation sediments (1450 Ma), including 18α(H)-neohopane ($C_{27}Ts$ and $C_{29}Ts$), 17α(H)-diahopane ($C_{27}D$ and C_{29}-$C_{35}D$), early eluting rearranged hopane ($C_{27}E$,
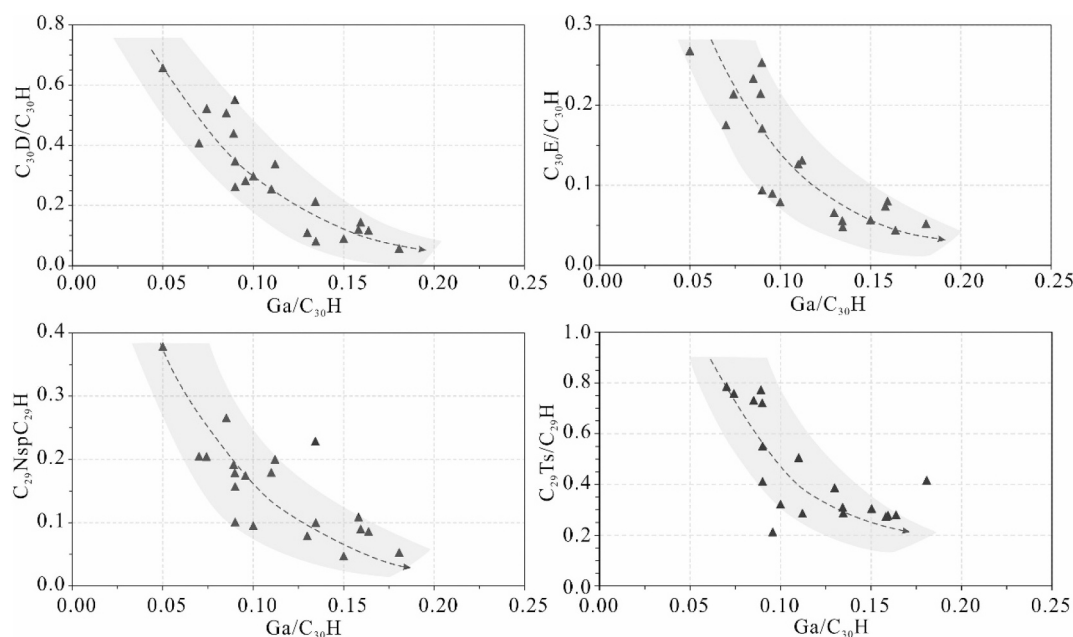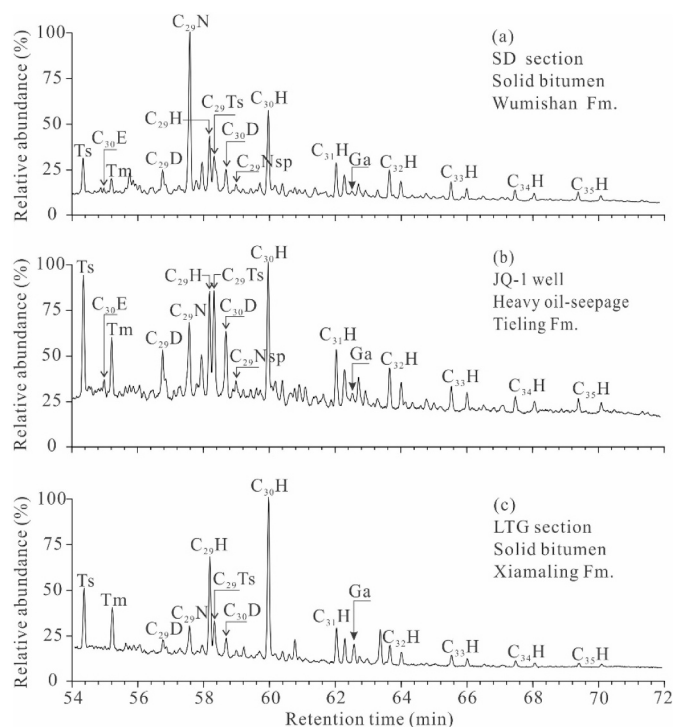

Fig. 9. Correlation between the relative abundance parameters ($C_{30}D/C_{30}H$, $C_{30}E/C_{30}H$, $C_{29}Nsp/C_{29}H$ and $C_{29}Ts/C_{29}H$ ratios) and the gammacerane index (Ga/$C_{30}H$ ratio).

Fig. 10. Mass chromatograms of *m/z* 191 showing the rearranged hopanes distribution of saturated hydrocarbons from the Mesoproterozoic oil seepages and solid bitumen. Note: $C_{29}N = C_{29}$ 25-norhopane.

C_{29}-C_{35}E), and 28-nor-spergulane (C_{29}Nsp). The four series rearranged hopanes have identical genetic biological source and similar formation mechanism. Different distribution pattern of four series of rearranged hopanes in the Mesoproterozoic sediments is directly controlled by biological source and indirectly by salinity of sedimentary water. The related parameters (e.g. C_{29}D/C_{29}H, C_{30}D/C_{30}H, C_{30}E/C_{30}H, C_{29}Nsp/C_{29}H and C_{29}Ts/C_{29}H) can be used as the effective parameters for determining Proterozoic oil source in the NCC.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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