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Original Paper

Discovery of a new Proterozoic paleo-reservoir and its oil source in the Jianchang Sag, Yanliao Faulted-Depression Zone, North China

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ABSTRACT

The discovery of many Proterozoic primary oil and gas reservoirs around the world testifies that the Meso-Neoproterozoic petroleum is an energy resources realm worthy of attention. This paper firstly reports the occurrence of hydrocarbon accumulations in the Neoproterozoic Luotuoling Formation in the Jianchang Sag, the Yanliao Faulted-Depression Zone. Petrography observation shows that the lower sandstone member of the Luotuoling Formation contains yellow fluorescent liquid hydrocarbons, while the upper sandstone member is rich in solid bitumen. Further analysis of the biomarkers and isotopic compositions reveals that the upper and lower reservoirs have different oil sources. The bitumen in the lower reservoir is rich in C_{19}–C_{20} tricyclic terpanes (TTs), 13α(n-alkyl)-tricyclic terpanes and rearranged hopanes, but lacks gammacerane and steranes and depletes ^{13}C isotope (−33.4‰ to −30.6‰). This is consistent with the properties of the Hongshuizhuang Formation source rocks. The upper reservoir bitumen has C_{23}TT as the major peak among C_{19}–C_{23}TTs, lacks 13α(n-alkyl)-tricyclic terpanes, has a low abundance of rearranged hopanes, obvious distribution of gammacerane and steranes, and depletion of the ^{13}C isotope; essentially the same as the Gaoyuzhuang Formation source rocks. The discovery of oil seepage in the Luotuoling Formation of the Han-1 well is a promising indicator of the Precambrian oil and gas exploration potential of the Jianchang Sag.

1. Introduction

Intensive study of the biological evolution of the early Earth has been confirmed that the biological diversity emerged in the Proterozoic ocean (Han and Runnegar, 1992; Javaux et al., 2004), and the material basis for oil and gas generation was established in the Meso-Neoproterozoic. Discoveries of organic-rich shales and commercial primary oil and gas reservoirs in many basins around the world have proved that Proterozoic petroleum is a huge potential energy resource (Meyerhoff, 1980; Al-Marjeby and Nash, 1986; Fowler and Douglas, 1987; Summons et al., 1988b; Kuznetsov, 1997; Volk et al., 2003; Grosjean et al., 2009; Craig et al., 2013).

Since the 1970s, many petroleum geologists have searched for oil and gas exploration in the Proterozoic strata of the Yanliao Faulted-Depression Zone, discovering oil seepages in the Mesoproterozoic Wumishan Formation (ca. 1485 Ma) in the Shuangdong area and bituminous sandstones in the Mesoproterozoic Xiamaling Formation (ca. 1400 Ma) in the Xiahuayuan area of Hebei Province (Wang, 1980; Hao and Feng, 1982; Liu and Fang, 1989; Gao et al., 1991). Hundreds of incidences of in-situ oil seepages and bitumen have been discovered in the Proterozoic strata, mostly in the Jibei and Liaoxi depressions (Wang and Gong, 2018). In addition, several sets of organic-rich rocks within the Gaoyuzhuang, Hongshuizhuang and Xiamaling formations have been discovered that are considered to be potential source rocks. These are at various stages of thermal evolution, ranging from immature to postmature (Luo et al., 2016; Sun and Wang, 2016; Wang et al., 2018). The organic matter of some sediments in the local area of the Yanliao Faulted-Depression Zone is still in the major oil-generation window. Moreover, Wang et al. (2016) concluded that the hydrocarbons charged in the early stage in the Xiamaling Formation basal oil

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reservoir of the Jibei Depression was sourced from the Gaoyuzhuang Formation source rock, while the late-stage hydrocarbons in the Xiamaling Formation basal oil reservoir and the liquid oil seepages found in the Wumishan and Tieling formations were derived from the Hongshuizhuang Formation source rock.

In recent years, PetroChina's Liaohe Oilfield Company has drilled several exploratory wells (including Han-1, Yang-1, and Xinglong-1 wells) in the Jianchang Sag, targeting Proterozoic petroleum resources. Although commercial oil and gas accumulations have not yet been found, oil- and bitumen-rich sandstone cores have been collected from the Neoproterozoic Luotuoling Formation in the Han-1 well with a depth range of 2116–2170 m. This is the first time that liquid oil has been found in drilling cores in the Jianchang Sag, offering good prospects for ancient oil and gas exploration in the basin. This study analyzes the molecular markers and stable carbon isotopic compositions of the oil-bearing sandstones and potential source rocks to identify the oil sources. The results are of great significance for future Proterozoic petroleum exploration in the Jianchang Sag.

2. Geological setting

The Yanliao Faulted-Depression Zone is the northern part of the North China Craton and contains five depressions and two uplifts (Fig. 1) (Sun and Wang, 2016; Wang et al., 2016). It is the oldest petroleum-bearing structural belt in China. The Jianchang Sag is an important structural unit of the Liaoxi Depression, trending NNE-SSW, with a width of 35 km and a length of 120 km, and covering an area of approximately 4700 km^2 (Fig. 1). The Meso-Neoproterozoic strata experienced a stable subsidence period during the Late Neoproterozoic-Paleozoic, and were then impacted by the Indosinian and the Yanshan movements, which resulted in the formation of a series of thrust fault zones. The orientation of the thrust faults is mainly NNE-SSW, and the corresponding thrust direction is NW-SE. Against this background of thrusting, various types of structural traps have developed in the Jianchang Sag (Yang, 2013).

Archean metamorphic rocks are exposed in the Jianchang Sag, as well as extremely thick sedimentary rocks, including the Mesoproterozoic Changcheng and Jixian systems, the Neoproterozoic Qingbaikou System, and Cambrian, Ordovician, Permian, Triassic, Jurassic, Cretaceous, and Cenozoic sequences (Ma et al., 2013). The Meso-Neoproterozoic strata are mainly composed of marine carbonate rocks with a thickness of several kilometers thick, interbedded with clastic rocks (Fig. 2). Observations of the Meso-Neoproterozoic filed outcrops in the Yanliao Faulted-Depression Zone have found scattered oil shows in the dolomite of the Gaoyuzhuang, Wumishan, and Tieling formations, the bottom sandstone of the Xiamaling Formation, and the quartz sandstone of the Luotuoling Formation (Ma et al., 2013). Previous studies have suggested that the Xiamaling Formation black shale (ca. 1400 Ma), the Hongshuizhuang Formation black shale (ca. 1450 Ma), and the Gaoyuzhuang Formation black argillaceous dolomite (ca. 1560 Ma) are organic-rich sediments, and may be the source rocks for the oil seepage areas that have been discovered (Wang and Han, 2011; Sun and Wang, 2016; Wang et al., 2016; Wang and Gong, 2018; Zhao et al., 2018, 2019b). The Jurassic Haifanggou Formation is also locally developed over the Proterozoic strata in the western Liaoxi Depression. It is a set of continental clastic rocks containing several organic-rich carbonaceous shale and coal measure interlayers (Tang et al., 2019).

3. Samples and methods

3.1. Samples and preparation for experiments

Hydrocarbon-bearing rocks were collected from the Luotuoling Formation in Han-1 well in the Jianchang Sag. Potential source rock samples were collected from JQ-1 and JQ-3 wells in the Jibei Depression, including samples from the Hongshuizhuang Formation black shales and the Gaoyuzhuang Formation black argillaceous dolomites. The sampling well locations are shown in Fig. 1.

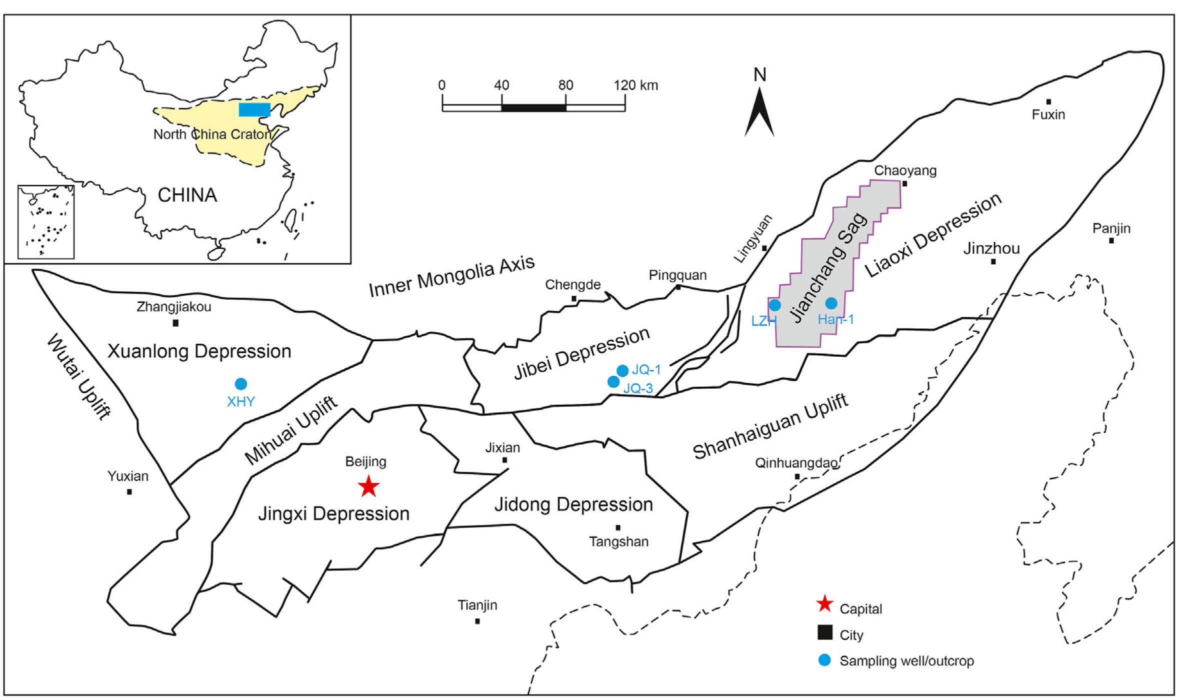

Fig. 1. Generalized geological map of architecture schematic structure of Yanliao Faulted-Depression Zone, and location of the Jianchang Sag.

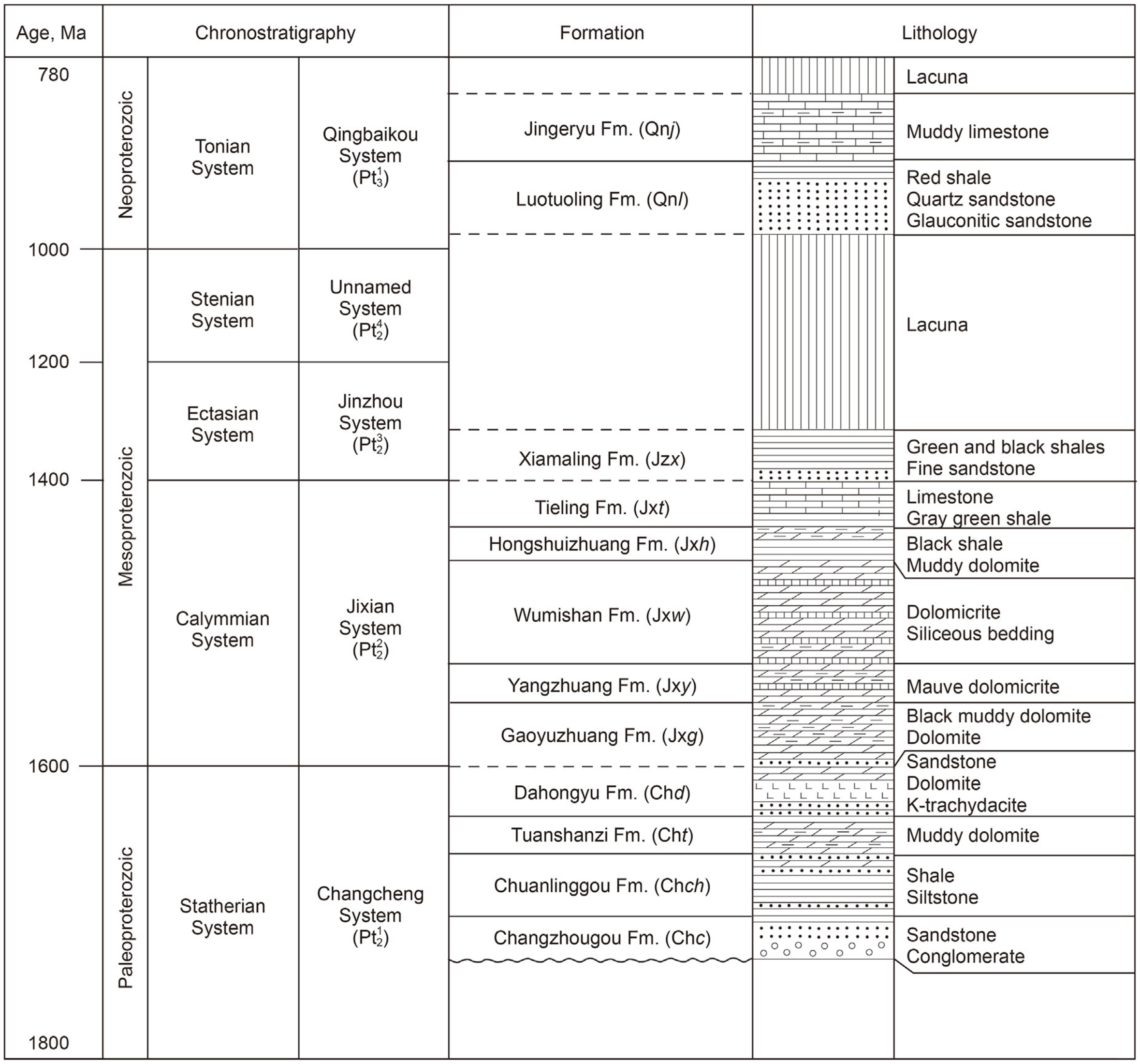

Fig. 2. Proterozoic stratigraphical column of the Yanliao Faulted-Depression Zone, North China.

Prior to beginning the experiments, a number of measures were taken to ensure the syngeneity and indigeneity of the soluble hydrocarbons, including deep cleaning of laboratory glassware, redistillation of reagents, removal of rock surfaces, and blank experiment analysis. The detailed experimental methods and procedures followed the approach used by (Xiao et al., 2021b).

3.2. Methods

3.2.1. TOC and rock-eval analyses

The samples were crushed and ground to less than 0.2 mm (80 mesh). Total organic carbon (TOC) was measured using a LECO CS-230 carbon analyzer after removal of inorganic carbon by diluted hydrochloric acid (1.5 mol/L). Rock-eval pyrolysis was carried out using a OGE-VI Rock Pyrolysis Instrument. The initial temperature was set at 300 °C, held for 3 min, then increased at 25 °C/min up to 600 °C to measure the volatile hydrocarbon content (S_1), the remaining hydrocarbon generation potential (S_2), and the temperature corresponding to maximum pyrolysis yield (T_{max}).

3.2.2. Soluble hydrocarbon extraction and fractionation

Soluble organic matter was extracted from more than 100 g ground samples using a Soxhlet apparatus for 72 h. The extracts were concentrated in a rotary evaporator, and then dissolved in 40–50 mL petroleum ether in a precleaned glass container. An N_2 stream was used to dry off the solvent as much as possible. The resulting extracts were filtered through a stuffed funnel to remove insoluble asphaltenes. The residual solution was further separated into saturated, aromatic, and resin fractions using a chromatography column filled with dry silica gel and alumina. The saturated fraction was isolated using redistilled petroleum ether as the eluent, the aromatic fraction using a mixed reagent of redistilled dichloromethane and redistilled petroleum ether (2:1, v/v), and the resin fraction using a mixed reagent of redistilled dichloromethane and redistilled methanol (93:7, v/v).

3.2.3. Gas chromatography–mass spectrometry (GC–MS)

An Agilent 6890 gas chromatography matched with an Angilent 5975i mass spectrometer (GC-MS) with an HP-5 MS fused silica capillary column (30 m × 0.25 mm internal diameter, with 0.25 μm film) was used to analyzed the molecular markers, with helium as the carrier gas. The initial temperature was set at 50 °C for 1 min, then increased to 120 °C at a rate of 20 °C/min, and then to 310 °C at 3 °C/min, and finally held for 10 min.

3.2.4. Stable carbon isotope analysis

The stable carbon isotopes of the crude oils and their four fractions were analyzed using a MAT 253 isotope ratio mass spectrometer. The detailed temperature program and conditions followed the procedure set out in (You et al., 2021).

4. Results and discussion

4.1. Discovery of neoproterozoic oil in Han-1 well

Han-1 well is in the southwest of the Jianchang Sag, in Jianchang Country, Liaoning Province (Fig. 1). The total drilling depth of the well is 2667 m and it encounters the Wumishan, Hongshuizhuang, and Tieling formations of the Jixian System (2163.90–2667.00 m), the Luotuoling Formation of the Qingbaikou System (2090.06–2163.90 m), as well as the Cambrian (1548.00–2090.06 m) and Cretaceous sequences (1548.00–0 m). Different types of oil shows have been found in the sandstones of the Neoproterozoic Luotuoling Formation (Fig. 3) (Xiao, 2020). Oil spots are mostly found in the gray quartz sandstone at a depth of 2152.00–2154.00 m, and brown sticky oil seeps out from the core. Oil traces are found in the gray-green quartz sandstone at depths of 2144.00–2147.00 m and 2150.00–2152.00 m. The gray sandstones at 2147–2150 m and 2154–2163.9 m are fluorescent (Fig. 3).

Interestingly, according to the physical property data from the Luotuoling Formation sandstone provided by the Liaohe Oilfield Company, the porosity of the upper sandstone member of the Luotuoling Formation (2116.00–2144.00 m) is greater than that of the lower sandstone member (2144.00–2163.90 m), but there are no oil shows in the upper sandstone member (Fig. 3). We carried out further microscopic observation of the petrographic characteristics and found that, as expected, the lower sandstone member of the Luotuoling Formation contains liquid hydrocarbons that fluoresce yellow under ultraviolet light. However, the upper sandstone member is unexpectedly rich in solid bitumen with no apparent fluorescence (Fig. 3). This suggests different oil sources and accumulation processes for the upper and lower sandstone members of the Luotuoling Formation in Han-1 well.

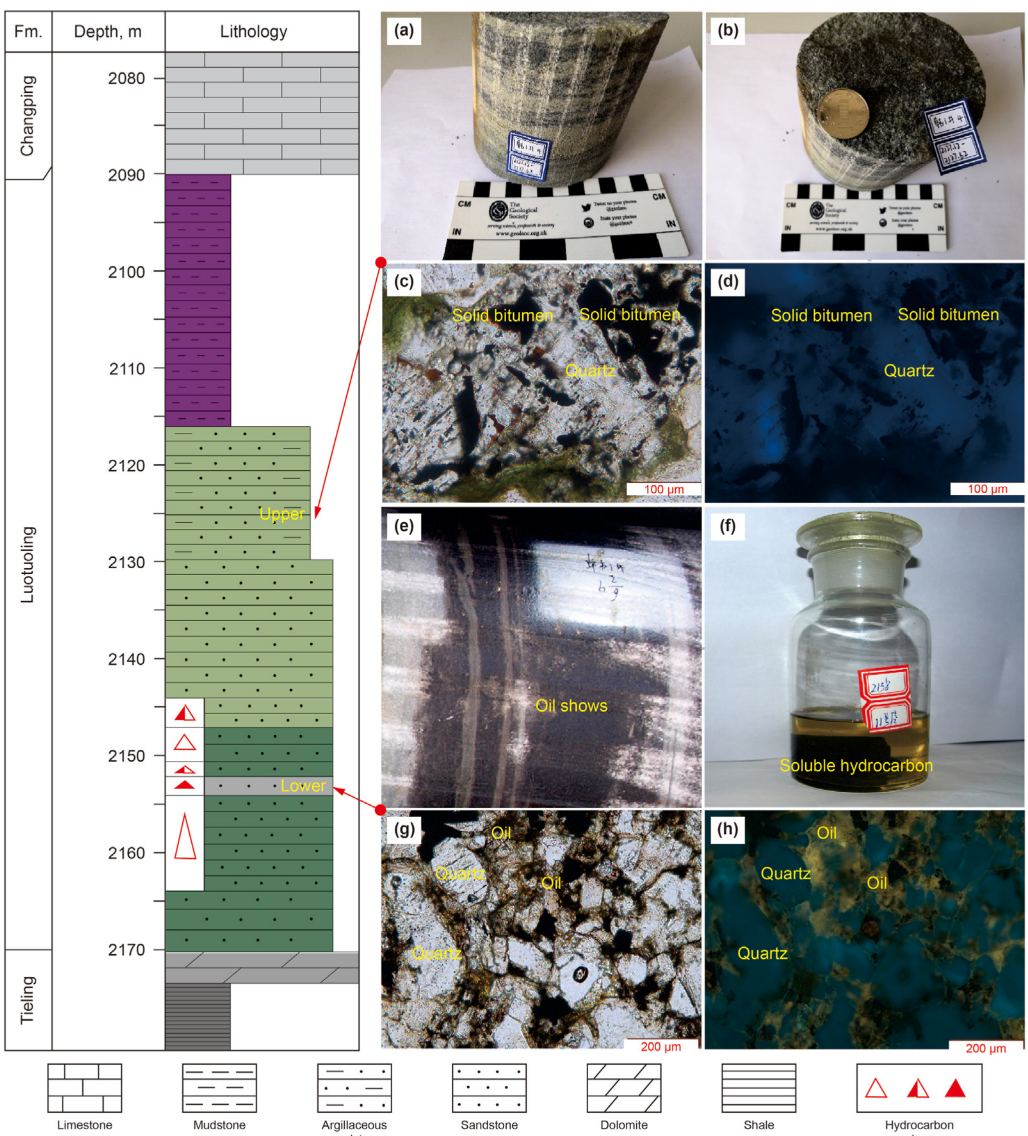

Fig. 3. Characteristics of Neoproterozoic Luotuoling Formation sandstones in the Han-1 well. (**a**–**b**) showing the core samples collected from the upper member; (**c**–**d**) showing the solid bitumen in the upper member under transmitted light and UV light; (**e**–**f**) showing the core samples with brown sticky oil seepage and the soluble hydrocarbon from the lower member; (**g**–**h**) showing hydrocarbon and corresponding yellow fluorescence in the lower member under transmitted light and UV light.

4.2. Potential source rocks in the Jianchang Sag

In order to determine the oil sources of the upper and lower reservoirs in the Neoproterozoic Luotuoling Formation sandstones in the Han-1 well, it is first necessary to identify the potential source rocks in the area. Previous studies have confirmed three sets of potential source rocks in the Yanliao Faulted-Depression Zone: the Xiamaling Formation black shales, the Hongshuizhuang Formation black shales, and the Gaoyuzhuang Formation black argillaceous dolomites (Sun and Wang, 2016; Wang et al., 2016).

4.2.1. The Xiamaling Formation source rock

During deposition period of the Xiamaling Formation, the depositional center in the Yanliao Faulted-Depression Zone moved westward from the Jibei-Liaoxi depressions to the Xuanlong Depression. The complete depositional cycle of the Xiamaling Formation can only be observed in the Xiahuayuan area of the Xuanlong Depression, where it has a total thickness of up to 500 m (Zhang et al., 2007). The black shale in the third member of the Xiamaling Formation contains abundant organic matter (mean TOC ≈ 4.20%) and is still in the early stage of the oil generation window (R_o ≈ 0.7%) (Sun and Wang, 2016).

However, the original sedimentary thickness of the Xiamaling Formation in the Liaoxi Depression is limited. Under the influence of the Yuxian movement at the end of the Mesoproterozoic, it was severely eroded and further thinned. Moreover, thermal baking of magmatic intrusions further reduced the potential hydrocarbon generation potential of the formation (Sun and Wang, 2016). Diabase sills are widespread in the remaining shale of the formation (Fig. 4a and b), which caused it to rapidly evolve into slate (Fig. 4c), completely losing its hydrocarbon generation potential. A large number of spherical weathering products of diabase sills have been observed in the Laozhuanghu (LZH) area, the Jianchang Sag (Figs. 1 and 4d).

4.2.2. The Gaoyuzhuang Formation source rock

Three samples of black argillaceous dolomite from the Gaoyuzhuang Formation were obtained from JQ-3 well. A large volume of the basic geochemical data of the Gaoyuzhuang Formation in JQ-3 (Sun and Wang, 2016) and L-1 wells (Tang et al., 2019) was also collected (Table 1). TOC values range from 0.11% to 4.29% (average 0.54%) for samples from JQ-3 and 0.29%–0.99% (average 0.65%) for those from L-1 (Table 1). The S_1+S_2 values are in the ranges of 0.05–2.39 (average 0.29) and 0.26–0.81 (average 0.52), respectively (Table 1). Sun and Wang (2016) found that the Gaoyuzhuang Formation samples in JQ-3 well contains 164 m organic-rich layer with TOC values of 0.5%–4.29%, and their equivalent vitrinite reflectance of 1.38%–1.75%.

Fig. 5 shows that the typical biomarker compositions of the black argillaceous dolomite extracts from the Gaoyuzhuang Formation are as follows: (I) absence or extremely low abundance of C_{18}–C_{23} 13α(n-alkyl)-tricyclic terpanes in m/z 123, (II) C_{23} tricyclic terpane (TT) as the dominant homologue among C_{19}–C_{23}TTs, (III) low abundance of rearranged hopanes, (IV) moderate abundance of gammacerane, and (V) complete distribution of C_{27} diasteranes and C_{27}–C_{29} regular steranes (Fig. 5a–d) (Xiao, 2020). These features indicate that the Gaoyuzhuang Formation was deposited in a reducing and saline water column, with biotic contributions from prokaryotes and eukaryotic algae.

4.2.3. The Hongshuizhuang Formation source rock

The Hongshuizhuang Formation samples were collected from the Han-1 and JQ-1 wells and mainly consist of black and dark gray shales. Compared with the Gaoyuzhuang Formation samples, the Hongshuizhuang Formation shales have relatively higher TOC contents, in the ranges of 0.42%–2.12% (average 1.35%) for Han-1 well and 1.09%–4.44% (average 2.39%) for JQ-1 well, and also have higher S_1+S_2 values with the range of 0.33 mg/g–2.32 mg/g (average 1.54 mg/g) and 3.20 mg/g–13.84 mg/g (average 6.79 mg/g), respectively (Table 1). In the Precambrian samples, the S_1+S_2

Fig. 4. Diabase intruded into the Xiamaling Formation in the Laozhuanghu area, Jianchang Sag. (**a**) Diabase intruding the Xiamaling Formation; (**c**) the slate of the Xiamaling Formation; (**b**) and (**d**) Diabase sills showing spherical weathering.

Table 1
TOC and S_1+S_2 values showing the hydrocarbon generation potential of the Hongshuizhuang and Gaoyuzhuang formations.

No.	Formation	Well	Quantity	TOC, %		S_1+S_2, mg/g	
				Range	Mean	Range	Mean
1	Hongshuizhuang	Han-1	8	0.42–2.12	1.35	0.33–2.32	1.54
2	Hongshuizhuang	JQ-1	3	1.09–4.44	2.39	3.20–13.84	6.79
3	Gaoyuzhuang	JQ-3	47	0.11–4.29	0.54	0.05–2.39	0.29
4	Gaoyuzhuang	L-1	4	0.29–0.99	0.65	0.26–0.81	0.52

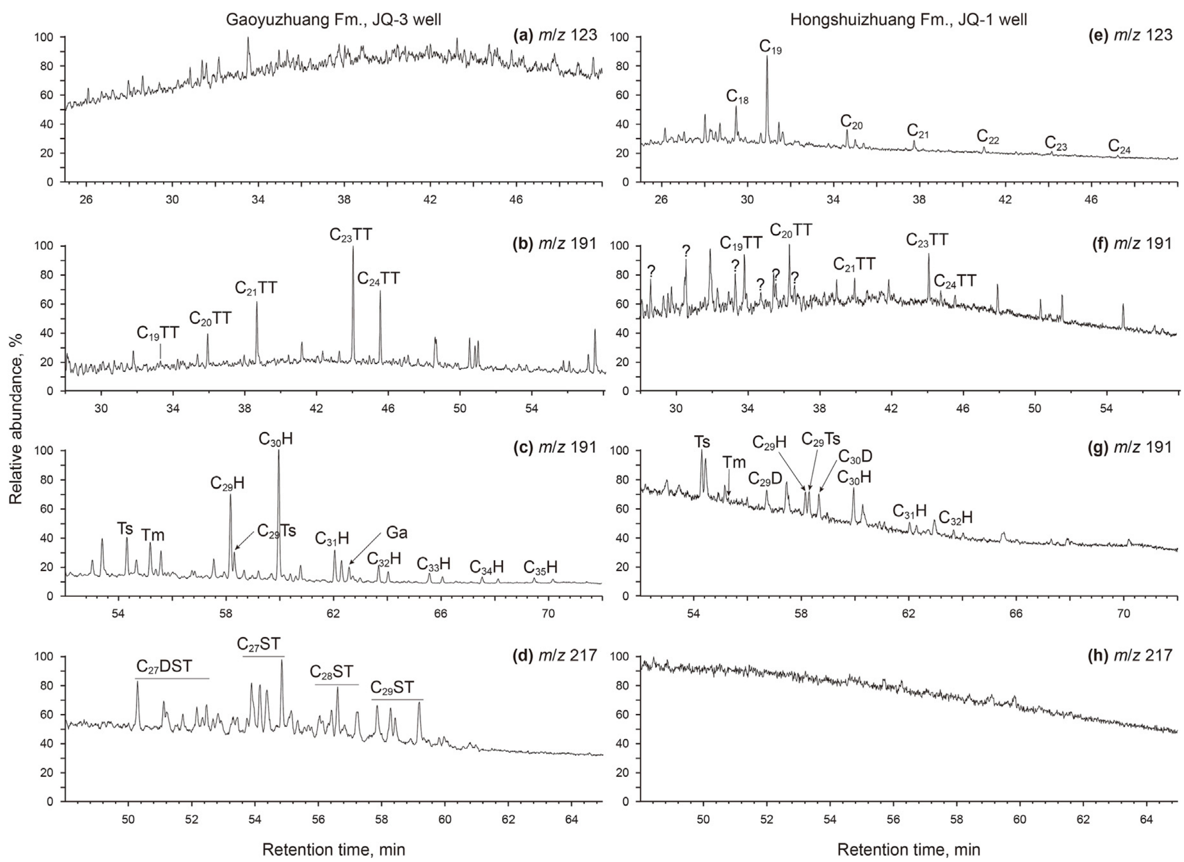

Fig. 5. Typical biomarker compositions of the representative samples of the Gaoyuzhuang and Hongshuizhuang formations. Notes: TT = tricyclic terpane; H = regular hopane; D = diahopane; DST = diasterane; ST = regular sterane; Ga = gammacerane.

value is always lower than the original value and therefore does not reflect the real hydrocarbon generation potential. Despite increasing of thermal maturity to 1.03% R_o equivalent (Luo et al., 2016), there is only limited reduction in TOC content, so the Hongshuizhuang Formation shales are still classified as moderate to good source rocks (Luo et al., 2016; Sun and Wang, 2016).

The biomarker compositions of the black shale extracts from the Hongshuizhuang Formation are as follows: (I) complete distribution of C_{18}–C_{23} 13α(n-alkyl)-tricyclic terpanes, (II) C_{19} or C_{20} short-chain tricyclic terpanes as the dominant homologue among C_{19}–C_{23}TTs and the presence of several unidentified tricyclic terpanes, (III) high abundance of rearranged hopanes, (IV) absence or extremely low abundance of gammacerane, and (V) absence of C_{27} diasteranes and C_{27}–C_{29} regular steranes (Fig. 5e–h) (Xiao, 2020). These features are distinctly different from those of the Gaoyuzhuang Formation and reveal that salinity was relatively low during deposition period of the Hongshuizhuang Formation, with a weakly stratified water column, and that there was only a limited contribution of eukaryotic algae to the original organic matter.

4.2.4. The Haifanggou Formation source rock

In addition to the Proterozoic organic-rich sediments, the Jurassic Haifanggou Formation has also been proposed as a potential source bed in the west Liaoxi Depression (Tang et al., 2019). N-1 well revealed that the Haifanggou Formation contains several organic-rich mudstone layers with a cumulative thickness of 45.93 m. The average TOC value of these mudstone layers is 4.96%, with a maximum value of 33.90% (Sun et al., 2019). The Haifanggou Formation was mainly deposited in a delta front with significant higher plant contributions (Zhao et al., 2019a), which is consistent with a predominance of high carbon number n-alkanes and C_{29} steranes among C_{27}–C_{29} regular steranes (Fig. 6). The other biomarkers in the Haifanggou Formation sediments include an odd carbon number preference between nC_{19} and nC_{35}, high abundance of the C_{29}–C_{35} moretane series, predominance of 22R over 22S isomers of C_{31}–C_{35} hopanes, and apparent predominance of biological configurations in C_{27}–C_{29} regular sterane isomers (Fig. 6) (Tang et al., 2019). These characteristics demonstrate that the organic-rich mudstone of the Haifanggou

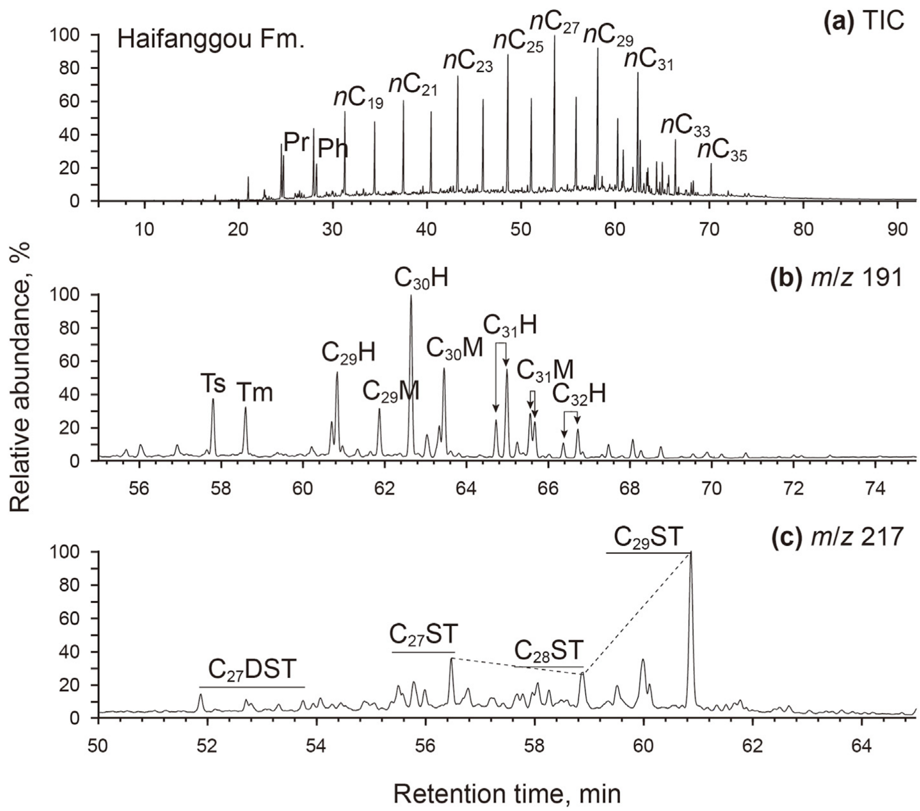

Fig. 6. Typical biomarker compositions of representative sample of the Jurassic Haifanggou Formation (Tang et al., 2019). Notes: H = regular hopane; M = moretane; DST = diasterane; ST = regular sterane.

Formation has not yet entered the main hydrocarbon generation stage.

4.3. Biomarker compositions of reservoir hydrocarbons

In order to determine the oil sources of the upper and lower reservoirs of the Luotuoling Formation in Han-1 well, we analyzed their biomarker compositions, including normal alkanes, regular tricyclic terpanes, 13α(n-alkyl)-tricyclic terpanes, rearranged hopanes and steranes.

4.3.1. Normal alkanes

Fig. 7 shows the total ion chromatogram of the saturated hydrocarbons in the soluble bitumens extracted from the upper and lower sandstone reservoirs in Han-1 well. The bitumens in both the upper and lower reservoirs show similar distribution patterns of normal alkanes; a complete distribution of normal alkanes with the carbon number range of C_{13}–C_{35} and an apparent baseline hump (UCM) (Fig. 7). This scenario was considered to be a typical feature of Proterozoic bitumen, which may be attributed to the reworking of primary lipids by bacterial microbial communities on benthic microbial mats (Pawlowska et al., 2013). In addition, the n-alkane series displays a unimodal distribution pattern, with C_{16} or C_{18} as the main peak and the values of nC_{21-}/nC_{22+} ratio greater than 1.0 (1.32–3.65) (Fig. 7 and Table 2). The strong predominance of low-molecular weight homologues and the abundance of mono-methyl alkanes suggest that cyanobacteria/bacteria were the major contributors to the primary biological materials (Blumenberg et al., 2012; Xiao et al., 2022). Based on this feature alone, we preliminarily conclude that the Proterozoic source rocks are more likely to be the source of the oil than the source rocks in the Haifanggou Formation (Figs. 5 and 6).

4.3.2. C_{19}–C_{23} regular tricyclic terpanes

There is a significantly different distribution pattern of C_{19}–C_{23} tricyclic terpanes (TTs) between the upper and lower reservoir bitumens (Fig. 8a and b). The upper reservoir bitumen shows a predominance of C_{23}TT among C_{19}–C_{23}TTs (Fig. 8a), with C_{19}–C_{20}/C_{23}TT value of 0.90–0.92 (Table 2), which is consistent with the typical marine sediments (such as the source rocks of the Gaoyuzhuang Formation in the study) (Fig. 5b) or saline lacustrine sediments (Xiao et al., 2019b). In contrast, high abundance of short-chain tricyclic terpanes (C_{19}–C_{20}TTs) was found in the lower reservoir bitumens (Fig. 8b), with C_{19}–C_{20}/C_{23}TT value of 1.43–1.70 (Table 2). These tricyclic terpanes are usually enriched in coal-bearing strata and the sediments with predominantly terrestrial higher plant input (Zumberge, 1987; Xiao et al., 2019b). In addition to the abundant short-chain tricyclic terpanes, several unidentified compounds were found in the m/z 191 of the lower reservoir bitumen, which are also found in the Hongshuizhuang Formation source rocks (Fig. 5f). It therefore follows that, even if the lower reservoir bitumen is proved to be derived from the Proterozoic source rock, the absolute predominance of C_{19}–C_{20}TTs suggests that prokaryotic microorganisms were the main source of C_{19}–C_{20}TTs, contradicting previous results that indicate predominantly terrestrial higher plant input in Phanerozoic sediments.

4.3.3. 13α(n-alkyl)-tricyclic terpanes

The 13α(n-alkyl)-tricyclic terpane series (αNATT) was initially detected in the Xiamaling bituminous sandstone in the Jibei Depression, and their molecular structures were determined by co-injection of synthetic standards (Wang and Simoneit, 1995). This

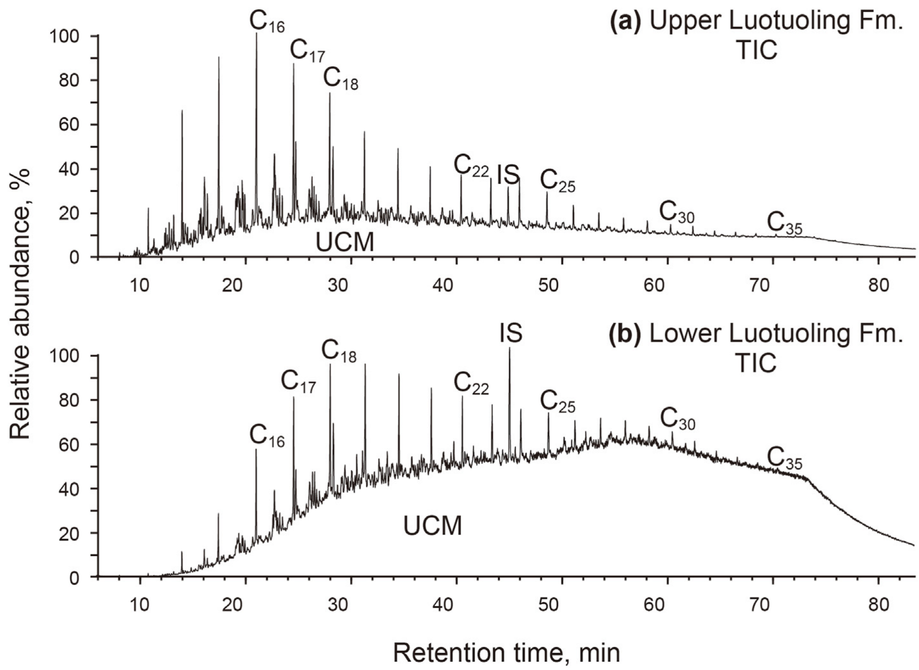

Fig. 7. Representative total ion chromatogram of the saturated hydrocarbon from the upper (**a**) and lower Luotuoling Formation sandstones (**b**) in the Han-1 well. Notes: IS = internal standard; UCM = unresolved complex mixture.

Table 2
Biomarker parameters in the upper and lower reservoir bitumens of the Luotuoling Formation in the Han-1 well.

No.	Formation	Depth, m	Main peak	$nC_{21}-/nC_{22}+$	$C_{19}-C_{20}/C_{23}TT$	$C_{19}\alpha NATT/C_{30}H$	$C_{30}D/C_{30}H$	Ga $/C_{30}H$	St/H
1	Luotuoling	2126.62–2127.12	C_{16}	3.65	0.90	–	0.08	0.15	0.60
2	Luotuoling	2127.12–2127.62	C_{16}	1.56	0.92	–	0.12	0.19	0.55
3	Luotuoling	2153.01–2153.51	C_{18}	1.77	1.70	16.50	7.92	–	–
4	Luotuoling	2153.54–2154.04	C_{18}	1.32	1.43	13.08	5.71	–	–

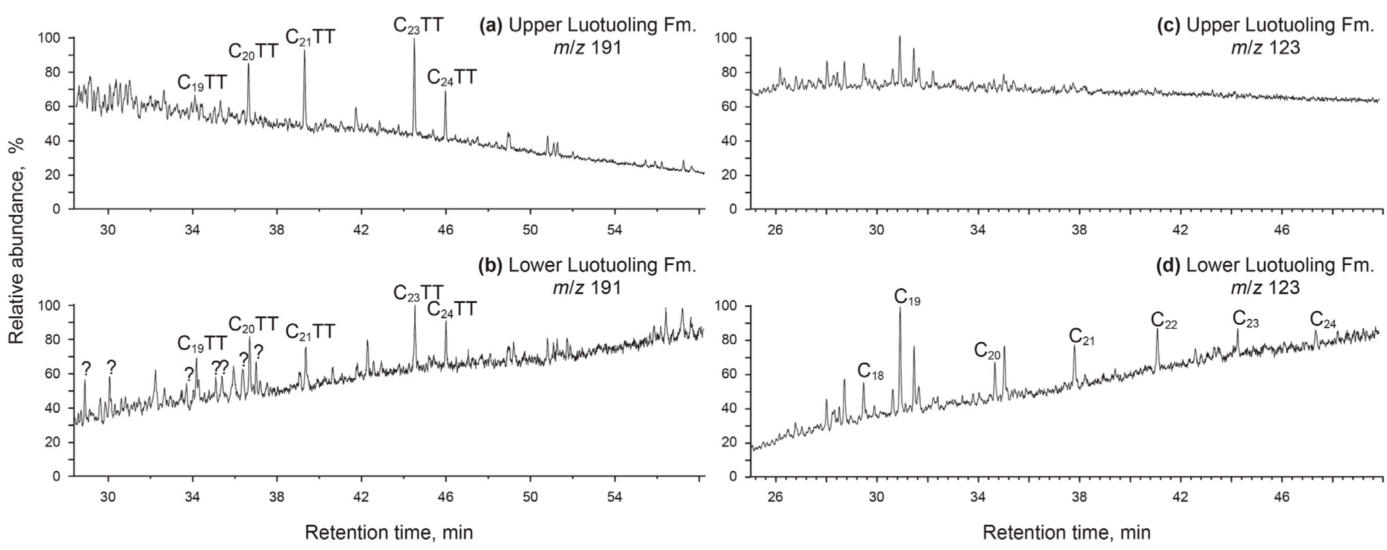

Fig. 8. Representative *m/z* 191 and 123 mass chromatograms showing the distribution of regular tricyclic terpanes (**a**–**b**) and 13α(*n*-alkyl)-tricyclic terpanes (**c**–**d**) in the saturated hydrocarbon from the upper and lower Luotuoling Formation sandstones in the Han-1 well. Notes: TT = tricyclic terpane; ? = unidentified compounds.

series has carbon numbers in the range of $C_{18}–C_{23}$, with a base peak at *m/z* 123 in their mass spectra (Wang et al., 2020). Recently, Xiao et al. (2021b) reported that the αNATT series had been observed in the Hongshuizhuang and Xiamaling formation black shales, but not in the Gaoyuzhuang Formation black argillaceous dolomite. Based on GC–MS–MS analysis of saturated hydrocarbons, it is found that the αNATT carbon number range can be extended to C_{33} (Xiao et al., 2021b). Further, we consider it likely that the carbon number range

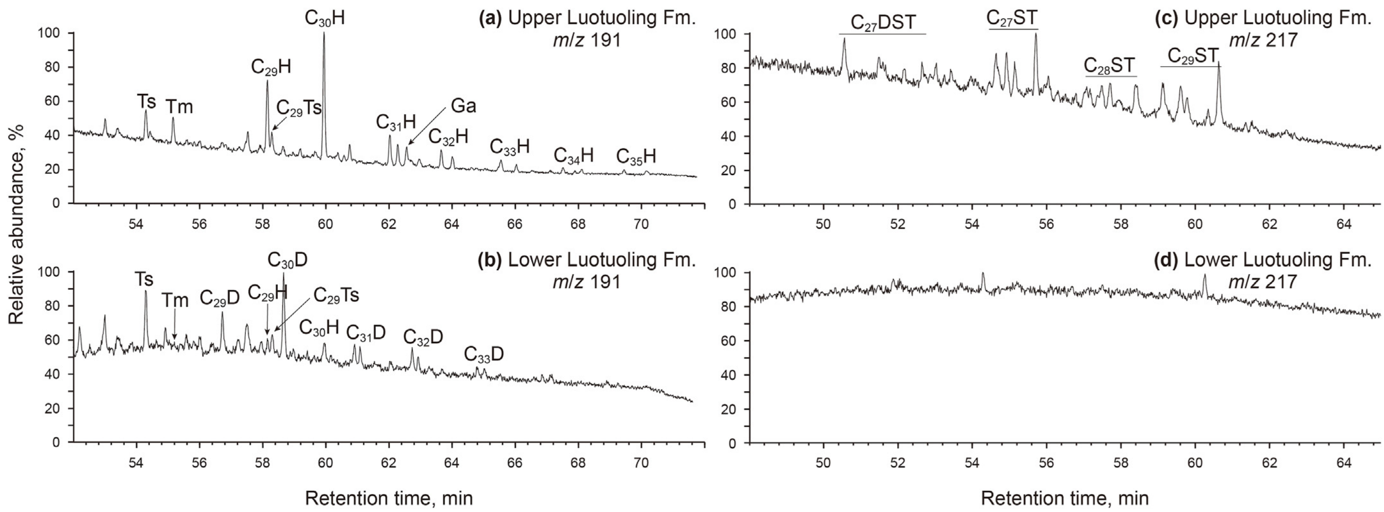

Fig. 9. Representative *m/z* 191 and 217 mass chromatograms showing the distribution of hopanes (**a**–**b**) and steranes (**c**–**d**) in the saturated hydrocarbon from the upper and lower Luotuoling Formation sandstones in the Han-1 well. Notes: H = regular hopane; D = diahopane; DST = diasterane; ST = regular sterane.

of αNATT is similar to that of regular tricyclic terpanes, and could accordingly be extended up to C_{54} (De Grande et al., 1993). As unique biomarkers in the Precambrian bitumen and sediments of the North China Craton, the αNATT series with carbon numbers in range of C_{18}–C_{24} was detected in the lower reservoir bitumen (Fig. 8d) (Xiao, 2020), with the ratio of C_{19}αNATT to C_{30} hopane (C_{19}αNATT/C_{30}H) being in the range of 13.08–16.50 (Table 2). However, the series is absent or below the detection limit in the upper reservoir bitumen (Fig. 8c) (Xiao, 2020), which is consistent with the potential source rock of the Gaoyuzhuang Formation (Fig. 5a).

4.3.4. Hopanes and gammacerane

Rearranged hopanes have similar molecular structures and carbon isotope compositions to regular hopanes, and are therefore also considered to derive from bacteriohopanetetrol from prokaryotic organisms (Rohmer et al., 1984; Moldowan et al., 1991). Recently, Xiao et al. (2021a) reported an abundance of four types of rearranged hopanes including 18α(H)-neohopane, 17α(H)-diahopane, early eluting rearranged hopane, and 28-nor-spergulane in the Hongshuizhuang and the Xiamaling formations black shales, but none in the Gaoyuzhuang Formation black argillaceous dolomite. The study further proposed that the rearranged hopanes may not be produced by ubiquitous bacteria but by other bacterial communities living in a restricted environment. This was considered to be an effective molecular fossil maker for identifying the source of the Proterozoic bitumen in the North China Craton (Xiao et al., 2021a). According to the study, the upper reservoir bitumen contains C_{27}–C_{35} regular hopanes with a predominance of C_{30} hopane (Fig. 9a). In contrast, the lower reservoir bitumen has a higher abundance of C_{29}–C_{35} 17α(H)-diahopanes compared to

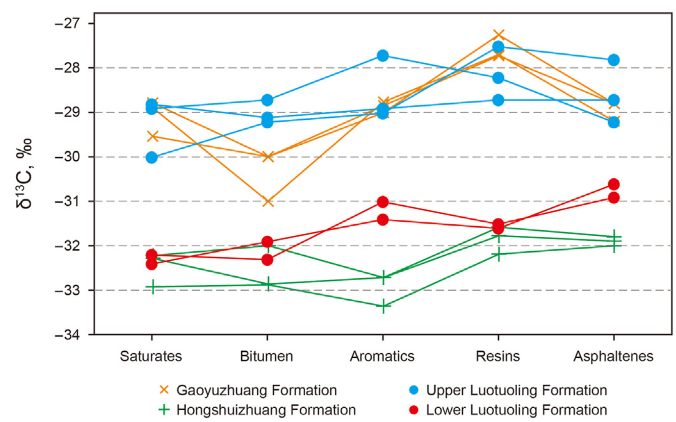

Fig. 10. Stable carbon isotope compositions of soluble hydrocarbons and their four fractions.

C_{29}–C_{35} regular hopanes, with C_{30} 17α(H)-diahopane as the major peak (Fig. 9b) and the ratio of C_{30} 17α(H)-diahopane to C_{30} hopane (C_{30}D/C_{30}H) of 5.71–7.92 (Table 2), consistent with the potential source rock of the Hongshuizhuang Formation (Fig. 5g). Both the upper and lower reservoir bitumens contain extremely low amounts of the moretane series (Fig. 9), which reinforces the suggestion that the oil is not from the Haifanggou Formation source rock (Fig. 6). Gammacerane (Ga) was first detected in the Green River shale (Hills et al., 1966) and is usually used to identify water column stratification environments resulting from hypersaline conditions. Gammacerane is also generally considered to derive from protozoa (Summons et al., 1988a). Considering the samples'

Table 3
The selected molecular markers and isotope compositions for oil source analysis and their distribution features.

No.	Molecular markers	Upper Luotuoling Fm. (Han-1)	Lower Luotuoling Fm. (Han-1)	Gaoyuzhuang Fm. (JQ-3 and L-1)	Hongshuizhuang Fm. (Han-1 and JQ-1)
1	C_{19}–C_{23}TT	major peak at C_{23}TT	major peak at C_{19} or C_{20}TT	major peak at C_{23}TT	major peak at C_{19} or C_{20}TT
2	13α(*n*-alkyl)-tricyclic terpanes	absence	high	absence	high
3	Rearranged hopanes	low	high	low	high
4	Gammacerane	moderate	absence	moderate	absence
5	Steranes	moderate	absence	moderate	absence
6	^{13}C isotope	enrichment	depletion	enrichment	depletion

Table 4
Stable carbon isotope data of the soluble hydrocarbons extracted from oil-bearing sandstones and potential source rocks, and their four fractions.

No.	Well	Formation	Saturates, ‰	Bitumen, ‰	Aromatics, ‰	Resins, ‰	Asphaltenes, ‰
1	Han-1	Upper Luotuoling	−28.8	−29.1	−28.9	−28.7	−28.7
2	Han-1	Upper Luotuoling	−28.9	−28.7	−27.7	−28.2	−29.2
3	Han-1	Upper Luotuoling	−30.0	−29.2	−29.0	−27.5	−27.8
4	Han-1	Lower Luotuoling	−32.2	−32.3	−31.0	−31.5	−30.9
5	Han-1	Lower Luotuoling	−32.4	−31.9	−31.4	−31.6	−30.6
6	JQ-3	Gaoyuzhuang	−29.5	−30.0	−29.0	−27.3	−28.8
7	JQ-3	Gaoyuzhuang	−28.8	−30.0	−28.9	−27.7	−28.8
8	JQ-3	Gaoyuzhuang	−28.9	−31.0	−28.8	−27.7	−29.2
9	JQ-1	Hongshuizhuang	−32.9	−32.9	−33.4	−32.2	−32.0
10	JQ-1	Hongshuizhuang	−32.2	−32.0	−32.7	−31.8	−31.9
11	JQ-1	Hongshuizhuang	−32.3	−32.9	−32.7	−31.6	−31.8

ages and general biological evolution, the gammacerane found in the Tuanshanzi Formation (1.7 Ga) in North China was considered to be from bacteria or ciliates (Peng et al., 1998). The upper reservoir bitumen contains moderately abundant gammacerane (Fig. 9a), with a gammacerane index of 0.15–0.19 (Table 2). However, gammacerane is absent or below the detection limit in the lower reservoir bitumen.

4.3.5. Steranes

Sterane series have been proved to be biomarkers of eukaryotic organisms (Peters et al., 2005). Their precursors are derived from the cell membranes of eukaryotes, including terrestrial higher plants, animals, algae, and fungi. Generally, C_{29} steranes are found in higher plants, planktonic green algae, and benthic brown algae, whereas a predominance of C_{27} regular steranes usually indicates contributions from benthic red algae, benthic green algae and planktonic dinoflagellates (Hoshino et al., 2017; Summons and Douglas, 2018; Xu et al., 2019). C_{27} diasteranes and C_{27}–C_{29} regular steranes were detected in the upper reservoir bitumen (Fig. 9c) with a ratio of steranes to hopanes (St/H) of 0.55–0.60 (Table 2), which indicates a certain contribution from eukaryotes. In contrast, C_{27} diasteranes and C_{27}–C_{29} regular steranes were not detected in the lower reservoir bitumen (Fig. 9d), which suggests that prokaryotes were the main source of organic matter, with a minimal contribution from eukaryotes. This is consistent with the Hongshuizhuang Formation black shales.

4.4. Oil sources of the Luotuoling Formation reservoirs in the Han-1 well

Oil-source correlation analysis relies primarily on stable carbon isotopes, and the source-related and sedimentary environment-related biomarkers that are comparatively unaffected by thermal maturity, including C_{19}–C_{23} regular tricyclic terpanes (Xiao et al., 2019b), 13α(n-alkyl)-tricyclic terpanes (Wang and Simoneit, 1995; Xiao et al., 2021b), rearranged hopanes (Xiao et al., 2019a, 2021a), and steranes (Brocks et al., 2017; Xiao et al., 2022).

Based on the predominance of odd carbon numbers, the abundance of the moretane series, the predominance of 22R over 22S isomers of C_{31}–C_{35} hopanes, and the apparent dominance of biological configurations in regular steranes, we can categorically conclude that the source rocks of the Haifanggou Formation made no contribution to the Luotuoling Formation reservoirs in Han-1 well. Oil-source correlation analysis shows that the upper reservoir bitumen originates from the Gaoyuzhuang Formation source rock, while the lower reservoir bitumen is derived from the Hongshuizhuang Formation source rock.

Both the upper reservoir bitumen and the Gaoyuzhuang Formation source rock have C_{23}TT as the major peak among C_{19}–C_{23} regular tricyclic terpanes (Table 3), an absence of 13α(n-alkyl)-tricyclic terpanes, low abundance of rearranged hopanes, and obvious distribution of gammacerane and steranes. The lower reservoir bitumen and the Hongshuizhuang Formation source rock are rich in C_{19}–C_{20}TTs, 13α(n-alkyl)-tricyclic terpanes and rearranged hopanes, and lack gammacerane and steranes.

The stable carbon isotope composition of bitumen directly reflects its kerogen types and the biogenetic organic matter (Galimov, 2006). In addition to the biomarkers, analysis of the stable carbon isotopic compositions of the bitumens/extracts and their four fractions in this study produces the same results as oil-source correlation (Fig. 10). The δ^{13}C values of both the upper reservoir bitumen and the Gaoyuzhuang Formation source rock and their four fractions (saturates, aromatics, resins, and asphaltenes) are in the range of −31.0‰ to −27.3‰, with almost all of the values being higher than −30‰ (Table 4). However, the lower reservoir bitumen and the Hongshuizhuang Formation source rocks and their four fractions are comparatively depleted in ^{13}C and have lower δ^{13}C values (−33.4‰ to −30.6‰) (Table 4). The ^{13}C enrichment of the upper reservoir bitumen and the Gaoyuzhuang Formation rock extracts indicates that, in addition to the primary contribution of bacteria and cyanobacteria, there may have a small amount of contribution from heterotrophic halophilic archaea (Li et al., 2003) or multicellular eukaryotes (Zhu et al., 2016).

5. Conclusions

This study firstly reports the hydrocarbon accumulations in the Neoproterozoic Luotuoling Formation of the Jianchang Sag, the North China. The discovery of liquid oil seepage in the lower member of the Luotuoling Formation sandstone is a promising indication of the Precambrian oil and gas exploration potential in the Jianchang Sag.

Observation of petrographic characteristics under the microscope found that the lower Luotuoling Formation reservoir contains yellow fluorescent liquid hydrocarbons, while the upper Luotuoling Formation sandstone is rich in non-fluorescent solid bitumen, which strongly suggests that the upper and lower reservoirs have different oil sources and/or accumulation processes. Further oil source analysis based on biomarkers (e.g., C_{19}–C_{23} regular tricyclic terpanes, 13α(n-alkyl)-tricyclic terpanes, rearranged hopanes, gammacerane, and steranes) and isotopic compositions (e.g., bitumen, rock extracts, and four fractions) indicates that the upper reservoir bitumen originates from the Gaoyuzhuang Formation source rock, while the lower reservoir bitumen is derived from the Hongshuizhuang Formation source rock.

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