Oil Shale, 2013, Vol. 30, No. 2, pp. 117–135
doi: 10.3176/oil.2013.2.03 ISSN 0208-189X

GEOCHEMICAL CHARACTERISTICS OF HIGH-QUALITY HYDROCARBON SOURCE ROCKS IN THE NANPU SAG OF THE BOHAI BAY BASIN, CHINA

GUANGYOU ZHU[(a)*], ZHENGJUN WANG[(b)], JIN SU[(a)]

[(a)] PetroChina Research Institute of Petroleum Exploration and Development, Beijing 100083, China
[(b)] PetroChina Jidong Oilfield Company Institute of Exploration and Development, Tangshan 063004, China

Abstract. *In recent years, the Nanpu Sag in the Bohai Bay Basin in eastern China has experienced great discoveries in exploration, and has become a sag most rich in oil and gas in the basin. However, the early evaluation believed that the source rocks were of low quality. Based on numerous samplings and analyses, this paper finds that* Es_3^4 *(the fourth sub-section of the third member of the Paleogene Shahejie Formation) is a high-quality hydrocarbon source rock, its TOC is above 5%. The thickness of high-quality hydrocarbon source rocks is 100 m and that of effective hydrocarbon source rocks about 250 m. The main buried depth of hydrocarbon source rocks is more than 3500 m, vitrinite reflectance (*R_o*) is more than 0.8%. The amorphous body and algae are an important source of organic matter in the hydrocarbon source rocks. The rocks are enriched with layers of clay and fine-grained calcite, which are the result of seasonal water stratification. The organic layer formed by algae breaking out and settlement is the main source of the organic-rich mudstone layer in* Es_3^4 *in the Nanpu Sag. The biomarkers in* Es_3^4 *reveal that the* Es_3^4 *oil shale has a higher content of 4-methyl steranes, which is significantly different from that in other source rocks. In addition, a detailed comparison of biomarkers and isotopes in the* Es_3^4 *oil shale and oil suggests that the oil in the Nanpu Sag comes mainly from the* Es_3^4 *source rock, which is an object of future exploration.*

Keywords: *high-quality hydrocarbon source rocks, lamellar structure, 4-methyl steranes, Paleogene Shahejie Formation, oil-rich Nanpu Sag, Bohai Bay Basin.*

1. Introduction

Oil and gas reservoirs are formed only when there are effective hydrocarbon source rocks. For a long time, hydrocarbon source rocks have been evaluated

* Corresponding author: e-mail *zhuguangyou@petrochina.com.cn*

by collecting rock and rock debris and gathering information on organic carbon content, kerogen type and maturity, and molecular geochemistry. Then a set of evaluation indexes and methods established provide an important reference and support for oil and gas exploration [1–9]. In recent years, with the discovery of the heterogeneity of hydrocarbon source rocks in lacustrine basins [10–15], and development of the concept of high-quality hydrocarbon source rocks [16–18], the above method cannot reflect the contribution or influence of strata of high- or low-abundant organic matter, even more, it leads to wrong conclusions. In some oil and gas basins, no good cores of hydrocarbon source rock can be obtained due to the restrictions of drilling and coring, which implies great challenges to the evaluation of hydrocarbon source rocks. Due to the lack of good samples of hydrocarbon source rocks from the Nanpu Sag in the Bohai Bay Basin, the past evaluation considered the sag's potential for oil and gas resources to be unpromising. In addition, previous studies have evaluated the Es_3 source rock as a whole [19–20], but this study also deals with its sub-sections and finds that oil and gas come mainly from the Es_3^4 source rock, whose discovery is of importance for planning next-step exploration and finding deep tight sandstones interbedded with this source rock.

2. Oil and gas geology in the Nanpu Sag

The Nanpu Sag, located in the northeast of the Huanghua Depression, Bohai Bay Basin, China, represents a syndepositional rift valley fault sag (Fig. 1). The favorable exploration area is approximately 1932 km^2, including 570 km^2 land and 1362 km^2 beach [21]. The Nanpu Sag is a typical dustpan-like sag with the characteristics of north broken and south overlap in the Tertiary [22]. The sag interior is divided into the southern and northern zones by the Gaoliu fault. The southern zone is the depositional center of the Shahejie Formation where the Liuzan and Gaoshangpu drape anticlinal structures and the Shichang sub-sag have been developed and is the main oil-bearing zone of the Shahejie Formation. The southern zone is the depositional center of the Dongying Formation. The Laoyemiao and Beipu reverse drag anticlines have been developed in the footwall of the Xinanzhuang fault; the structural belts of Nanpu I, Nanpu II, Nanpu III, Nanpu IV and Nanpu V have been developed in the beach area. Two negative structural units of the Linque and Liunan sub-sags have been developed, from west to east, in the central area and are also important hydrocarbon-generating centers (Fig. 1). The Lower Tertiary Minghuazhen, Guantao, Dongying and Shahejie formations are important petroleum-bearing formations [23].

The Nanpu Sag is a mature area in terms of exploration. In recent years, a number of large petroliferous structures and traps have been discovered by in-depth exploration, and a great breakthrough has been achieved in the beach area where the large Nanpu oilfied has a resource of a billion tons. So,

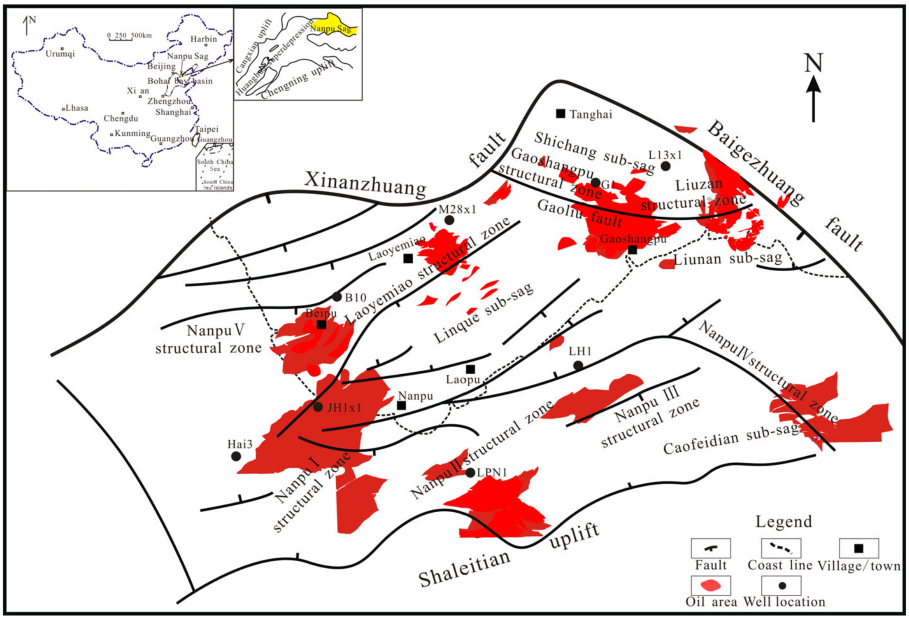

Fig. 1. The tectonic map of and oil-gas distribution in the Nanpu Sag.

it is needed for petroleum geologists to further study the generation and accumulation of oil and gas in the Bohai Bay Basin. It is noteworthy that the values of TOC in source rocks that were used in the past resource evaluations are generally low [24] and greatly differ from the lower TOC value of effective source rocks in the Bohai Bay Basin. So far, effective and excellent source rocks have not been identified. In fact, few wells have been drilled in deep depressions in the Nanpu Sag, coring wells are even fewer, and wells from which the Shahejie Formation mudstone is obtained are almost next to nothing. In the evaluation of source rocks, the parameters of mudstones obtained from the coring wells in the margin of the sag served as features of source rocks of the whole sag. As a result, it appeared that earlier estimated reserves exceeded resources. Combining the latest data on exploration in the oilfield, this paper examines the Tertiary source rocks in the Nanpu Sag, observes and analyzes all the cores, and finds that multiple source rocks have been developed in the sag, with Es_3^4 as a major source rock. In combination of geology and geochemistry, this paper discusses the characteristics and mechanism of formation of the Es_3^4 source rock and points out its geological significance.

3. Sample collection and analysis

Due to rare drilling and coring, the parameters of the mudstone from coring wells in the sag's margin were used to evaluate hydrocarbon source rocks of the sag. In the past resource evaluations, the adopted TOC values of rocks in the Nanpu Sag were low (most actual measured data were low), about 0.8–1.2%. However, in the Bohai Bay Basin as a whole, the lower value of TOC of effective hydrocarbon source rocks is over 1.0%, amounting to 1.5%. So, a contradictory situation occurs that the earlier estimated reserves exceed the calculated resources.

The organic carbon content, pyrolysis parameters, kerogen composition, vitrinite reflectance, and isotope composition of the source rock and oil were determined and GC-MS performed in the National Key Laboratory of PetroChina Research Institute of Petroleum Exploration and Development. All the samples were analyzed using conventional methods, the analysis standards met international standards.

4. Geochemical characteristics

4.1. Lithological association and geochemical characteristics of hydrocarbon source rocks in the Paleogene Shahejie Formation

The Paleogene Shahejie Formation is the most important sedimentary association and hydrocarbon source rock developing stratum [25–27]. During the sedimentary evolution process, the lake basin was broad and water deep and lacustrine mudstones were most developed in Es_3. This was the most important period in the development of high-quality hydrocarbon source rocks, and exhibits strong reflections in seismic response. According to lithological features, Es_3 can be divided into five submembers, Es_3^5, Es_3^4, Es_3^3, Es_3^2, Es_3^1 from bottom to top (Fig. 2). Of them, Es_3^4 contains widely spread mudstones and oil shale, which are the best hydrocarbon source rocks discovered in this study, followed by Es_3^3 and other submembers. Es_1, the first Member of the Shahejie Formation, developed lacustrine deposition, which provides a good geological background for formation of hydrocarbon source rocks. The Dongying Formation developed dark grey mudstones, which are also good hydrocarbon source rocks. The hydrocarbon-generating system composed of many sets of hydrocarbon source rocks are the foundation for the enrichment of hydrocarbons in the Nanpu Sag.

4.2. Geochemical characteristics and distribution of high-quality hydrocarbon source rocks in Es_3^4

Es_3^4 is a set of high-quality hydrocarbon source layers where TOCs are mostly more than 2%, and some are over 8% (Table 1). This set of hydrocarbon source rocks has a well-developed lamellar structure (Fig. 3). These rocks developed in the deepest water at the most well developed stage of the lake, and are also called a “condensed section” in the study of continental sequence stratigraphy. This means that they are characterized by low deposition rate, and fine grains, corresponding to the largest undercompensation sedimentation, and the lake has the largest accommodation space. This set of

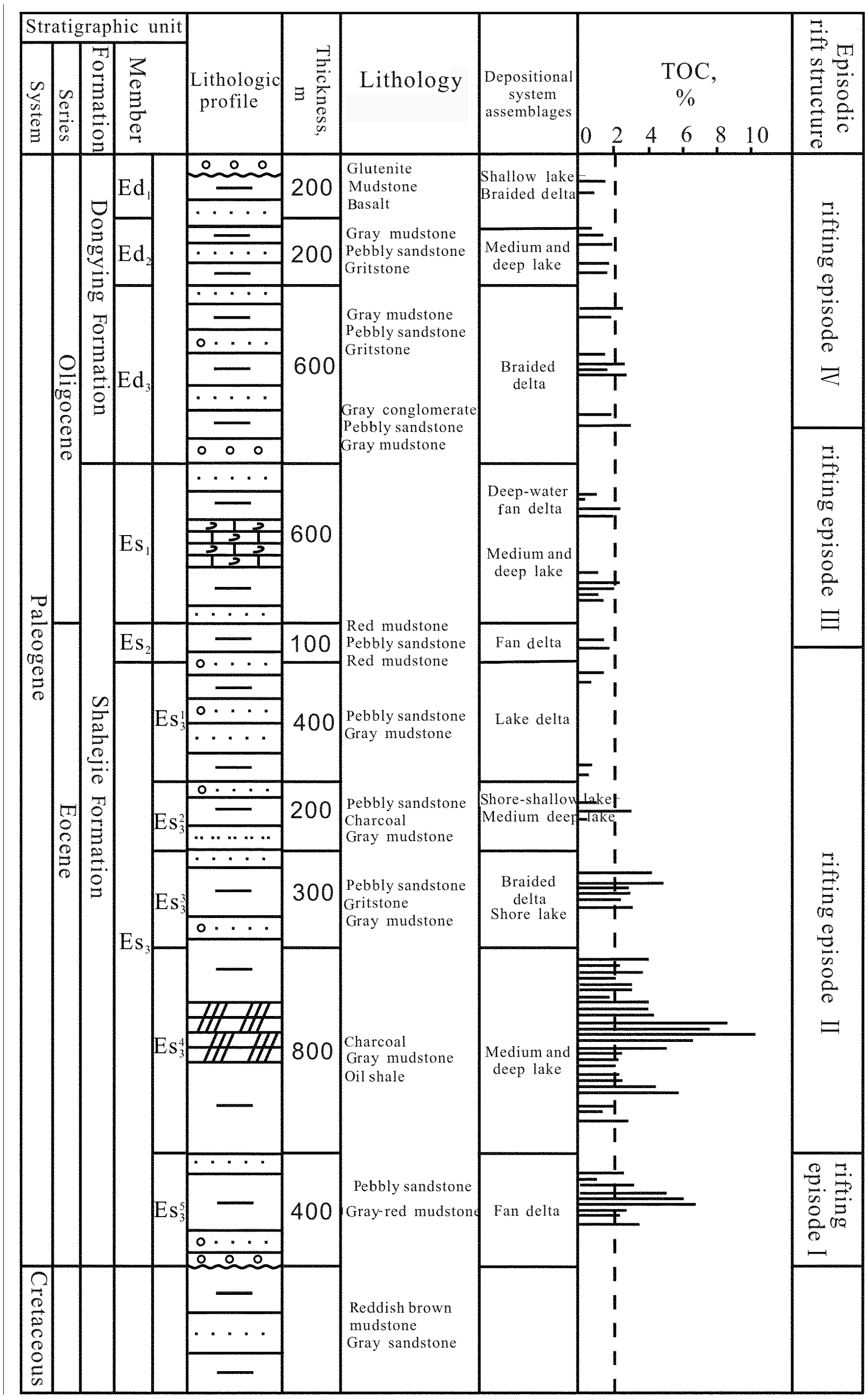

Fig. 2. A comprehensive lithological-geological histogram of and vertical distribution of organic carbon in the Nanpu Sag.

Table 1. Geochemical data of the high-quality hydrocarbon source rock in Es_3^4 in the Nanpu Sag

Well	Depth, m	Stratum	Lithology	TOC, %	Tmax, ℃	S_1, mg/g	S_2, mg/g	S_1+S_2, mg/g	HI, mg/g.TOC
G190×1	4003.00	Es_3^4	Mudstone	4.20	442	1.19	22.28	23.47	530
G190×1	4014.50	Es_3^4	Mudstone	3.55	439	1.35	17.71	19.06	499
G19-10	4043.54	Es_3^4	Mudstone	3.44	444	3.74	16.80	20.54	488
G19-10	4043.69	Es_3^4	Mudstone	3.37	441	3.71	18.97	22.68	563
G19-10	4043.84	Es_3^4	Mudstone	7.37	439	6.21	48.15	54.36	653
G19-10	4044.04	Es_3^4	Mudstone	6.50	439	5.11	44.57	49.68	686
G19-10	4044.24	Es_3^4	Mudstone	8.78	442	6.06	57.20	63.26	651
G19-10	4044.32	Es_3^4	Mudstone	5.65	442	4.64	38.31	42.95	678
G19-10	4044.5	Es_3^4	Mudstone	4.34	442	4.45	25.79	30.24	594
G19-10	4045.36	Es_3^4	Mudstone	1.92	441	1.76	8.93	10.69	465
G19-10	4045.70	Es_3^4	Mudstone	1.97	440	2.24	9.33	11.57	474
G19-10	4045.78	Es_3^4	Mudstone	2.12	443	2.73	10.29	13.02	485
G19-10	4045.92	Es_3^4	Mudstone	3.79	439	4.58	22.37	26.95	590
G19-10	4046.41	Es_3^4	Mudstone	4.91	442	4.89	29.87	34.76	608
G19-10	4050.00	Es_3^4	Mudstone	4.00	441	3.27	19.02	22.29	476
G62	4054.00	Es_3^4	Mudstone	1.11	431	8.51	3.86	12.37	348
G65×1	3228.95	Es_3^4	Mudstone	3.56	439	0.33	19.25	19.58	541
G65×1	3277.00	Es_3^4	Mudstone	2.24	440	0.13	8.80	8.93	393
G8	3501.80	Es_3^4	Mudstone	3.14	437	0.56	16.81	17.37	535
G8	3505.28	Es_3^4	Mudstone	3.01	436	0.56	16.64	17.20	553
G8	3508.00	Es_3^4	Mudstone	2.96	433	0.45	14.80	15.25	500
G18	3523.62	Es_3^4	Mudstone	2.43	439	1.02	12.98	14.00	534
G18	3525.20	Es_3^4	Mudstone	3.86	491	0.51	20.73	21.24	537
G18	3527.48	Es_3^4	Mudstone	2.83	439	0.46	10.48	10.94	370
GC1	3923.50	Es_3^4	Mudstone	4.93	442	0.65	21.49	22.14	436
GC1	3994.50	Es_3^4	Mudstone	4.82	445	0.62	18.53	19.15	384
GC1	3996.50	Es_3^4	Mudstone	4.81	446	0.64	19.65	20.29	409
L38×1	3383.00	Es_3^4	Mudstone	2.71	437	0.23	13.53	13.76	499
L38×1	3384.57	Es_3^4	Mudstone	2.42	439	0.34	19.95	20.29	824
L38×1	3385.86	Es_3^4	Mudstone	3.44	438	0.34	20.30	20.64	590
L12	3300.00	Es_3^4	Mudstone	2.67	435	0.43	16.8	17.23	629
L12	3300.00	Es_3^4	Mudstone	2.67	435	0.43	16.8	17.23	629
L12	3320.00	Es_3^4	Mudstone	2.27	436	0.37	12.05	12.42	530
L12	3340.00	Es_3^4	Mudstone	2.20	436	0.37	10.67	11.04	485
L12	3360.00	Es_3^4	Mudstone	2.50	436	0.39	14.24	14.63	569
L12	3380.00	Es_3^4	Mudstone	2.32	436	0.38	12.52	12.9	539
L13	3566.00	Es_3^4	Mudstone	4.07	425	1.36	28.56	29.92	701
L13	3604.00	Es_3^4	Mudstone	4.19	425	1.56	30.96	32.52	738
L13	3653.00	Es_3^4	Mudstone	2.50	428	1.00	14.12	15.12	564
LS11	3384.00	Es_3^4	Mudstone	2.13	437	0.42	11.96	12.38	562
LS11	3414.00	Es_3^4	Mudstone	2.42	440	0.47	15.08	15.55	623
LS11	3424.00	Es_3^4	Mudstone	2.25	433	0.71	11.8	12.51	524
LS11	3490.00	Es_3^4	Mudstone	2.29	442	0.42	13.52	13.94	590
PG2	4665.30	Es_3^4	Mudstone	1.95	462	0.48	2.14	2.62	110
PG2	4665.35	Es_3^4	Mudstone	2.00	463	0.50	2.24	2.74	112
PG2	4665.90	Es_3^4	Mudstone	2.11	461	0.51	2.38	2.89	113
PG2	4666.17	Es_3^4	Mudstone	1.63	463	0.54	1.78	2.32	109
PG2	4666.72	Es_3^4	Mudstone	1.74	459	0.50	1.95	2.45	112
PG2	4666.80	Es_3^4	Mudstone	1.95	464	0.47	2.07	2.54	106

Table 1 (continuation)

Well	Depth, m	Stratum	Lithology	TOC, %	Tmax, ℃	S_1, mg/g	S_2, mg/g	S_1+S_2, mg/g	HI, mg/g.TOC
PG2	4667.72	Es_3^4	Mudstone	1.54	466	0.46	1.57	2.03	102
NP280	4324.00	Es_3^4	Mudstone	2.33	447	0.51	2.33	2.84	100
NP280	4296.00	Es_3^4	Mudstone	1.92	450	0.72	2.24	2.96	117
NP280	4340.00	Es_3^4	Mudstone	2.32	445	1.37	2.66	4.03	115
NP2-82	4647.00	Es_3^4	Mudstone	2.18	443	0.85	4.01	4.86	184
NP2-82	4730.00	Es_3^4	Mudstone	2.21	443	0.95	3.96	4.91	179
NP2-82	4810.00	Es_3^4	Mudstone	2.33	448	1.56	3.56	5.12	153
NP288	4052.00	Es_3^4	Mudstone	1.55	449	0.37	3.18	3.55	205
NP288	4372.00	Es_3^4	Mudstone	1.58	455	0.32	1.02	1.34	65
NP288	4421.00	Es_3^4	Mudstone	2.33	450	0.94	2.53	3.47	109

TOC – weight percent organic carbon; S_1 – mg HC/g dry rock distilled by pyrolysis; S_2 – mg HC/g dry rock cracked from kerogen by pyrolysis; Tmax – temperature, °C; HI – $S_2 \times 100$/TOC.

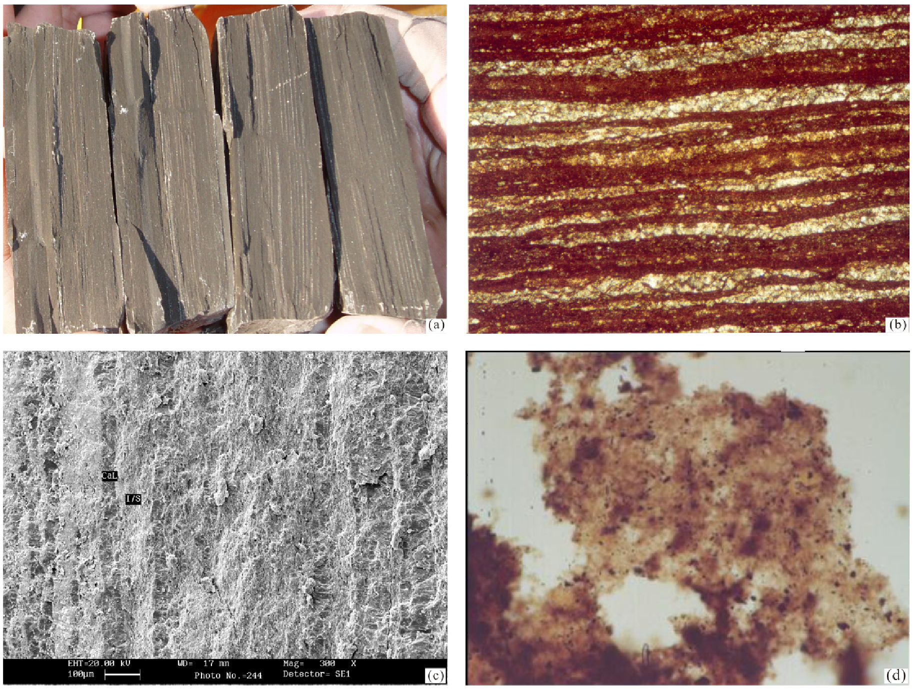

Fig. 3. Characteristics of high-quality hydrocarbon source rocks in Es_3^4: (a) grey-brown sheath of oil shale showing a very good pattern of bedding; (b) lamellar structure of high-quality hydrocarbon; (c) clay layer rich in organic matter; (d) amorphous solid algae and mud rot, transmission light.

high-quality hydrocarbon source rocks have a light mass, are rich in crude oil, and have a chocolate color and a high content of organic matter [25]. They can be burnt, with emission of heavy smoke and a scent of asphalt

(Fig. 3). The rocks are composed of layers of fine-grained calcite and clay enriched in organic matter. The clay layers are mainly composed of organic matter, clay minerals (illites are over 95%), quartz, feldspars, ankerite, pyrite, etc., and the horizontal layers show the characteristics of standing water sedimentation. Of kerogen macerals and soluble organic matter, the abundant amorphous body and algae are important sources of organic matter (Fig. 3).

The formation of laminated high-quality hydrocarbon source rocks of Es_3^4 is closely related to the stratification of lake water. The difference in water temperature between the lake surface and bottom could cause the formation of thermocline, and the separation of the lake water caused the seasonal division of water density, so the suspended fine-grained sediments were deposited with seasonal changes [28–34]. The lamellation of the deep lacustrine oil shale represents a seasonal deposition process. By cores observation, the oil shale is lack of benthic fossil and has terrigenous clastics, preserved fish fossils and pyrites. These characteristics and geochemical analysis suggest that the bottom water of the lake had a strong reducing condition without oxygen during the formation of oil shale, which results from the stratification of water. A microscopic observation reveals stratified fossilized algae whose outbreak and sedimentation are an important reason for the development of the organic lamina. Overall, the hydrocarbon source rocks are dominantly floating algae in the Nanpu Sag. Photosynthesis, respiration and decomposition of algae can affect the concentrations of oxygen and carbon dioxide in some complex ways. The intensity of this effect is controlled by algal colony, while algal colony is controlled by nutrition, light, temperature and salinity. After the death of the algae, the debris is preserved in the bottom of the lake and the calcium and magnesium in the algae debris are released to form magnesium carbonate. Thus, the formation of organic and carbonate laminae is related to plankton. The outbreak of algae can enhance the formation of high-organic oil shale. The kerogen is mainly sapropel and is composed of types II_1 and I (Fig. 4), and the cloud misty, cottony, crumble amorphism degraded by aquatic low algae are over 80%, associated with large quantities of globular pyrite. There is a low content of fine crushing or small flake terrestrial detritus of higher plants. The content of the biomarker, such as tricyclene, gammacerane and oleanane, is low, suggesting a freshwater sedimentary environment with a minor input of continental source.

There are strong reflections in the geophysical response and logging parameters have good response. The value of apparent resistibility is high, and the value of apparent density is low. It is easy to track, identify and evaluate.

The thickness of effective source rocks is over 100 m (TOC > 2.0%), being about 250 m in the center of the Nanpu Sag (TOC > 2 %). The thickness of high-quality hydrocarbon source rocks is over 100 m (TOC 2–5%) and they are widely distributed (Fig. 5). The rocks are one of the most important hydrocarbon source rocks in the Nanpu area, their formation potential is tremendous.

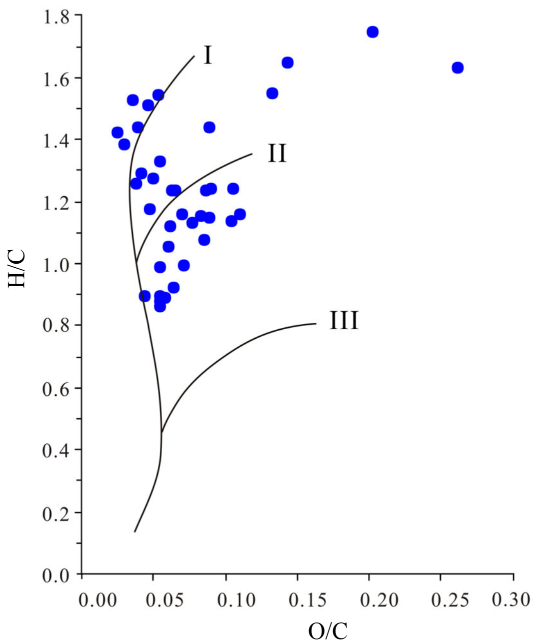

Fig. 4. The kerogen type of high-quality hydrocarbon source rocks in Es_3^4. Atomic H/C versus O/C diagram based on elemental analysis of kerogen can be used to describe the type of organic matter in source rocks.

The extent of thermal evolution of source rocks in the Nanpu Sag is one of the highest in the Shahejie Formation of the Bohai Bay Basin. The burial bottom depth of Es_3 in the Nanpu Sag is about 5800–6400 m (Fig. 6). The authors obtained a great number of black mudstone samples of various source rock strata, analyzed their vitrinite reflectance, and also collected analytic data about predecessors. The source rocks in the deepest depression are over-matured and the vitrinite reflectance (R_o) is already over 1.0% (Fig. 7). In addition, the rapid sedimentation speed leads to the high extent of thermal evolution of source rocks. The expulsive efficiency of mature source rocks of Es_3 is over 80% [23].

4.3. Biomarker characteristics of Es_3^4 source rock

The Es_3^4 dark brown oil shale is one of the best source rocks in the Nanpu Sag, with foliation developed, and is composed mainly of dark organic and light calcareous laminae. The seasonal fluctuation of lake water and the corresponding bloom of phytoplankton are the main reasons for the formation of the laminae. The shale is rich in algae and fish fossils, suggesting that it was formed in a deep-lake oxygen-poor environment. Limited by coring conditions, this study takes the oil shale from well G19-10 well as an example.

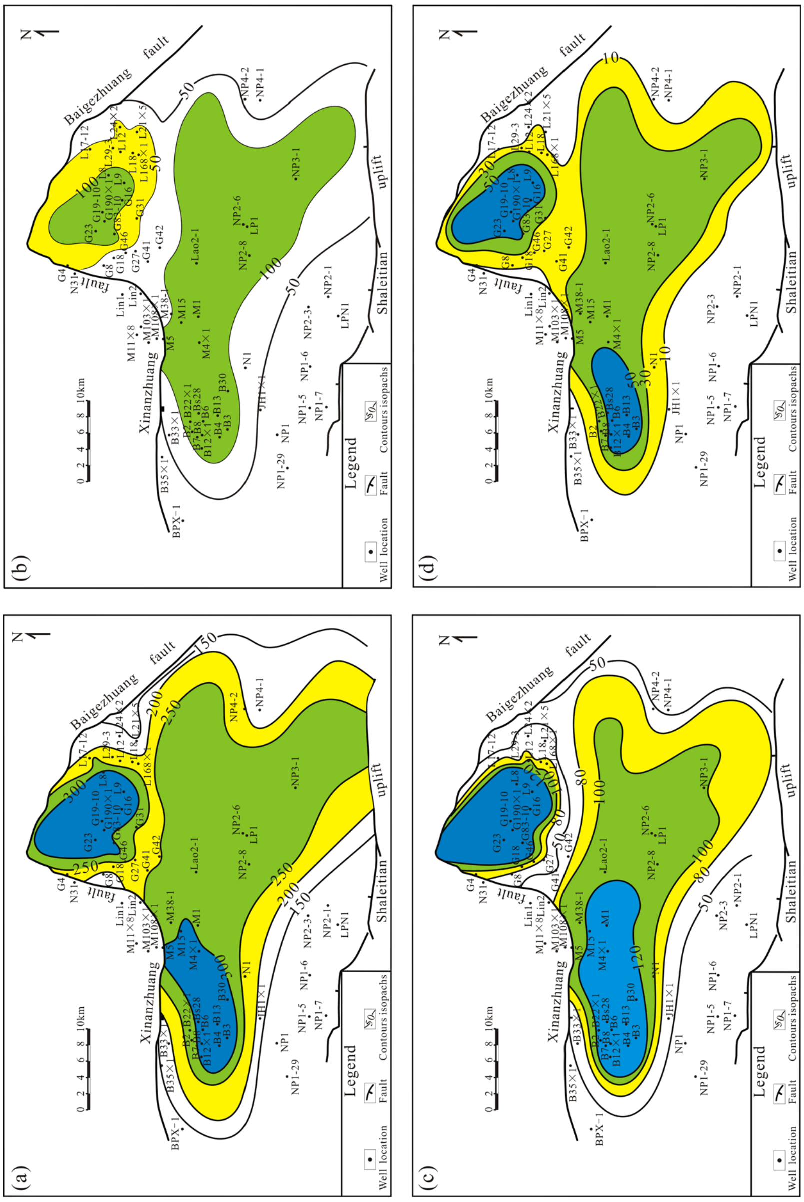

Fig. 5. Contour of the Es_3^4 source rock in the Nanpu Sag: (a) thickness contour of dark mudstones; (b) thickness contour of the source rock of 1–2% TOC; (c) thickness contour of the source rock of 2–5% TOC; (d) thickness contour of the source rock of more than 5% TOC.

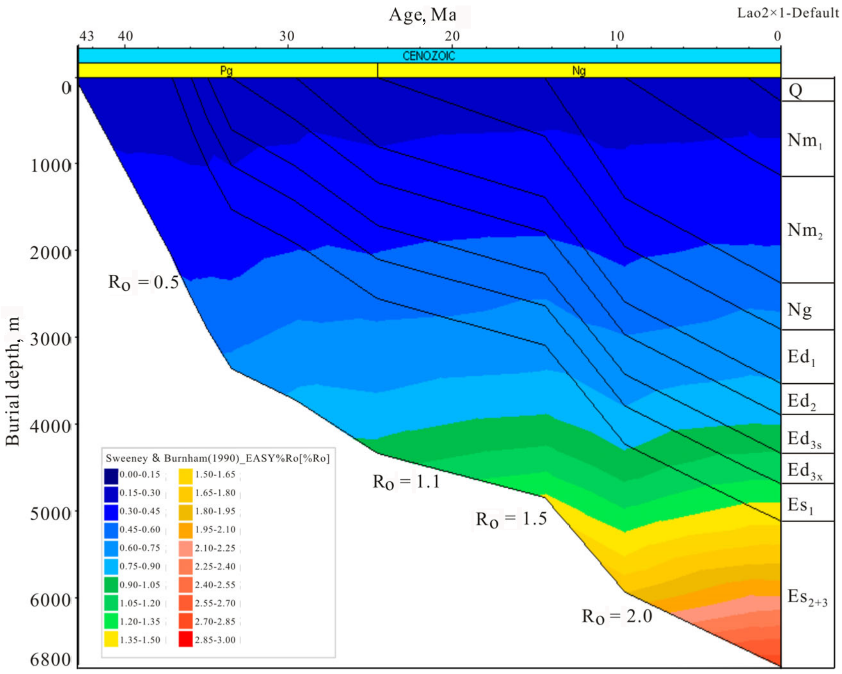

Fig. 6. The burial history curve of source rocks in the Linque-Liunan area, Nanpu Sag.

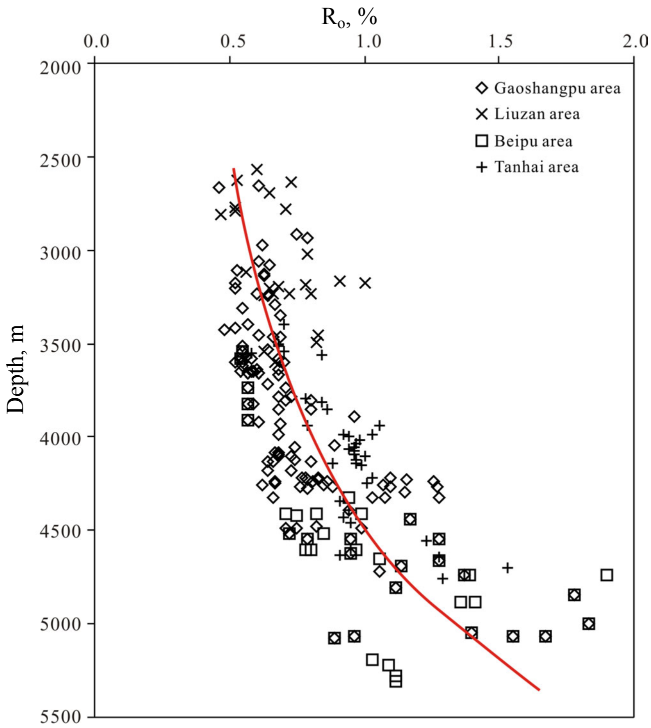

Fig. 7. The relation between the vitrinite reflectance (R_o) and depth of source rocks in the Nanpu Sag.

The biomarkers of steranes and terpanes in the Es_3^4 source rock have the following characteristics (Fig. 8). Tricyclic terpanes are low, tricyclic terpanes of low carbon number have a normal distribution, C_{21} or C_{23} is the main peak, C_{26}/C_{25} tricyclic terpanes are mostly above 1.0 typical of lake source rock, tricyclic terpanes of high carbon number (C_{28} or C_{29}) are of a relatively high content, gammaceranes are underdeveloped with a ratio of gammacerane to C_{30}H less than 0.04. Ts/Tm is approximately 1.0; C_{29} Ts and C_{30} rearranged hopanes and normoretanes have a relatively low content; oleananes are even lower and can not be observed. The distribution of regular steranes is dominately C_{27} and C_{29} steranes with the ααα-20R configuration, with a low content of C_{28} regular steranes. Regular steranes are distributed in a "V" shape, the content of C_{27} steranes is slightly higher than that of C_{29} steranes, similarly to source rocks in other strata. The difference is that rearranged steranes are underdeveloped, with a ratio of rearranged to regular steranes about 0.2 (Table 2). 4-melhyl steranes are highly developed, equivalent in content to C_{29} steranes (Fig. 8).

The m/z 231 mass chromatogram of saturated hydrocarbons in the Es_3^4 source rock shows that the distribution of C_{28}–C_{30} methyl steranes is significantly different from that in other source rocks (Fig. 8). C_{28} and C_{30} methyl steranes are abundant, while C_{29} methyl steranes are relatively low in abundance. Among C_{30} methyl steranes, 4α-methyl and 24-ethyl C_{30} steranes are the most abundant, being significantly more abundant than dinosteranes and 3β-methyl and 24-ethyl C_{30} sterane.

In summary, there are source rocks with highly abundant organic matter, good kerogen type, a high degree of thermal evolution and hydrocarbon-generating as well as expulsive efficiency, and of great thickness and wide distribution in Es_3 in the Nanpu Sag. The potential of source rocks is tremendous. In the Es_3^4 source rock, 4-methyl steranes are abundant, the presence of C_{30} methyl steranes is an important feature, which distinguishes this source rock from other rocks.

4.4. Component content and isotopic chararacteristics

The carbon isotopes of kerogen in the Es_3^4 source rock are distributed in the range of –26 to –27‰, the carbon isotopes of saturated hydrocarbons are mostly around –28‰. The carbon isotopes of aromatic hydrocarbons are predominantly in the range of –26 to –27‰, but the carbon isotopes of non-hydrcarbons and bitumen vary greatly. Compared to the carbon isotopes of kerogen, the carbon isotopes of crude oil in the Es_3^4 source rock are generally lower by 1 to 2‰, and are prevailingly distributed in the range of –27.2 to –28.9‰. The carbon isotopes of saturated hydrocarbons are mainly in the range of –27.3 to –30.0‰, being mostly from –27.3 to –28.9‰. The carbon isotopes of aromatic hydrocarbons mainly range from –26 to –27.9‰, the carbon isotopes of non-hydrcarbons vary from –24.8 to –26.7‰, and the carbon isotopes of bitumen from –25.3 to –26.9‰ (Table 3).

Table 2. Biomarker parameters of the Es_3^4 source rock and oil

Well	Depth, m	Age of reservoir rock	Sample type	C29Ts/C30H	NorM/C_{30}H	Ol/Hop	TT/Hop	Ts/Tm	Mor/Hop	C_{31} S/R	C_{32} S/R	$C_{29}\alpha\alpha\alpha S/(S+R)$	$C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$	$\alpha\alpha\alpha(R)C_{27}/C_{29}$	$\alpha\alpha\alpha(R)C_{28}/C_{29}$	C_{27}, %	C_{28},%	C_{29},%	$C_{27}\alpha\alpha\alpha(R)$%	$C_{28}\alpha\alpha\alpha(R)$%	$C_{29}\alpha\alpha\alpha(R)$%	S/(S + T)	C_{25}/C_{26}	C_{24}/C_{26}
G19-10	4043.84	Es_3^4	Mudstone	0.15	0.06	0.02	0.03	0.94	0.14	1.42	1.45	0.53	0.36	1.10	0.73	0.35	0.24	0.41	0.39	0.26	0.35	0.14	2.76	0.28
G19-10	4044.24	Es_3^4	Mudstone	0.17	0.06	0.02	0.03	0.91	0.14	1.39	1.36	0.53	0.35	0.96	0.68	0.35	0.24	0.42	0.36	0.26	0.38	0.13	2.72	0.27
G8	3501.8	Es_3^4	Mudstone	0.22	0.16	0.06	0.04	0.66	0.19	1.42	1.31	0.32	0.28	1.46	0.63	0.47	0.17	0.36	0.47	0.20	0.32	0.20	1.46	1.01
L38×1	3384.57	Es_3^4	Mudstone	0.12	0.06	0.03	0.02	0.66	0.11	0.87	0.70	0.10	0.29	1.69	0.63	0.48	0.20	0.32	0.51	0.19	0.30	0.39	3.95	0.45
G17-16	3497.2–3794.2	Es_3	Oil	0.20	0.05	0.04	0.06	1.11	0.14	1.30	1.48	0.37	0.54	0.55	0.33	0.34	0.21	0.45	0.29	0.18	0.53	0.12	0.56	1.36
G22	4114–4156	Es_3	Oil	0.25	0.05	0.02	0.05	1.33	0.14	1.53	1.39	0.41	0.59	0.61	0.51	0.36	0.22	0.42	0.29	0.24	0.47	0.13	0.56	1.71
G29	2224–2229.6	Ng	Oil	0.17	0.07	0.07	0.04	0.80	0.16	1.46	1.25	0.31	0.39	0.85	0.79	0.37	0.29	0.34	0.32	0.30	0.38	0.21	0.71	1.91
G32	2799.4–2828	Ed_3	Oil	0.18	0.05	0.08	0.08	1.12	0.14	1.29	1.40	0.41	0.53	0.75	0.66	0.38	0.26	0.36	0.31	0.27	0.41	0.19	0.60	1.10
G40	3185–3187.4	Ed_3	Oil	0.23	0.08	0.12	0.03	1.03	0.14	1.43	1.28	0.30	0.39	0.90	0.85	0.37	0.30	0.33	0.33	0.31	0.36	0.28	0.78	2.15
G76-12	2954–3017.8	Es_3	Oil	0.12	0.05	0.04	0.10	1.08	0.14	1.32	1.26	0.53	0.46	0.78	0.61	0.36	0.19	0.46	0.33	0.25	0.42	0.16	1.23	0.85
G76-42	3124.8–3202.2	Es_1	Oil	0.17	0.06	0.06	0.12	1.35	0.19	1.39	1.30	0.50	0.38	0.65	0.51	0.35	0.20	0.45	0.30	0.24	0.46	0.18	1.27	0.83
G104-5P32	2129.1–2199.57	Ng	Oil	0.15	0.06	0.10	0.09	0.88	0.16	1.30	1.21	0.37	0.38	0.74	0.73	0.34	0.30	0.36	0.30	0.30	0.40	0.23	1.17	0.88
G69-10	2169.8–2170.0	Ng	Oil	0.13	0.05	0.05	0.07	0.96	0.14	1.33	1.25	0.51	0.48	0.93	0.82	0.35	0.26	0.38	0.34	0.30	0.36	0.15	1.07	0.88
G105×1	2569.4–2599.6	Ed_1	Oil	0.19	0.04	0.08	0.06	1.73	0.15	1.35	1.24	0.44	0.43	0.74	0.69	0.39	0.23	0.38	0.30	0.28	0.41	0.19	1.05	0.85
G29-10	1989.6–1993.2	Nm	Oil	0.11	0.05	0.04	0.08	0.80	0.13	1.31	1.30	0.51	0.50	0.79	0.73	0.34	0.26	0.40	0.31	0.29	0.40	0.13	1.08	0.89
G69-14	2377–2382	Ng	Oil	0.14	0.05	0.06	0.08	1.10	0.14	1.34	1.30	0.43	0.40	0.71	0.63	0.35	0.27	0.38	0.30	0.27	0.43	0.17	1.20	0.84
G59-5	2564.4–2563.2	Ed_1	Oil	0.21	0.04	0.11	0.07	1.96	0.15	1.31	1.23	0.45	0.46	0.75	0.74	0.40	0.24	0.35	0.30	0.30	0.40	0.25	1.21	0.78
G3	2876–3600	Es_3^3	Oil	0.10	0.07	0.02	0.03	0.56	0.15	1.38	1.32	0.43	0.28	0.93	0.65	0.35	0.23	0.42	0.36	0.25	0.39	0.15	1.06	0.90
LB2-21-2	2622.8–2697.0	Es_3^3	Oil	0.26	0.03	0.05	0.05	2.21	0.14	1.35	1.27	0.47	0.46	0.53	0.46	0.35	0.19	0.47	0.27	0.23	0.50	0.19	1.07	1.17
L27×6	2685.6–2695.4	Es_3^2	Oil	0.17	0.04	0.03	0.04	1.26	0.14	1.36	1.30	0.50	0.40	0.58	0.48	0.33	0.19	0.48	0.28	0.23	0.49	0.15	0.92	1.12
L125×1	2043–2045	Ng	Oil	0.15	0.05	0.06	0.13	0.82	0.15	1.19	1.23	0.48	0.38	0.65	0.52	0.35	0.20	0.45	0.30	0.24	0.46	0.26	1.20	0.89
L10	3367.4–3641.5	Es_3	Oil	0.24	0.07	0.06	0.07	1.20	0.16	1.28	1.50	0.38	0.49	0.82	0.54	0.38	0.24	0.39	0.35	0.23	0.42	0.18	0.55	1.18
L12-6	3588.4–3659.3	Es_3^5	Oil	0.22	0.05	0.04	0.05	1.57	0.16	1.37	1.31	0.50	0.38	0.85	0.63	0.36	0.22	0.42	0.34	0.25	0.40	0.19	1.16	1.04

C29Ts/C30H – 17α,21β-30-norhopane/17α(H), 21β(H)-hopanes; NorM/C_{30}H – normoretane/17α(H), 21β(H)-hopanes; Ol/Hop – oleanane/17a hopane; Mor/Hop – moretane 17a hopane; TT/Hop – all tricyclic terpanes/all hopanes; S/(S + T) – all steranes/(all steranes + all terpanes); $C_{27}\alpha\alpha\alpha$ – C_{27}aaa20R sterane/(C_{27} + C_{28} + C_{29})aaa20R steranes; $C_{28}\alpha\alpha\alpha$ – C_{28}aaa20R sterane/(C_{27} + C_{28} + C_{29})aaa20R steranes; $C_{29}\alpha\alpha\alpha$ – C_{29}aaa20R sterane/(C_{27} + C_{28}+ C_{29})aaa20R steranes; Dia/Hop – 15a-methyl-27-nor-17a-hopane/17a hopane; C_{24}/C_{26} – C24 tetracyclic terpane/C_{26}(S+R) tricyclic terpanes; C_{25}/C_{26} = C_{25}(S + R) tricyclic terpanes/C_{26}(S+R) tricyclic terpanes

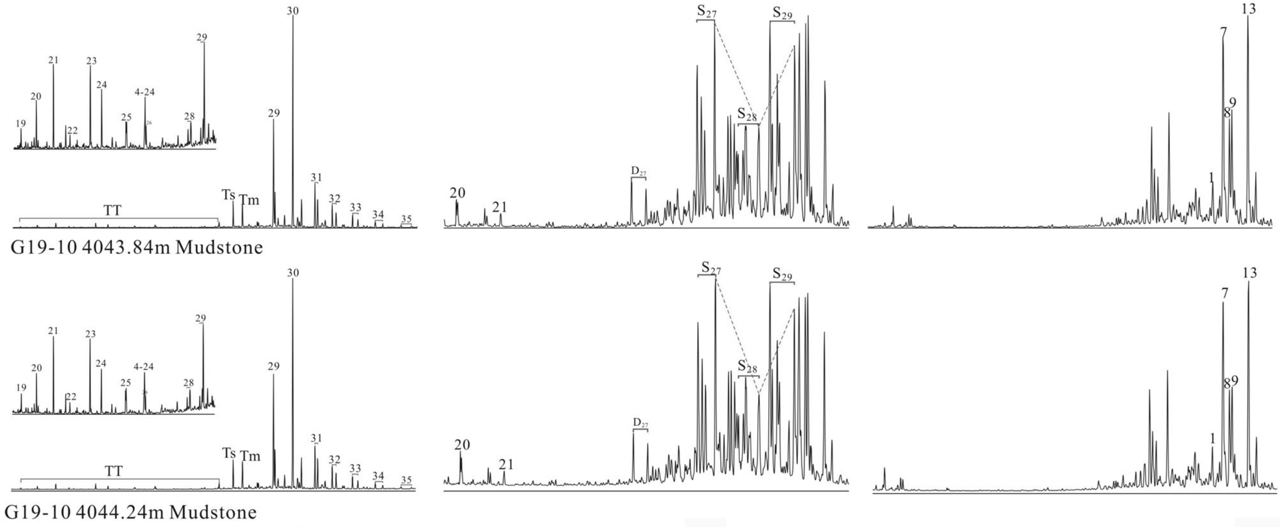

Fig. 8. Biomarker compound characteristics of the Es_3^4 source rock.

TT – tricyclic terpanes (C_{19}-C_{29}); Ts – 18α,-22,29,30-trisnorhopane; Tm – 17α,-22,29,30- trisnorhopane; 29 – 17α-, 21β-30-norhopane; 30 – 17α(H)-, 21β(H)-hopanes; 31–35 – C_{31}-C_{35} 17α(H)-, 21β(H)-hopanes; G – gammacerane; 20 – pregnane; 21 – homopregnane; D_{27} – C_{27} diasteranes; S_{27} – C_{27} regular steranes; S_{28} – C_{28} regular steranes; S_{29} – C_{29} regular steranes; 5, 6, 10: 3β-methyl, 24-ethyl C_{30} sterane; 7, 8, 9, 13: 4α-methyl, 24-ethyl C_{30} sterane 1: 4α-methyl, 24-methyl C_{29} sterane; 11, 12, 14, 15: 4α-, 23-, 24-trismethyl C_{30} sterane (dinosterane), respectively.

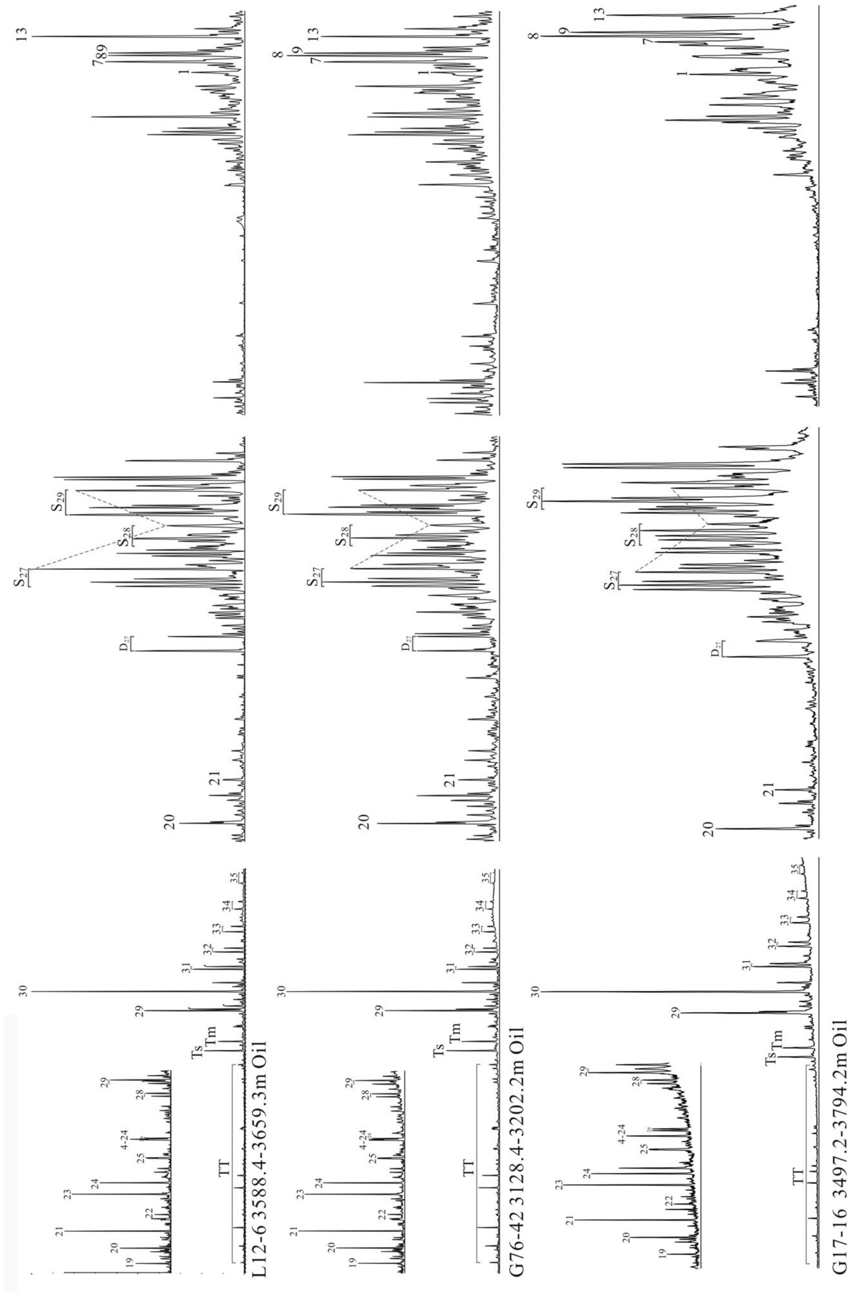

Fig. 8 (continuation).

Table 3. Component content and isotopic chararacteristics of oils in the Es_3^4 source rock

Well	Depth, m	Age of reservoir rock	Sample	Fraction, wt%				Stable carbon isotope, ‰				
				Sat.	Aro.	Res.	Asph.	Fraction /oil	Sat.	Aro.	Res.	Asph.
L35-4	2863.7	Es_3^4	Mudstone					–26.8	–28.6	–26.3	–25.9	–25.5
G3105	3780.8	Es_3^4	Mudstone					–26.9	–28.3	–27	–27.1	–26.1
G32-30	3504.7	Es_3^4	Mudstone	39.41	41	17.64	1.95					
G19-10	4043.8	Es_3^4	Mudstone	52.82	22.41	22.14	2.63					
G19-10	4044.2	Es_3^4	Mudstone	49.64	24.97	22.18	3.21					
G8	3501.8	Es_3^4	Mudstone	41.39	34.15	23.25	1.21					
G65×1	3229.0	Es_3^4	Mudstone	40.13	35.7	22.23	1.94					
G65×1	3277.0	Es_3^4	Mudstone	34.77	41.14	22.69	1.40					
G104-5P118	2013.0–2098.9	Ng	Oil	50.22	39.04	4.98	5.76	–27.5	–28.3	–26.1	–25.6	–26.4
G104-5P32	2129.1–2199.6	Ng	Oil	51.20	23.80	17.61	7.39	–28.1	–28.8	–26.2	–25.9	–26.0
G105×1	2569.4–2599.6	Ed_1	Oil	82.75	5.59	9.64	2.02	–27.7	–28.0	–26.3	–25.9	–25.8
G17-15	3630.4–3924.0	Es_3^3	Oil	66.58	16.37	4.77	12.28	–28.1	–28.9	–27.9	–25.5	–26.9
G17-16	3497.2–3794.2	Es_3	Oil	67.62	17.67	1.67	13.04	–27.9	–27.3	–26.8	–25.6	–26.2
G29-10	1989.6–1993.2	Nm	Oil	47.23	20.52	21.85	10.40	–28.9	–30.0	–26.5	–26.0	–26.1
G60-21	3016.5–3070.7	Es_1	Oil	73.42	9.01	0.95	16.62	–27.2	–27.3	–26.4	–25.9	–26.1
G69-10	2169.8–2170.0	Ng	Oil	54.46	21.71	17.27	6.56	–27.9	–28.9	–26.3	–25.8	–25.9
G69-14	2377.0–2382.0	Ng	Oil	68.08	14.79	13.19	3.94	–28.3	–28.6	–26.7	–26.1	–25.3
G76-12	2954.0–3017.8	Es_3^1	Oil	73.32	5.15	15.57	5.96	–27.2	–27.7	–26.4	–26.0	–26.1
G76-42	3124.8–3202.2	Es_1	Oil	77.67	2.09	11.34	8.90	–28.5	–28.4	–26.9	–26.1	–25.8
L10-2	3322.3–3484.1	Es_3	Oil	82.68	10.13	0.63	6.56	–27.3	–27.4	–26.6	–26.0	–26.4
L10-3	3534.8–3547.6	Es_3	Oil	75.90	5.90	–	18.20	–27.5	–27.8	–26.6	–25.7	–26.4
L125×1	2043.0–2045.0	Ng	Oil	58.92	18.37	13.74	8.97	–28.6	–28.8	–26.6	–25.9	–26.1
L12-6	3588.4–3659.3	Es_3^5	Oil	54.98	7.90	9.28	27.84	–27.7	–28.3	–27.0	–26.0	–26.1
L1-3	2540.0–2721.6	Es_3^{2+3}	Oil	58.77	18.86	4.13	18.24	–28.0	–28.8	–27.0	–25.8	–26.1
L16-11	2608.0–2648.2	Es_3	Oil	55.42	16.15	2.91	25.52	–27.9	–28.9	–26.7	–26.1	–25.8
L17-16	2968.5–3024.7	Es_3	Oil	73.93	17.74	1.48	6.85	–27.4	–28.3	–26.7	–25.5	–25.4
L25-6	1705.4–1708.0	Nm	Oil	55.10	27.01	11.01	6.88	–27.5	–28.6	–26.4	–25.7	–26.0
L27×6	2685.6–2695.4	Es_3^2	Oil	58.13	10.80	14.63	16.44	–28.1	–28.7	–27.0	–26.0	–26.3
L28-1	2827.0–2871.4	Es_3	Oil	55.60	18.19	2.75	23.46	–28.1	–28.8	–26.7	–25.7	–25.8
L90-20	2669.5–2794.8	Es_3	Oil	59.52	16.35	2.89	21.24	–27.8	–28.8	–26.8	–25.5	–26.4
LB1-29	2938.0–2960.0	Es_3	Oil	59.24	28.69	4.12	7.95	–27.3	–28.2	–26.1	–24.8	–25.6
LB2-21-2	2622.8–2697.0	Es_3^3	Oil	68.27	12.53	12.50	6.70	–27.6	–28.3	–26.0	–25.2	–25.8
LN3-5	1683.2–1699.6	Nm	Oil					–27.5	–28.4	–26.2	–26.2	–26.1
T2-17	1846.0–1866.0	J	Oil					–27.8	–28.3	–26.9	–26.7	–26.7
T31×1	2964.6–2990.4	Es_1	Oil					–27.9	–29.6	–26.9	–26.7	–26.5

Sat. – saturates; Aro. – aromatics; Res. – resins; Asph. – asphaltenes.

5. Conclusions

Highly abundant hydrocarbon source rocks are developed in Es_3^4 in the Nanpu Sag, the TOCs are above 5%. This set of mudstones in Es_3^4 was formed at the main rift stage, and is of wide distribution and great thickness. The thickness of effective hydrocarbon source rocks is about 250 m (TOC > 1.0%), while that of high-quality hydrocarbon source rocks is over 100 m (TOC 2–5%). The vitrinite reflectance (R_o) is above 0.8%. The amorphous mass and algae are an important source of the organic matter of source rocks. The kerogens are of I and II_1 types. The highly organic laminar structure was developed during the period of algae outbreak. The analysis of biomarkers and isotopes in the Es_3^4 source rocks and oil suggests that the rocks have a high content of 4-methyl steranes and developed C_{30} methyl steranes, which distinguishes them from the other source rocks.

Acknowledgement

The authors are thankful for permission to publish this paper, and acknowledge data contribution and sample collection by PetroChina Jidong Oilfield Company. This study was supported by the Scientific and Technological Research Project from PetroChina (Grant No. 2008A-0607).

REFERENCES

1. Zhao, W. Z., Zhang, G.Y., Wang, H. J. New achievements of petroleum geology theory and its significances on expanding oil and gas exploration field. *Acta Petrolei Sin*., 2005, **26**(1), 1–7 (in Chinese with English abstract).
2. Zhou, H. M., Dong, Y. X., Xie, Z. A. *Precise Exploration of Fault-Depression Basin – Practice and Understanding of Precise Exploration of Napu Depression, Bohai Bay Basin*. Petroleum Industry Press, Beijing, 2004 (in Chinese).
3. Zhou, C. N. Geological theory and exploration technology for lithostratigraphic hydrocarbon reservoirs. *Petroleum Exploration and Development*, 2007, **34**(2), 2–5 (in Chinese with English abstract).
4. Jin, Q., Wang, R., Zhu, G. Y., Zeng, Y., Rong, Q. H. The lacustrine Liangjialou fan in the Dongying depression, eastern China: deep-water reservoir sandstones in a non-marine rift basin. *J. Petrol. Geol*., 2005, **28**(4), 397–412.
5. Zhu, G. Y., Zhang, S. C., Liu, K. Y., Yang, H. J., Zhang, B., Su, J., Zhang, Y. G. A well-preserved 250 million-year-old oil accumulation in the Tarim Basin, western China: Implications for hydrocarbon exploration in old and deep basins. *Mar. Petrol. Geol*., http://dx.doi.org/10.1016/j.marpetgeo.2012.12.001.
6. Zhu, G. Y., Zhang, S. C., Su, J., Huang, H. P., Yang, H. J., Gu, L. J., Zhang, B., Zhu, Y. F. The occurrence of ultra-deep heavy oils in the Tabei Uplift of the Tarim Basin, NW China. *Org. Geochem*., 2012, **52**, 88–102.
7. Zhu, G. Y., Jiang, N. H., Su, J., Yang, H. J., Hu, J. F., Cui, J. Distribution and implication of adamantane in crude oils in Lunnan area, Tarim basin in China. *Energ. Explor. Exploit*., 2012, **30**(6), 957–970.
8. Zhu, G. Y., Cui, J., Su, J., Yang, H. J., Zhang, B., Hu, J. F., Zhu, Y. F. Accumulation and Reformation of Silurian Reservoir in the Northern Tarim Basin. *Acta Geol. Sin-Engl*., 2012, **86**(1), 209–225.
9. Zhu, G. Y., Zhang, S. C., Huang, H. P., Liang, Y. B., Meng, S. C., Li, Y. G. Gas genetic type and origin of hydrogen sulfide in the Zhongba gas field of the western Sichuan Basin, China. *Appl. Geochem*., 2011, **26**(7), 1261–1273.
10. Bertrand, P., Lallier-Verges, E., Boussafir, M. Enhancement of accumulation and anoxic degradation of organic matter controlled by cyclic productivity: a model. *Org. Geochem*., 1994, **22**(3–5), 511–520.

11. Derenne, S., Largeau, C., Brukner-Wein, A., Hetenyi, M., Bardoux, G., Mariotti, A., Origin of variations in organic matter abundance and composition in a lithologically homogeneous maar-type oil shale deposit (Gérce, Pliocene, Hungary). *Org. Geochem*., 2000, **31**(9), 787–798.
12. Carroll, A. R., Bohacs, K. M. Stratigraphic classification of ancient lakes: balancing tectonic and climatic controls. *Geology*, 1999, **27**(2), 99–102.
13. Carroll, A. R., Bohacs, K. M. Lake-type controls on petroleum source rock potential in nonmarine basin. *Am. Assoc. Petr. Geol. B*., 2001, **85**(6), 1033–1053.
14. Jin, Q., McCabe, P. J., Genetic features of petroleum systems in rift basins of eastern China. *Mar. Petrol. Geol*., 1998, **15**(4), 343–358.
15. Zhu, G. Y., Jin, Q. Study on source rock heterogeneity – a case of Nu-38 well in Dongying depression. *Acta Petrolei Sin*., 2002, **23**(5), 34–39 (in Chinese with English abstract).
16. Zhu, G. Y., Jin, Q. Geochemical characteristics of two sets of excellent source rocks in Dongying depression. *Acta Sedimentologica Sinica*, 2003, **21**(3), 506–512 (in Chinese with English abstract).
17. Zhu, G. Y, Jin, Q., Zhang, S. C., Dai, J. X., Zhang, L. Y., Li, J., Distribution characteristics of effective source rocks and their control on hydrocarbon accumulation: a case study from the Dongying Sag, Eastern China. *Acta Geol. Sin-Engl*., 2004, **78**(6), 1275–1288.
18. Zhu, G. Y., Gu, L. J., Su, J., Dai, J. X., Ding, W. L., Zhang, J. C., Song, L. C. Sedimentary association of alternated mudstones and tight sandstones in China's oil and gas bearing basins and its natural gas accumulation. *J. Asian Earth Sci.*, 2012, **50**, 88–104.
19. Li, S. M., Pang, X. Q., Wan, Z. H., Mixed oil distribution and source rock discrimination of the Nanpu depression, Bohaibay basin. *Earth Science* (*Journal of China University of Geosciences*), 2011, **36**(6), 1064–1072 (in Chinese with English abstract).
20. Gang, W. Z., Wu, Y., Gao, G., Ma, Q., Pang, X. Q., Geochemical features and geologic significances of source rocks in Nanpu Sag, Bohai Bay Basin. *Petroleum Geology & Experiment*, 2012, **34**(1), 57–61 (in Chinese with English abstract).
21. Wang, Z. J., Ma, Q., Zhao, Z. X., Xia, J. S., Zhang, Y. C., Liu, Y. C., Wang, J. W. Natural gas origin and gas accumulation model for deep volcanic rocks in Nanpu Sag, Bohai Bay Basin. *Acta Petrolei Sin*., 2012, **33**(5), 772–780 (in Chinese with English abstract).
22. Zhang, C. M., Liu, X. F. The boundary faults and basin-formation mechanism of Nanpu Sag. *Acta Petrolei Sin*., 2012, **33**(4), 581–587 (in Chinese with English abstract).
23. Zhu, G. Y., Zhang, S. C., Wang, Y. J., Wang, Z. J., Zheng, H. J., Xiong, Y., Dong, Y. X., Wang, X. D., Zhang, B. High quality source rocks and hydrocarbon accumulation in Nanpu Sag, Bohai Bay basin, China. *Acta Geol. Sin*., 2011, **85**(1), 97–113.
24. Liu, Y. H., Liu, X. Evaluation methods for petroleum resource of Nanpu Sag in Bohai Bay Basin. *Acta Petrolei Sin*., 2005, **26**(suppl.), 58–63 (in Chinese with English abstract).
25. Zheng, H. J., Dong, Y. X., Zhu, G. Y., Wang, X. D., Xiong, Y. High-quality source rocks in Nanpu Sag. P*etroleum Exploration and Development*, 2007, **34**(4), 385–450 (in Chinese with English abstract).

26. Zhu, G. Y., Zhang, S. C., Dai, J. X., Liang, Y. B., Jin, Q., Zhang, L. Y. Accumulation periods of hydrocarbon and its distribution in Dongying Sag, Jiyang Depression, Eastern China. In: *Petroleum Geochemistry and Exploration in the Afro-Asian Region* (Liang, D. G., Wang, D. R., Li, Z. X., eds.). Taylor & Francis Group, Balkema, 2008, 47–58.
27. Zhu, G. Y., Zhang, S. C., Jin, Q., Dai, J. X., Zhang, L. Y., Li, J. Origin of the Neogene shallow gas accumulations in the Jiyang superdepression, Bohai bay basin. *Org. Geochem.*, 2005, **36**, 1650–1663.
28. Robbins, L. L., Blackwelder, P. L. Biochemical and ultrastructural evidence for the origin of whitings: A biologically induced calcium carbonate precipitation mechanism. *Geology*, 1992, **20**(5), 464–468.
29. Kelts, K., Hsu, K. J. Freshwater carbonate sedimentation. In: *Lakes: Chemistry, geology, physics* (Lerman, A., ed.). Springer-Verlag, Berlin, 1978, 295–320.
30. Dean, W. E. The carbon cycle and biogeochemical dynamics in lake sediments. *J. Paleolimnol*., 1999, **21**, 375–393.
31. Chen, J. A., Wan, G. J., Chen, Z. L., Huang, R. G. Chemical elements in sediments of Lake Erhai and palaeoclimate evolution. *Geochimica*, 1999, **28**, 562–570 (in Chinese with English abstract).
32. Kilham, P. Mechanisms controlling the chemical composition of lakes and rivers: data from Africa. *Limnol. Oceanogr*., 1990, **35**(1), 80–83.
33. Deng, H. W., Qian, K. The genetic types and association evolution of deep lacustrine faces mudstones. *Acta Sedimentologica Sinica*, 1990, **8**(3), 1–21 (in Chinese with English abstract).
34. Zheng, H. J., Dong, Y. X., Wang, X. D., Zhang, S. C., Zhang, D. J., Zhu, G. Y., Xiong, Y., Yu, H. D. The generation and characteristics of source rocks in Nanpu oil-rich Depression, Bohai Bay Basin. *Natural Gas Geoscience*, 2007, **18**(1), 78–83 (in Chinese with English abstract).

Presented by I. Valgma
Received July 9, 2012