

The controls on the composition of biodegraded oils in the Liuhua11-1 Oilfield, Pearl River Mouth Basin, South China Sea

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Abstract (1) The geochemical characteristics of extracted oils in three oil columns from the Liuhua11-1 Oilfield in the Pearl River Mouth Basin of South China Sea were analyzed in detail. The results show that the oil of Liuhua 11-1 Oilfield is generated from a single source rock, and belongs to mature oil and their maturities have little difference. (2) The characteristics of saturated hydrocarbon gas chromatography, bulk composition, concentrations of biomarkers and gas chromatography–mass spectrometry of saturated hydrocarbon indicate that all samples studied were biodegraded, and the maximal level of biodegradation is less than PM level 6. (3) Bulk composition and the degree of biodegradation presented excellent gradient variations in the oil columns, and the highest degradation rates occurred at or near the oil–water contact (OWC). The key biomarkers of steranes and terpanes and maturity parameters of saturated hydrocarbon were not affected by degradation, which means that they are stable in slight to moderately biodegraded oils. Across the oilfield, the degree of biodegradation of LH11-1-3 was higher than that of LH11-1-A and LH 11-1-4 in general. (4) We infer that the strong hydrodynamic conditions (tectonic control) and high reservoir temperatures (50–65 °C) are the primary controllers

of the degree of oil biodegradation in the Liuhua 11-1 Oilfield and the late hydrocarbon accumulation may also have an important effect. The bulk composition and degree of biodegradation with excellent gradient variations in the oil columns were obviously controlled by the vertical distance from its in situ place to OWC. The highest supply of nutrient at the OWC results in high abundance of microorganisms and the highest degradation rate. And the lateral variation in level of biodegradation across the oil reservoir may be mainly control by the salinity of bottom water, the supply of nutrient and the energy of the bottom water.

Keywords Biodegradation · Geochemical characteristics · Controllers · Liuhua 11-1 Oilfield · Pearl River Mouth Basin

1 Introduction

Biodegradation of crude oil and natural gas in the reservoir is an important alteration process during the history of hydrocarbon migration and accumulation, which contributes to changes in hydrocarbon composition (Peters and Moldowan 1993; Peters et al. 2005; Head et al. 2003). In recent years, the advanced molecular biological techniques have been used to discover the mechanisms of aerobic and anaerobic degradation of hydrocarbons to establish the prediction model of biodegradation in reservoir (Jones et al. 2007). During the process of oilfield exploration and development, the model of biodegradation can be used to predict the degree of biodegradation in the reservoir to reduce the exploration risk and optimize the production (Hongjing et al. 2004; Chunming et al. 2007; Larter et al. 2008). The degree and rate of the biodegradation is controlled by oil composition, reservoir temperature (<80 °C),

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reservoir property, water salinity, the relative volumes of oil column to water column, the oil–water contact (OWC) area, nutrients (nitrogen, potassium, phosphorus, etc.) and history of hydrocarbon accumulation (Wenger et al. 2002; Larter et al. 2006).

To ensure more accurate assessment of fluid heterogeneity in heavy oil reservoir, accurate predictions on the degree of biodegradation, oil density and viscosity are needed (Larter et al. 2003, 2006; Huang et al. 2004; Bennett et al. 2013). So, further researches on the rules of biodegradation in the oil reservoir are needed. Since the oil reservoir formation is very complicated by natural geological and geochemical process in sedimentary basin, and factors influencing the biodegradation are multitudinous, the control factors and details of the biodegradation process are still poorly understood. Liuhua11-1 Oilfield is a massive reef limestone reservoir located at Dongsha Uplift, Pearl River Mouth Basin (PRMB). It has one OWC with the simple trap shape, which is an ideal natural laboratory for studying the controls on the composition of biodegraded oils. This paper, with three coring wells LH11-1-4, LH11-1-1A and LH11-1-3 as the research objects, adopted the analyses of bulk compositions, gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) of the extracted oils. The spatial distribution characteristics of biodegradation degrees in the oil reservoir had been studied, and the controls on the composition of biodegraded oil were investigated in detail.

2 Geological setting

The Liuhua 11-1 Oilfield is located at the carbonate platform formed on Dongsha Uplift in the PRMB (Fig. 1). The PRMB is a typical passive margin basin in the South China

Sea. The Huizhou Sag is the most important petroleum-generating center in northern depression of PRMB. The Eocene Wenchang Formation and Oligocene Enping Formation were the two sets of petroleum source rocks in Huizhou Sag. The Wenchang Formation was deposited in the middle-deep water lakes. The average organic carbon (TOC) value in mudstone of Wenchang Formation was 2.36 %. The organic matters were composed of Type I-II kerogens. A transition from lacustrine deposits to swamp-fluvial and fluvial deposits is present in the Enping Formation. The organic-rich mud and coals were deposited and were composed of Type I-II kerogens, with average TOC value of 1.45 %. The Liuhua 11-1 Oilfield was discovered in 1987 in 310 m water depth. It is 200 km southeast of Hong Kong and covers an area of 16.4 km². The crude oil was from 75 m of productive Lower Miocene Zhujiang carbonate (Tyrrell and Christian 1992). The OWC is at the depth of 1247 m. The Liuhua 11-1 Oilfield is a reef limestone reservoir, and has excellent porosity and permeability. The average reservoir porosity is 22.4 %, and the average reservoir permeability is $652 \times 10^{-3} \mu\text{m}^2$ (Dali et al. 2005; Junzhang et al. 2007).

3 Samples and methods

3.1 Sampling

The core samples were collected from LH11-1-4, LH11-1-1A and LH11-1-3, where cores were collected from the oil column, and into the supporting aquifer under the oil column. The distribution of wells is showed on Fig. 1. The core samples were kept under frozen conditions during shipping and subsequent storage period.

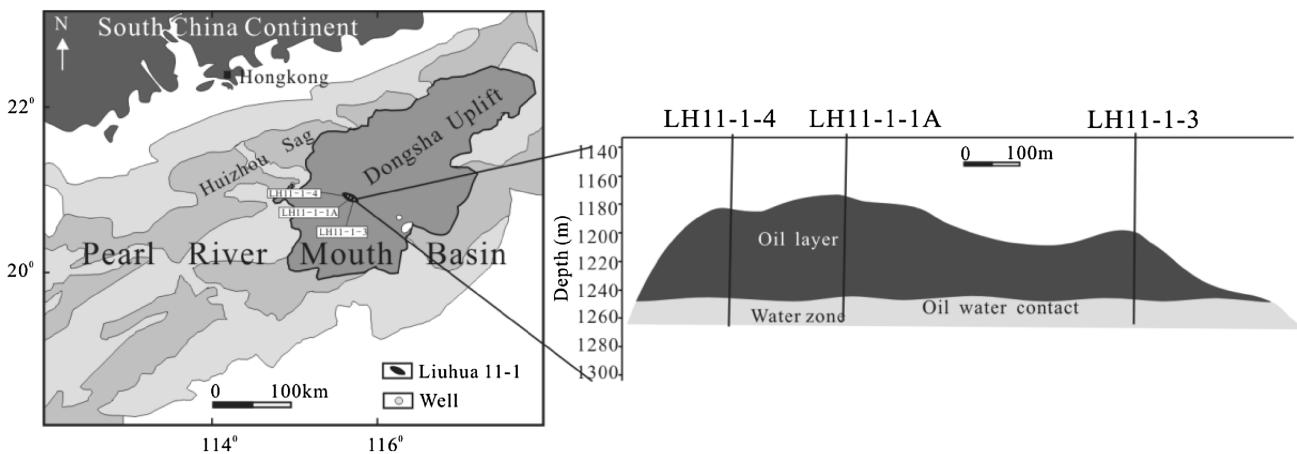


Fig. 1 Structure framework of Pearl River Mouth Basin and the cross-section of Liuhua11-1 Oilfield

3.2 Experimental methods

The core samples were crushed to 100 meshes and extracted for 72 h with dichloromethane by Soxhlet extraction. Asphaltenes in the core extracts were removed by n-hexane precipitation. The de-asphalted core extracts were separated into saturated and aromatic hydrocarbon fractions by silica gel and alumina column chromatography. Bulk fraction characterization of the extracted oils was carried out using an Iatroscan method. GC analyses of the extracted oils were performed on an HP6890N system equipped with an HP-PONA fused silica capillary column ($50\text{ m} \times 0.20\text{ mm} \times 0.3\text{ }\mu\text{m}$) by using N_2 as carrier gas at 1.0 ml/min . The over temperature was programmed at 35°C for 10 min, then ramped to 300°C at $4^\circ\text{C}/\text{min}$, and finally held for 50 min at 300°C . The injection and detector temperature was 300°C . All extracted oils analyzed in this study suffered biodegradation at different levels. The feature of biodegraded extracted oils is the “baseline hump” in gas chromatograms (Fig. 2).

GC-MS was conducted on the saturated fractions by using an Agilent 7890-5975c system equipped with an HP-5 ms capillary column ($60\text{ m} \times 0.25\text{ mm} \times 0.25\text{ m}$). The temperature program for saturated hydrocarbons was 50°C for 1 min, $50\text{--}120^\circ\text{C}$ at $20^\circ\text{C}/\text{min}$, $120\text{--}250^\circ\text{C}$ at $4^\circ\text{C}/\text{min}$, $250\text{--}310^\circ\text{C}$ at $3^\circ\text{C}/\text{min}$, and finally held for 30 min at 310°C . The temperature of the injector was 300°C . Helium was used as carrier gas at a flow rate of 1 ml/min . The scan range was from 50 to 550 Da by using full scan and multiple ion detection (MID) at 70 eV . And 5α -androstanes was used as an internal standard for the saturated hydrocarbons quantitative analysis.

4 Results

4.1 Oil source and thermal maturity

The mature oils have been found in Huizhou Sag and its neighboring area can be classified into three types by their geochemical characteristics (Shuichang et al. 2004; Junzhang et al. 2007; Youchuan et al. 2009). Type A oil, with high content of $\text{C}_{30}\text{-methylsteranes}$ and low content of

bicadinanes, was derived from the middle-deep lacustrine source rock in Wenchang Formation. Type B oil, with abundant bicadinanes and absent $\text{C}_{30}\text{-methylsteranes}$, was derived from source rock of Enping Formation. Type C oil was the mixed oil of Type A and Type B, with high content of $\text{C}_{30}\text{-methylsteranes}$ and bicadinanes. The oils of Liuhua 11-1 Oilfield sourced from Huizhou Sag and migrated up-dip along the Hui-Liu Structure Ridge through the marine sandstone carriers within the Zhuhai Formation to accumulate in the trap of Liuhua 11-1 carbonate platform (Tyrrell and Christian 1992). The detailed study of geochemical characteristics of extracted oils leads to a deeper understanding of the origin of oils in Liuhua 11-1 Oilfield.

Since the distribution of terpanes and steranes appears to be unaffected by the degradation process that affected the investigated oils, these biomarkers are used to assess the characteristics of the source rock that generates these oils. In the case of Liuhua 11-1, oleanane in the extracted oils is much lower than $\text{C}_{30}\text{-hopane}$ and the oleanane/ $\text{C}_{30}\text{-hopane}$ ratio is between 0.14 and 0.19. This ratio suggests the algal source of the Liuhua 11-1 oils and the absence of higher plant or terrestrial input. The abundance of $\text{C}_{30}\text{-methylsteranes}$ has been used as an indicator of oil types. The higher relative amount of $\text{C}_{30}\text{-methylsteranes}$ has been observed in the Liuhua 11-1 extracted oils. The $\text{C}_{30}\text{-methylsteranes}/\text{C}_{29}\text{steranes}$ ratio shows high value between 0.60 and 1.12. The $\text{C}_{27}\text{-C}_{29}\text{steranes}$ distributed in “V” shape, which is the common feature of A Type oil. The Liuhua 11-1 extracted oils had low content of bicadinanes. The bicadinane chemical (W) is extremely low and the bicadinane chemical (T) is much lower than $\text{C}_{30}\text{-hopane}$. T/ $\text{C}_{30}\text{-hopane}$ ratio is between 0.33 and 0.54 (Fig. 3; Table 1). The relative amount of $\text{C}_{27}\text{-C}_{29}\text{steranes}$ can be used to determine the source rock differences. It has now been found that the presence of $\text{C}_{29}\text{steranes}$ does not necessarily mean an input of higher plant material, as $\text{C}_{29}\text{steranes}$ can also have an algal source (Peters and Moldowan 1993). The slightly higher relative amount of $\text{C}_{29}\text{steranes}$ in the Liuhua 11-1 extracted oils would be expected for organic matter of lacustrine origin (Fig. 4). The uniform distribution patterns in the Liuhua 11-1 extracted oils are indicative of their similarity in terms of organic matter type and paleoenvironment of deposition.

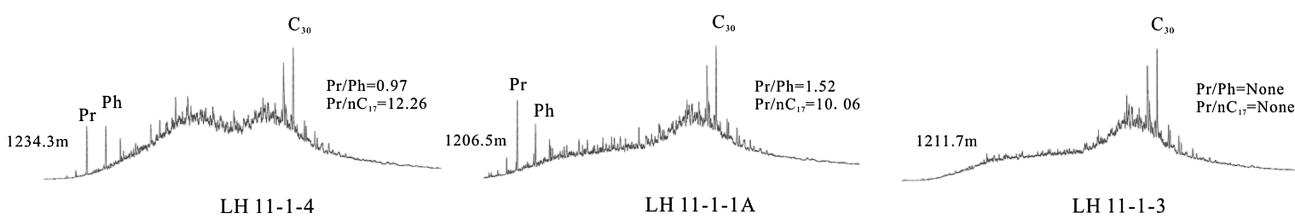


Fig. 2 Gas chromatograms of extracted oils from reservoir cores from the Liuhua 11-1 Oilfield

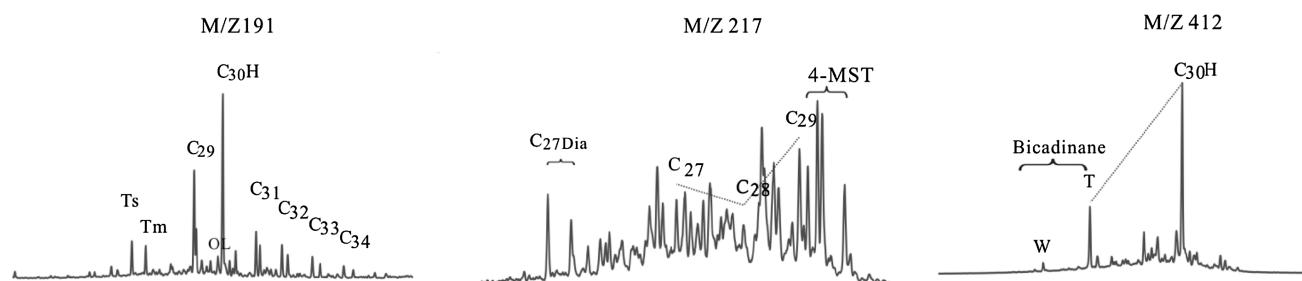


Fig. 3 Typical biomarker characteristic of saturated hydrocarbon for extracted oil from the Liuhua11-1 Oilfield (a case from LH11-1-4)

Table 1 Biomarker parameters of saturated hydrocarbons for extracted oils from the Liuhua11-1 Oilfield

Well	Depth (m)	a	b	c	d	e	f	g	h	i	j
LH11-1-4	1223.8	0.15	0.94	0.37	29	28	43	0.58	0.50	0.49	1.26
LH11-1-4	1234.3	0.16	1.01	0.39	30	28	41	0.59	0.52	0.48	1.25
LH11-1-4	1243.9	0.15	0.78	0.37	27	30	43	0.58	0.52	0.48	1.24
LH11-1-4	1248.5	0.15	0.97	0.39	29	28	43	0.58	0.53	0.47	1.26
LH11-1-4	1254.5	0.14	0.75	0.34	33	30	37	0.60	0.52	0.47	1.42
LH11-1-4	1263.3	0.14	0.86	0.37	28	27	44	0.60	0.54	0.46	1.37
LH11-1-4	1274.7	0.15	0.72	0.33	31	28	41	0.59	0.54	0.48	1.18
LH11-1-4	1283.2	0.14	0.87	0.35	29	31	41	0.58	0.50	0.49	1.38
LH11-1-1A	1183.8	0.19	0.99	0.54	24	31	45	0.59	0.56	0.49	1.35
LH11-1-1A	1201.7	0.15	1.12	0.40	31	20	49	0.58	0.52	0.48	1.30
LH11-1-1A	1206.5	0.14	1.05	0.36	32	23	45	0.58	0.54	0.47	1.25
LH11-1-1A	1215.5	0.15	0.60	0.38	29	27	44	0.58	0.61	0.39	1.29
LH11-1-1A	1223.2	0.15	1.05	0.40	31	20	49	0.58	0.60	0.45	1.24
LH11-1-1A	1229.9	0.15	1.06	0.38	28	27	45	0.58	0.54	0.47	1.28
LH11-1-1A	1237.2	0.15	1.07	0.39	28	27	45	0.58	0.52	0.48	0.99
LH11-1-1A	1242.1	0.16	1.07	0.40	28	27	46	0.58	0.52	0.48	1.25
LH11-1-3	1200.0	0.16	1.00	0.41	29	20	51	0.58	0.55	0.47	1.38
LH11-1-3	1205.0	0.15	0.99	0.40	27	23	50	0.59	0.53	0.49	1.39
LH11-1-3	1214.4	0.15	1.02	0.40	30	21	49	0.58	0.53	0.50	1.36
LH11-1-3	1218.0	0.15	1.04	0.43	32	20	48	0.58	0.52	0.50	1.39
LH11-1-3	1226.9	0.14	1.01	0.41	26	24	50	0.58	0.53	0.49	1.36
LH11-1-3	1238.5	0.15	0.78	0.41	37	20	42	0.57	0.61	0.44	1.38
LH11-1-3	1258.8	0.15	0.96	0.42	26	30	44	0.57	0.55	0.49	1.35
average	–	0.15	0.94	0.39	29	26	45	0.58	0.54	0.47	1.30

a Oleanane/C₃₀hopane, b C₃₀4-methylsteranes/C₂₉steranes, c bicadinane chemicals(T)/C₃₀hopane, d C₂₇ααα-Rsterane/(C₂₇αααRsterane+C₂₈αααRsterane+C₂₉αααRsterane), e C₂₈αααRsterane/(C₂₇αααRsterane+C₂₈αααRsterane+C₂₉αααRsterane), f C₂₉αααRsterane/(C₂₇αααRsterane+C₂₈αααRsterane+C₂₉αααRsterane), g C₃₁hopaneαβ2S/(22S+22R), h C₂₉steranes20S/20 (S+R), i C₂₉steranesββ/(αα+ββ), j Ts/Tm

The mature parameters of C₃₁hopaneαβ2S/(22S+22R) with an average value of 0.58, C₂₉steranes20S/20 (S+R) with an average value of 0.54, C₂₉steranesββ/(αα+ββ) with an average value of 0.47 and Ts/Tm with an average value of 1.30 are indicative of the mature oil (Seifert and Moldowan 1986; Peters and Moldowan 1993; Peters et al. 2005) (Table 1). According to those mentioned above, the oils of Liuhua 11-1 are typical A Type mature oil and derived from the middle-deep lacustrine source rock in Wenchang Formation in Huizhou Sag.

4.2 Biodegradation level

The observed depletion of n-alkanes and acyclic isoprenoid alkanes (phytane and pristane) indicated that all extracted oils studied were biodegraded (Fig. 5). The analysis of the fractions derived from the extracted oils did not reveal a preservation of 25-norhopanes. Therefore, all extracted oils studied were biodegraded to PM level <6 on the scale proposed by Peters and Moldowan (1993). Through comprehensive analysis of n-alkanes, acyclic isoprenoid

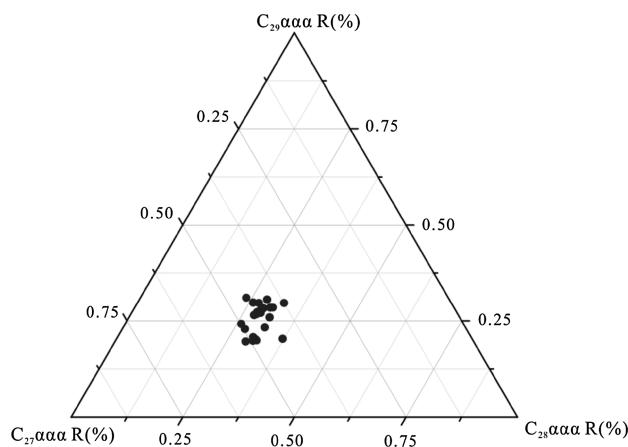


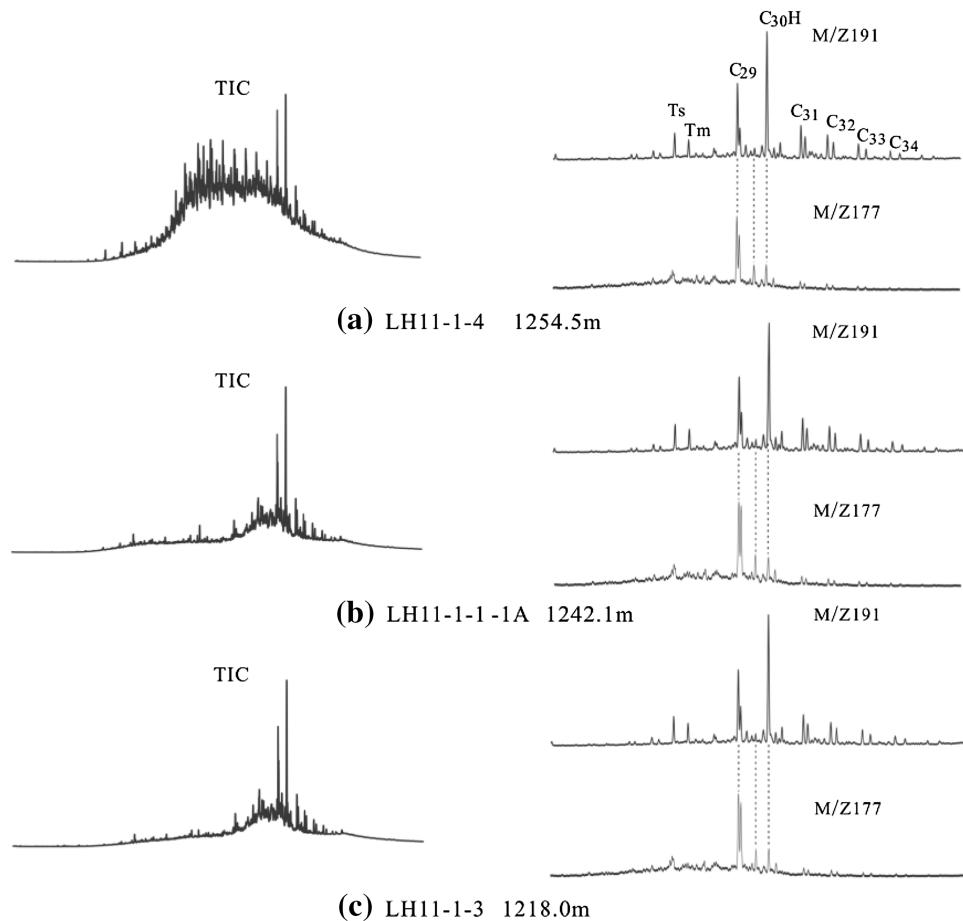
Fig. 4 Ternary diagram of the relative abundance of $C_{27}\alpha\alpha\alpha R$, $C_{28}\alpha\alpha\alpha R$ and $C_{29}\alpha\alpha\alpha R$ regular steranes in extracted oils from the Liuhua11-1 Oilfield

alkanes, monocyclic alkanes etc., the biodegradation levels of extracted oils from LH11-1-4, LH11-1-1A and LH11-1-3 have been divided into five biodegradation levels: PM3, PM4 medium, PM4 serious, PM5 medium and PM5 serious.

4.3 Concentration variation in biodegraded oil columns

The buck composition data (saturated hydrocarbons, aromatic hydrocarbons, non-hydrocarbon and asphaltenes) acquired by Iatroscan analysis enabled an assessment of the compositional changes occurring within each oil column. Variations in the abundance of residual oil, the saturated hydrocarbon fraction and of the non-hydrocarbon+asphaltene in each extracted oils of the LH11-1-4, LH11-1-1A and LH11-1-3 are presented in Fig. 6. The residual oil abundance firstly increases and then decreases towards the OWC, while the percentage content of the saturated hydrocarbon shows a progressively decreasing trend from 56 % at the top to about 27 % at the bottom (Fig. 6). And the percentage content of the non-hydrocarbon+asphaltene shows a progressively increasing trend from 23 % at the top to about 55 % at the bottom (Fig. 6). This well developed vertical gradient, which indicates a systematic loss of saturated hydrocarbon and a systematic gain of non-hydrocarbon+asphaltene with increasing depth. This is the remarkable characteristics of the effects of biodegradation

Fig. 5 Total ion current (left) showing the saturated hydrocarbons and m/z 191, m/z 177 mass chromatograms (right) showing hopanes and 25-norhopanoids for extracted oils from the Liuhua11-1 Oilfield



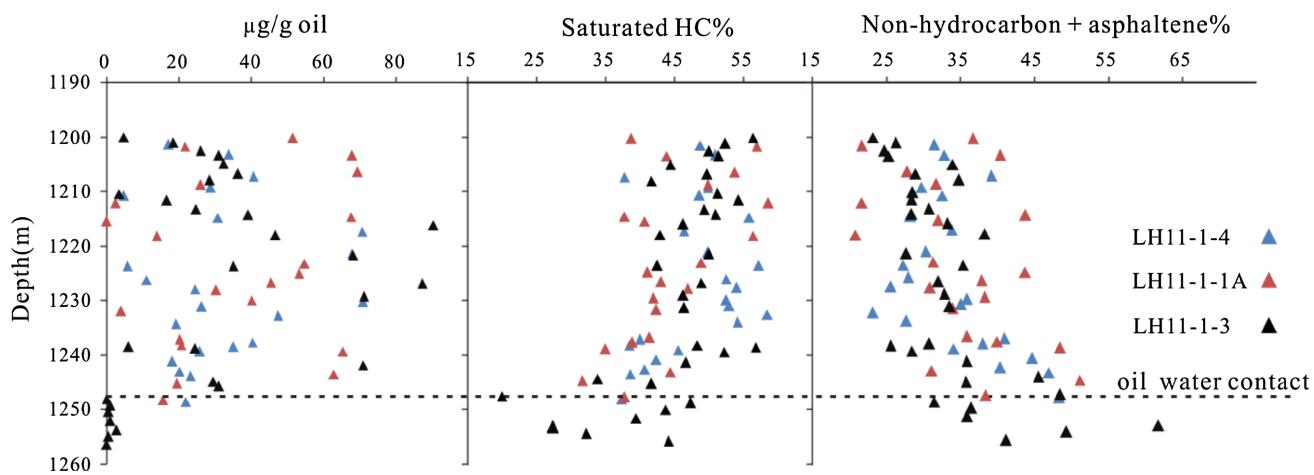


Fig. 6 Variation of residual oil, saturated hydrocarbon and non-hydrocarbon+asphaltene in three wells from Liuhua 11-1 Oilfield

(Huang et al. 2004; Haiping et al. 2010; Larter et al. 2012; Bennett et al. 2013).

The quantitative analysis of saturated hydrocarbons has been used to determine the differences in biodegradation level in the oil column (Fig. 7). The high abundance of $C_{30}\alpha\beta$ -hopane has been regarded as the characteristics of lacustrine oil. Regular steranes and $C_{30}4$ -methylsteranes are removed before $C_{30}\alpha\beta$ -hopane, while the gammacerane, being resistant until very severe levels of biodegradation, are achieved (Peters and Moldowan 1993). The concentration of $C_{30}\alpha\beta$ -hopane had no definite trend in oil column, which indicated that the terpanes had not been significantly affected by biodegradation. Only the concentrations of $C_{30}\alpha\beta$ -hopane in two samples of LH11-1-3 are obviously too low, and the two samples are near the OWC. A slight trend of increasing abundance of regular steranes with increasing depth can be observed over the OWC. The abundance of gammacerane and $C_{30}4$ -methylsteranes had no definite trend in oil column, but we found that the sample of lower concentration of gammacerane of LH11-1-3 is corresponding to lower concentrations of $C_{30}\alpha\beta$ -hopane, regular steranes and $C_{30}4$ -methylsteranes. As all extracted oils studied were biodegraded to PM level <6, it was not caused by biodegradation, while it may be influenced by water washing near the OWC. The variations in concentrations of $C_{30}\alpha\beta$ -hopane, regular sterane, gammacerane and $C_{30}4$ -methylsteranes with increasing depth that mentioned above indicate that the extracted oils have not reached a biodegradation level of PM6, and the energy of the bottom water is sufficient in the oil reservoir.

4.4 Variation in level of biodegradation in the oil reservoir

Due to the limitations of the existing oil biodegradation scales (for example, the Peters and Moldwans scale, 1993), GC-MS

characteristics of pristine (Pr), phytane (Ph) and other compounds can be used to identify the minor differences of biodegradation degrees of extracted oils, even in the same biodegradation degree in slight to moderately biodegraded oils. The eight samples of LH11-1-4 were biodegraded to PM levels between PM4 medium and PM5 serious through the oil column. Most of the n-alkanes of all extract were lost in the extracted oils of LH11-1-4. Isoprenoid hydrocarbons (Pr and Ph) were biodegraded and small residues were preserved (Fig. 8). The eight samples of LH11-1-1A above the OWC were biodegraded to PM levels between PM3 and PM5 serious through the oil column. The biodegradation degrees show a progressively increasing trend with increasing depth. The seven samples of LH11-1-3 were biodegraded to PM levels between PM5 medium and PM5 serious through the oil column. It also shows the greater degrees of biodegradation with increasing depth. Characteristics of biodegradation in the oil column of three wells indicate that degradation gradient in the oil column was controlled by the vertical distance from its in situ place to OWC.

Across the oil reservoir, the degree of biodegradation of LH11-1-3 was higher than that of LH11-1-1A and LH 11-1-4 in general. And we can also found that the most degraded oils of three wells are near OWC, which suggests that the site of most biodegradation is near the OWC. The differences of biodegradation degrees through the lateral of oil reservoir may be associated to the conditions that are the most conductive to microbial activity, such as bottom water salinity, supply of nutrients, the energy of bottom water, etc.

4.5 Effect of biodegradation on maturation parameters

The maturation parameters of steranes are observed with a narrow range in the oil columns (Fig. 9). The ratios of

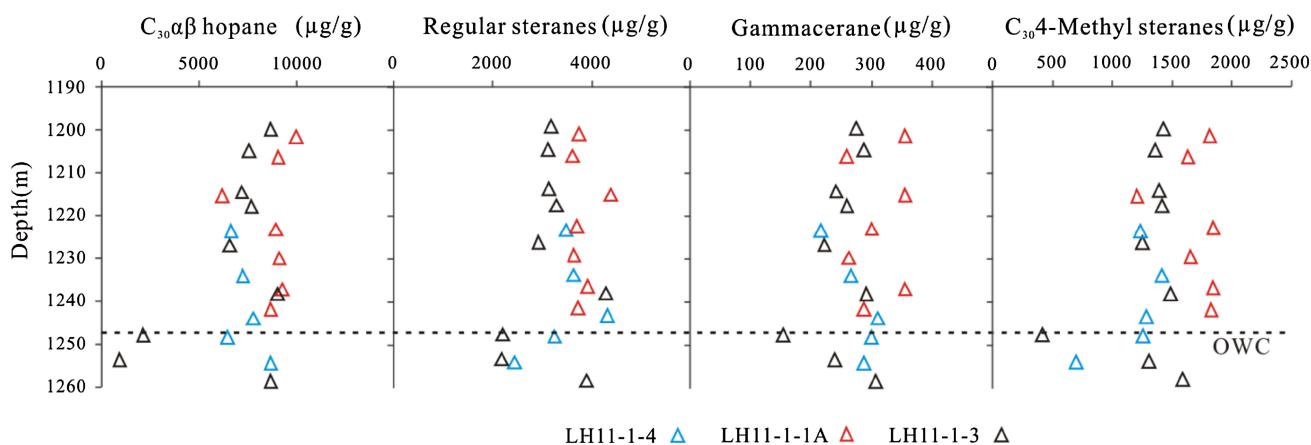


Fig. 7 Variation of $C_{30}\alpha\beta$ hopane, regular sterane, gammacerane and $C_{30}4$ -Methylsteranes contents in three wells from Liuhua 11-1 Oilfield

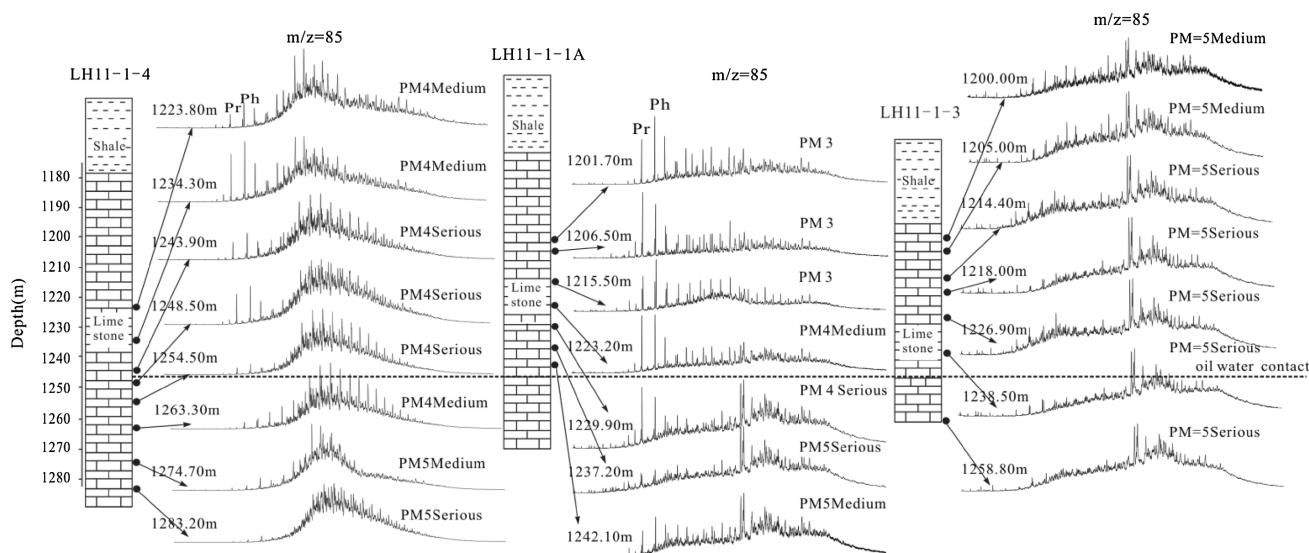


Fig. 8 The $m/z = 85$ mass chromatograms showing n-alkanes and branched isoprenoid alkanes in saturated hydrocarbon fractions from extracted oils of the Liuhua 11-1 Oilfield

C_{29} steranes $\beta\beta/(\alpha\alpha+\beta\beta)$ and C_{29} steranes 20S/20 (S+R) present no rules with increasing depth (also the increasing levels of biodegradation), and these parameters are reliable. The ratios of C_{31} hopane $\alpha\beta 22S/(22S+22R)$ generally stayed the same with increasing depth, and were unaffected by degradation. And it is the most stable in those maturation parameters with increasing depth. The abundance of Ts relative to Tm was used to indicate thermal maturity. The existing researches have shown that the value of Ts/Tm was almost impossible to be affected by degradation even in the heavy biodegraded oils. The Ts/Tm ratios in the all extracted oils have no trends of rising or declining with increasing depth (Fig. 9). But the Ts/Tm ratios of LH11-1-3 are higher than those in LH11-1-1A and LH11-1-4, which reflects that the maturity of extracted oils of LH11-1-3 is slightly higher. According to the above mentioned

analysis, the saturated hydrocarbon maturity parameters are reliable in very slight to moderately biodegraded oils (PM level <6).

5 Discussion

LH11-1 Oilfield kept the groundwater hydrodynamic in the low value since the later period of early Miocene (Xichun et al. 2010) (Fig. 10). The strong bottom water controls the supply of key nutrients, such as nitrogen, phosphorus, potassium etc., which are essential for the microorganisms living in the oil reservoir, and biodegradation of petroleum occurs throughout the reservoir. The geothermal gradient of Liuhua 11-1 Oilfield is higher than that of Huizhou Sag. The present temperatures in the reservoir varied from 52.9–

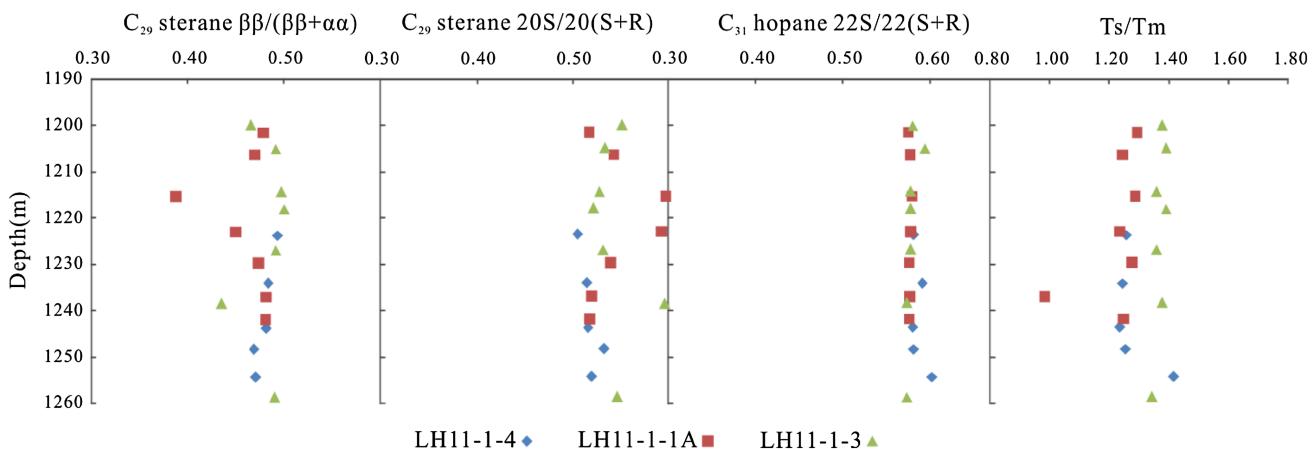


Fig. 9 Plot of $C_{29}\text{sterane } \beta\beta/(\beta\beta+\alpha\alpha)$, $C_{29}\text{sterane } 20\text{S}/20(\text{S}+\text{R})$, $C_{31}\text{hopane } 22\text{S}/22(\text{S}+\text{R})$ and Ts/Tm versus depth for core extracts from the Liuhua11-1 Oilfield

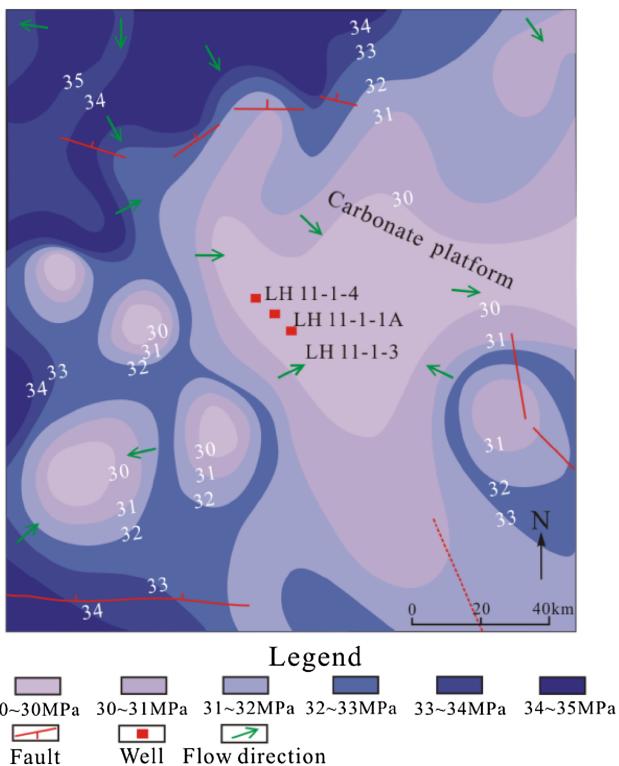


Fig. 10 Characteristics of groundwater hydrodynamic trend of Liuhua carbonate platform

61.5 °C, and the geothermal gradient was determined as 4.04 °C/100 m, with paleotemperatures varying from 50–65 °C. The microorganisms live in the oil reservoir with moderate temperatures, and the optimum temperatures are about 25–30 °C, with the upper limit temperatures being about 37–40 °C. Only the optimum temperatures of thermo stable microorganism are over 60 °C (Henry and Dianne

2008). Consequently, the strong bottom water, higher temperatures and the late hydrocarbon accumulation (the age of hydrocarbon accumulation is $10 \pm \text{Ma}$) (Shi et al. 2011) were the critical factors for petroleum biodegrading to PM level <6.

Saturated hydrocarbon contents show a progressive increase in biodegradation in three wells of Liuhua 11-1 Oilfield. Hydrocarbons diffuse towards the OWC, and they are degraded by microorganisms living in the oil column (Fig. 11). In the oil–water system, the active bottom water can support the nutrient to the OWC and even in the oil column (the oil column with the continuous water). The nutrients are probably by in situ place buffered mineral dissolution or carried by groundwater. The abundance of microorganism is increasing towards the OWC, and reaches its maximum near the OWC, which is an important factor controlling the biodegradation gradient (Bennett et al. 2013). The variations of bulk composition reflect this complex degradation phenomenon.

Until recently, it was generally accepted that the water–leg salinity has a repressing effect on petroleum degradation. The main mineral composition of LH11-1 Oilfield water is CaCl_2 . In the oil reservoir with depth varying from 1258.8 to 1278.8 m, the total amount of mineral matter of LH11-1-A and LH 11-1-3 are 87131.85 and 34286.2 mg/l, respectively (Fig. 12). The salinity of LH11-1-3 was lower, and low salinity water is a favorable condition for biological activity. The supply of nutrient from the bottom water is also an important factor that controls the degradation rate. It is speculated that nutrient supply capabilities of LH11-1-4 and LH11-1-1A are weaker than that of LH 11-1-3 by the water flow (Fig. 12). And both of these key factors make the biodegradation level of LH11-1-3 higher than that of LH11-1-4 and LH11-1-1A.

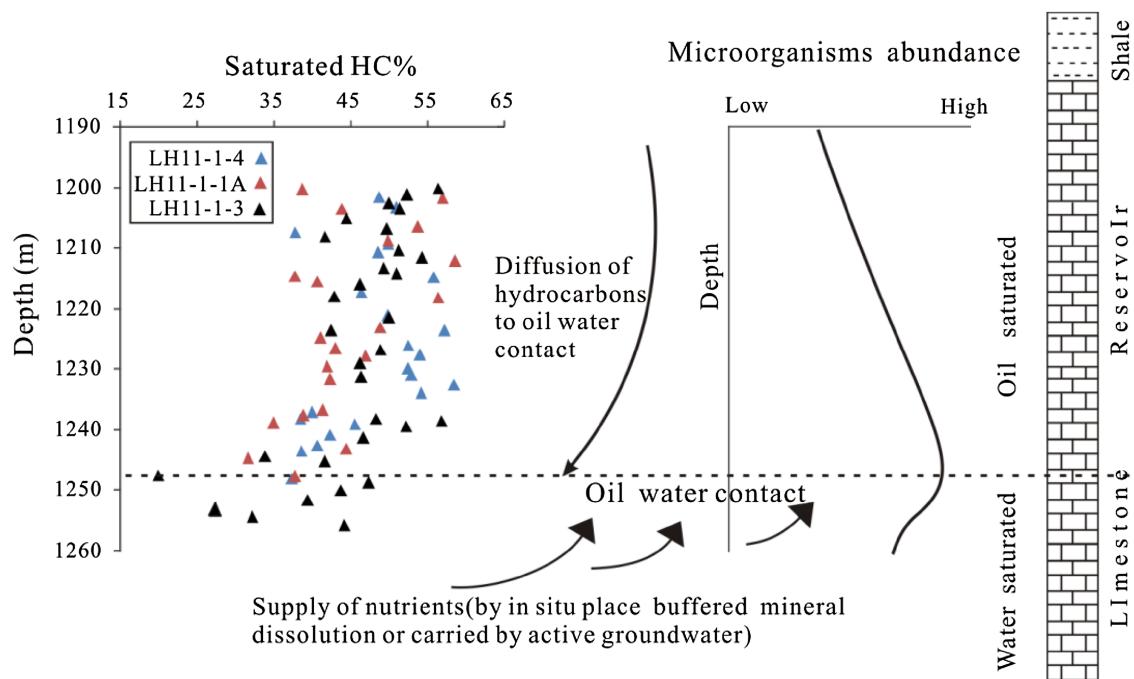
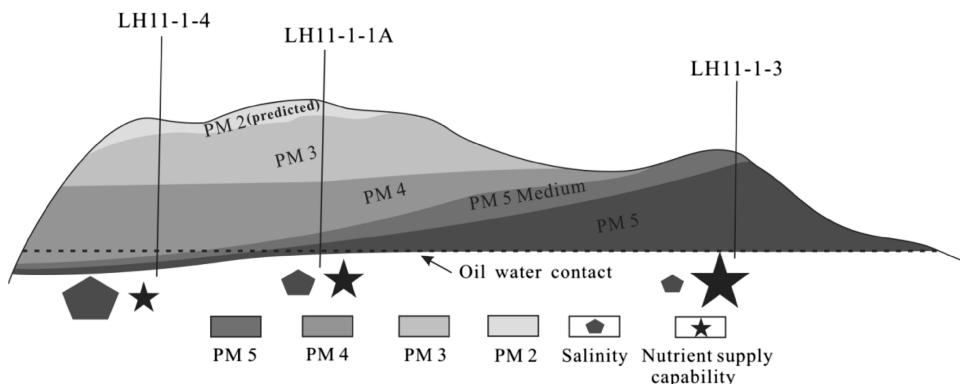


Fig. 11 The controls on biodegradation gradient in the oil column

Fig. 12 The controls on the levels of biodegradation across the Liuhua11-1 Oilfield



6 Conclusions

The oils of Liuhua 11-1 were derived from the middle-deep lacustrine source rock in Wenchang Formation in Huizhou Sag. The oils belong to mature oil, and their maturities have little difference. The characteristics of saturated hydrocarbon GC, bulk composition, concentrations of biomarkers and GC-MS of the saturated hydrocarbon indicate that all samples studied were biodegraded, and the maximal level of biodegradation is less than PM level 6. The saturated hydrocarbon maturity parameters were not affected by degradation, which means that they are reliable in slight to moderately biodegraded oils. Bulk compositions and the degrees of biodegradation present evident gradient variation in

the oil columns, and the highest degradation rate occurred at or near the OWC. Across the oilfield, the degree of biodegradation of LH11-1-3 was higher than that of LH11-1-1A and LH 11-1-4 in general.

Liuhua 11-1 Oilfield is located at the carbonate platform with strong hydrodynamic conditions (tectonic control) and high reservoir temperatures (50–65 °C). These factors are the primary controllers of the degree of oil biodegradation in the Liuhua 11-1 Oilfield, and the late hydrocarbon accumulation may also have an important effect. The bulk compositions and degree of biodegradation with excellent gradient variations in the oil columns were obviously controlled by the vertical distance from its in situ place to OWC. The highest supply of nutrient at the OWC results in high abundance

of microorganisms and the highest degradation rate. And the lateral variation in level of biodegradation across the oil reservoir maybe mainly controlled by the salinity of bottom water, the supply of nutrient and the energy of the bottom water.

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