The Occurrence of Oleananes in the Beibuwan Basin and Its Application to the Study of Maturity and Oil-Source Rock Correlation

LI Meijun^{1, *}, WANG Tieguan¹, LIU Ju², ZHANG Meizhu², LU Hong³, MA Qinglin² and GAO Lihui²

1 State Key Laboratory of Petroleum Resource and Prospecting, Earth Sciences and Geoinformatics School, China University of Petroleum, Beijing 102249, China 2 Southern Oil Exploration and Development Company, PetroChina, Guangzhou 510640, China 3 Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510240, China

Abstract: The oleanane parameter, i.e., OP (oleananes/(oleananes+ C_{30} hopanes)) in the two sedimentary columns of the Beibuwan Basin, South China Sea, can be used to definit the top of oil generation window, with R_0 (/%) of 0.53 in Well M1 and 0.55 in Wells H1/Hd1/Hd2, respectively. Comparing with vitrinite reflectance (R_0 /%), the OP features a dynamic range and can indicate the oil generation window more precisely. By using OP and other geochemical indices, the oil-source correlation is also conducted. It suggests that the oils in wells M1 and M2 are derived from the source rocks in situ. The mudstone in Huachang uplift is not the main source rocks for oils in this area. The OP is also a useful oil-source correlation parameter in some Tertiary lacustrine basins.

Key words: oleanane parameter (OP), biomarker, maturity, oil-source correlation, Fushan Depression

1 Introduction

Oleananes were first discovered in Nigerian petroleum more than three decades ago (Whitehead, 1974). Their apparent restrictions, initially to Tertiary Nigerian Basin, made them appear to be geochemical "oddities" — too provincial to be of wide geochemical applicability unlike their more ubiquitous hopane counterparts (Ekweozor and Udo, 1988). However, the compounds have been found in oils and rock extracts in many other late Mesozoic-Cenozoic basins around the world. Examples include the Po Basin (Riva et al., 1986), the Beaufort-Mackenzie Delta (Brooks, 1986a, b; Curiale, 1991), the Gippsland Basin (Philp and Gilbert, 1986), Brazil (Mello et al., 1988), Taranaki Basin (Killops et al., 1994, 1995), Japan (Waseda and Nishita, 1998), lignites in Greece (Fowler et al., 1991), and China (Fu and Sheng, 1989). Hao et al. (1998) has reported the present of high content of oleananes in oils from the Yinggehai Basin, South China Sea.

Due to its origin from betulins (Grantham et al., 1983), teraxerene (ten Haven and Rullkötter, 1988) and other 3β -functionized pentacyclic triterpenoids (e.g., aymyins) (Whitehead, 1974; Rullkötter et al., 1994) that are known exclusively from angiosperm higher land plants

(Moldowan et al., 1994, and references therein), oleanane has become a useful marker for both source input and geological age (Peters et al., 2005). Nevertheless, several observations show that the abundance of oleananes in an oil or sediment is not simply controlled by the degree of land plant contribution of the organic matter (Murray et al., 1994; Murray et al., 1997). Some researchers thought that the main fate of the precursor oleanenes in coal swamps and lakes is not hydrogenation but partial or complete aromatization (Murray et al., 1997). The abundance of oleananes is likely to be highly sensitive to changes in E_h and pH during early diagenesis. Murray et al. (1997) also found that a marine influence during early diagenesis increases the abundance of oleananes in sediments and oils and reduces skeletal alteration and aromatization.

Two isomers of 18α -(H) and 18β -(H) oleanane are found in petroleum, and the latter is thermally less stable (Riva et al., 1986). Therefore, the relative concentration of these two isomers can be used as maturity index.

The oleanane parameter (OP) proposed by Ekweozor and Udo (1988) is used to monitor the combined abundance of 18α -(H) and 18β -(H) oleananes relative to the C_{30} hopane. The OP (oleananes/(oleananes + C_{30} hopane)) increases from low values in immature rocks to a maximum at the top of the oil-generation window (TOGW),

^{*} Corresponding author. E-mail: meijunli2008@hotmail.com

remaining relatively stable at greater depth (Ekweozor and Udo, 1988; Ekweozor and Telnæs, 1990).

This paper reports the occurrence of oleanane in rock extracts and oils from the Fushan Depression, Beibuwan Basin, South China Sea, and studies the depth-trend with thermal evolution and its application to oil-source rock correlation in the Tertiary hydrocarbon-bearing basin.

2 Geological Setting

Situated north of the Hainan Island and south of the Qiongzhou Strait, the Fushan Depression is one of the many Mesozoic-Cenozoic rifting half-grabens in the northern continental shelf of the South China Sea. This NE-E trending depression forms the southeastern portion of the Beibuwan Basin (Fig.1), filled with over 9000 m of Cenozoic sediments in an area of approximately 3000 km², one third of which is offshore.

Hydrocarbon exploration in the Fushan Depression began at the end of 1950's, with approximately 70 wells being drilled in the subsequent three decades. Major discoveries up to date include light oils and gas condensates in the Huachang uplift and Jinfeng faulted nose structure, and normal gravity oils in the Meitai fault blocks (Fig.1).

Four orogenic events occurring during the late Mesozoic to Neogene controlled the tectonic evolution and sedimentary filling of the Beibuwan Basin (Gong, 1997; Oiu and Gong, 1999; Zhao, 2007). The Late Cretaceous Shenhu orogeny resulted in a number of grabens and halfgrabens. The Paleocene to Eocene Zhuqiong orogeny was the main period of rifting, responsible for the formation of the present Beibuwan basin configuration. In the early rifting stage, the basin was mainly filled with alluvial and fluvial red pebbled sandstones and mudstones of the Changliu Formation (E_1c) . In the late rifting stage, organicrich mudstones of the Liushagang Formation (E_2l) were deposited in a series of well-developed lakes, forming the most important hydrocarbon source rocks. The Liushagang Formation is the time equivalent of the Wenchang Formation in the Pearl River Mouth Basin (PRMB) (Zhang et al., 2004; Qiu and Gong, 1999). Major boundary faults occurring in this period controlled the framework of the Fushan Depression. During the late Oligocene Nanhai orogeny, the area was dominated by a shallow lake and swamps, leading to the formation of organic-rich mudstones with thin coal interbeds of the Weizhou Formation (E_3w) , the second important source unit in the basin. At the late stage of the Nanhai orogeny, the area was filled with shallow marine deposits, intercalated with fluvial sediments in the second member of the Weizhou Formation. During the Neogene Dongsha orogeny, block faulting dominated the basin evolution. The orogenic events described above were usually accompanied by extrusive volcanism, resulted in a series of uplifted and subsided blocks during the deposition of the Jiaowei $(N_U j)$, Dengloujiao $(N_1 d)$ and Wanglougang $(N_2 w)$ Formations (Li et al., 2007a).

The Fushan Depression is bounded by the Lingao Fault in the northwest, Anding Fault in the south, and Changliu Fault in the southeast (Fig. 1). It bears the characteristics of typical half-graben rifting basin. The structural subunits include the northern fault blocks (deep slope), central structural belt and southern slope. Majority of oil and gas discoveries occur in the central structural belt, mainly in the Huachang uplift. The known petroleum reservoirs in the Fushan Depression include payzones in the E_2l^3 , E_2l^2 and E_2l^1 Members of the Liushagang Formation (Fig. 2). Oils in the Huachang and Meitai oil and gas fields mainly occur in E_2l^3 and are dominated by light oil or condensate with an average gravity of 45° (API).

The coarse sandstones formed in the braided fan delta front are the main reservoirs in the E_2l^3 pools, with an average porosity of 16.8% in the Huachang oil/gas field and 13.1% in the Meitai. The fine-grained sandstones of the fan delta front facies form the main reservoir rocks in the E_2l^1 pools, with an average porosity of 15.5% in the Huachang oil/gas field, and 8.8% in other areas. Regional hydrocarbon seals include the 100-500 m of thick lacustrine dark mudstones in the E_2l^2 section and the upper E_2l^1 to middle E_2l^3 section (Li et al., 2007a).

3 Experiment

Twenty one core and cutting samples were collected from Well M1 (in Meitai structure) and Wells Hd1/Hd2/H1 (in Huachang uplift) for vitrinite reflectance measurement. The vitrinite reflectance values $(R_o/\%)$ were measured on polished rock blocks using a Leica Model MPV-SP microscopic photometer. Rock-Eval analyses were carried out on approximately 50mg crushed cores, using a Rock-Eval 6 instrument in which the oxidation oven was programmed to ramp temperature between 400°C and 800°C. The rock samples were extracted using a Soxhlet extractor with about 500mL solvents of dichloromethane and methanol (83:17 v/v). Five oil samples from 5 wells were collected from the Huachang and Meitai oil and gas fields. The oils and the extracted bitumens were fractionated into saturated, aromatic hydrocarbons, and polar compounds (NSOs and asphaltenes) using open column chromatography and a series of elution solvents with increasing polarity.

The saturate fractions were analyzed by using gas chromatography (GC) and GC-selected ion and full scan mass spectrometry (GC-MS). Gas chromatography

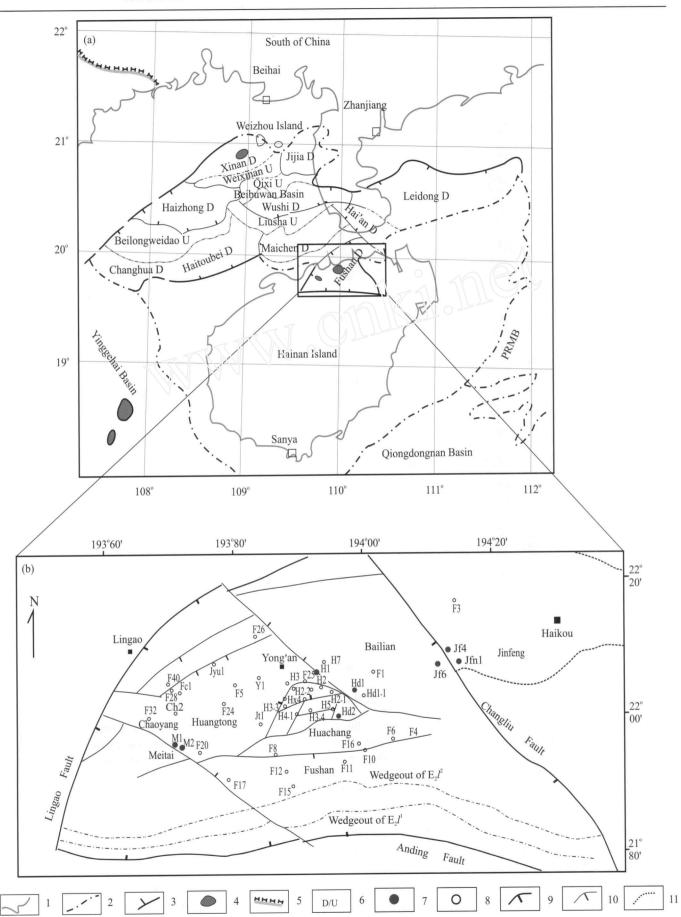


Fig. 1 Map (a) showing the location of the Fushan Depression, Beibuwan Basin; map (b) showing the schematic structures of the Fushan Depression, and the sampling wells.

Legend: 1 – Coastline; 2 – Boundary of basin; 3 – Fault; 4 – Oil/gas field; 5 – National boundary; 6 – Depression/Uplift; 7 – Well sampled; 8 – Well; 9 – Main fault; 10 – Fault; 11 – Hypothetical boundary (after Li et al., 2007a).

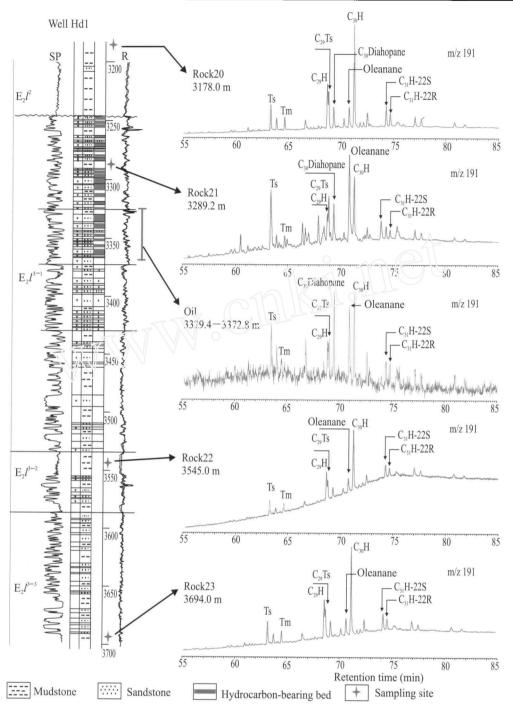


Fig. 2 Stratigraphic column showing the lithology and sampling sites in this study, and Mass Chromatograms (m/z 191) showing the distribution and composition of hopanes, oleananes, diahopane and other triterpanes of source rock and oils samples from Well Hd1, the Fushan Depression.

Note: $C_{29}H = C_{29}$ norhopane; $C_{29}Ts = 18\alpha(H)-30$ -normeohopane; $C_{30}H = C_{30}17\alpha(H)$ -hopane; $C_{31}H-22S = C_{31}$ -homohopane (22S); $C_{31}H-22R = C_{31}$ -homohopane (22R).

analysis was carried out using a Agilent 6890 GC equipped with a SE-54 fused silica capillary column (30m \times 0.25mm ID) with a 0.25 μm coating thickness. Helium was used as the carrier gas. The oven temperature was initially set at 100°C and programmed to 300°C at 4°C /min, with a final hold at 300°C for 30 minutes. GC-MS analyses were made using a Thermal Finnigan Trace-DSQ mass spectrometer coupled to a HP 6890 GC equipped with a HP-5MS column (30m \times 0.25mm ID) with a 0.25 μm coating. Helium was

used as the carrier. The oven temperature was initially set at 50°C, and programmed to 120°C at 20°C /min, to 250°C at 4°C /min, then to 310°C at 3°C /min with a final hold of 30 min. Electron ionization was employed (70 eV).

The oleananes were identified on the mass chromatograms (m/z 191), by the relative retention time and mass spectra, referring data published (Nytoft et al., 2002). The compound lupane could coelute with the peak of oleananes. However, the absence of diagnostic m/z 369

peak on mass spectra (referring Nytoft et al., 2002) indicate that the lupane in the studied rock and oil samples is present only in trace amount.

4 Results and Discussion

4.1 Characterization of organic matter

TOC (total organic carbon) values of Wells H1/Hd1/Hd2 range from 0.33% to 1.59% with an average of 1.08%. Except for the Rock21 (0.33%), all samples can be served as effective source rocks. The average TOC value in Well M1 is 1.42% with a minimum of about 1.0%.

Based on the pseudo-van Krevelen diagram (HI-Tmax) and maceral compositions, the organic matter in the Eocene Liushagang Formation (E_2l) of Wells M1, and H1/Hd1/Hd2 is dominated by type II_B to III kerogen (Li et al., unpublished data). It is better in quality for the Well M1 than the Wells H1/Hd1/Hd2.

4.2 Depth-trend of OP

Figs. 3a and 4a present the profiles of the downhole variations of OP for Wells M1 and H1/Hd1/Hd2. In the former, the OP value increases from 0.06 at a depth of 1820.0 m to a maximum of 0.19 at 3115.4 m, and then decreases to 0.15 at a depth of 3326.0 m (Fig. 3a). Wells H1/Hd1/Hd2 shows a similar relationship except for Rock21. The OP value increases from 0.11 at a depth of 2437.0 m to a maximum of 0.21 at 3545.0 m (Fig. 4a). This trend is similar to those found by Ekweozor and Telnæs (1990) in Niger Delta. However, the OP values are relatively lower in the Fushan Depression.

The OP of Rock21 is abnormally higher than that of adjacent samples. It is as high as 0.62. The oleanane peak in mass chromatogram (m/z 191) is apparently higher than that of C_{30} hopane (Fig. 2). This abnormality can be caused by three possible processes, including diagenesis, variations in organic facies or contaminating.

The trend of OP in Niger Delta also gets a maximum point at certain depth (Ekweozor and Telnæs, 1990) and is interpreted as the generation of oleananes during diagenesis. However, this abnormally high OP in Well Hd1 is apparently different from the maximum value of Niger Delta. It is three times higher than that of the sample approximately 110 m shallower.

The alternation interpretation is variations in local organic matter input or depositional environment, namely the organic facies. This conclusion may be supported by extra higher Ts/(Ts + Tm) and C_{30} diahopane/ C_{30} hopane (0.88 and 0.73, respectively)(Fig. 3b, c and Fig. 4b, c). Ts/ (Ts + Tm) is a useful maturation parameter to correlate source rocks with similar depositional environment (Peters et al., 2005).

The diahopane is also affected by depositional environment. It is usually abundant in oxic and acid clay environment (Peters et al., 2005). The characteristics of high OP, Ts/(Ts + Tm) and Diahopane/C₃₀hopane supported the conclusion that the abnormality of Rock21 sample is likely due to variations in depositional environment and source input. However, all rock samples in Wells H1/Hd1/Hd2 have similar Pr/Ph value. It ranges from 2.41 to 4.18 with an average of 3.0, which indicate typical oxic depositional environment (Table 1). Furthermore, the bitumen of this sample is featured by very high maturity. For example, the MPI-1 and TNR-2 is 0.77 and 1.19 respectively, which is apparently not consistent with the maturation of rocks reflected by vitrinite reflectance $(R_0 = 0.54\%)$ and much higher than that of samples with a depth only 111m shallower (0.77 vs. 0.49, 1.19 vs. 0.94, respectively). Thus the variations in organic facies can be ruled out.

The possible reason is the contaminating. Rock21 was sampled from the mudstone interval of Well Hd1. It is only about five meters thick and embedded by sandstone beds. The sandstone beds are payzones in Well Hd1 (Fig. 2). This rock sample is likely contaminated by oils from sandstones. This conclusion can be supported by the similarity of mass chromatograms of Hd1 oil and Rock21 rock samples. Both of them have special high concentration of oleananes, diahopane, high Ts/(Ts + Tm) values and high maturation molecular parameters. Another piece of evidence is that this rock sample has especially lower organic carbon content (TOC: 0.33%). The bitumen "A" to TOC ratio, however, is much higher (0.17) than any other samples (with an average of about 0.07) (Table 1). The high content of bitumen "A" might be contributed by migrated oils. Therefore, the abnormality in molecular compositions of Rock21 may be contributed by contamination of oils from Well Hd1.

4.3 Relationship between OP and some maturity indices

The relationship between the OP maturation profile and the corresponding downhole variations of vitrinite reflectance $(R_o/\%)$, Ts/(Ts + Tm), and the compound ratios derived from C₃₁homohopane epimerization maturity indices are shown in Figs. 3 a, b, c and Figs. 4 a, b, c for Wells M1 and H1/Hd1/Hd2, respectively. Table 1 lists the OP values for the studied section and the corresponding molecular geochemical parameters and reflectance maturity measurements. In Well M1, the OP turning point, which occurs at ~3100 m (Fig. 3a), corresponds to 0.53% $(R_o/\%)$. The Ts/(Ts + Tm) value apparently increases gradually with the increasing of burial depth. It gets a maximum of 0.64 at the lowermost of the studied stratigraphic column (Fig. 3b). The values of C₃₁hopane-

1.15

1.04

0.49 0.54 0.75 0.75 0.76 0.90 0.90 0.77

0.64

0.94

0.95

1.07

TNR-2

0.83

0.87

0.67

0.38 0.73 0.77 0.77 0.78 0.35 0.38 0.46 0.39 0.45 0.43 0.620.65 0.58 69.0 0.49 1.07 0.51 0.28 0.47 0.45 89.0 0.90 0.23 0.21 0.63 (1,2,5-+1,2,7-)TMN/ (1,6,7-+1,2,7-)TMN 2.82 1.12 0.84 0.30 0.46 2.23 1.30 2.20 1.36 1.18 2.01 0.61 1.86 06.0 2.17 1.33 89.1 90.1 1.43 1.25 1.95 1.55 1.67 2.01 90.0 0.08 0.20 0.73 0.18 0.22 09.0 0.03 0.10 0.16 0.16 0.15 0.04 0.03 0.04 0.04 0.04 0.97 0.03 0.02 0.02 0.07 0.04 0.01 0.31 0.09 0.17 0.15 0.19 0.12 0.13 0.50 0.24 0.10 0.13 0.15 0.16 0.19 0.10 0.10 0.10 0.17 0.13 0.18 90.0 0.14 0.17 0.14 0.09 0.62 $^{\circ}$ 0.11 0.21 0.31 0.34 0.47 0.47 0.59 0.88 0.68 0.88 0.38 0.350.36 0.62 0.59 0.64 0.56 0.58 0.58 Table 1 Geochemical parameters for the source rocks and oils from the Fushan Depression, South China Sea 0.47 0.15 0.45 0.51 0.64 0.61 0.84 0.31 0.47 0.51 0.81 (S+R)0.59 0.59 0.59 0.59 0.59 0.59 0.62 0.58 0.52 09.0 0.60 0.60 0.60 0.65 0.60 09.0 0.38 0.42 0.55 0.59 0.600.59 0.61 0.31 0.61 0.610.61 C₂₉ 20S/(S+R) 0.20 0.62 0.45 0.19 0.49 0.48 0.52 0.49 0.57 0.18 0.17 0.58 0.72 0.50 0.52 0.52 0.52 0.65 99.0 0.62 0.23 0.53 0.53 0.55 0.61 090 3.45 4.18 2.75 2.80 2.95 3.39 2.87 4.13 3.48 2.50 3.18 2.32 2.41 3.73 3.47 3.63 4.22 96.0 1.21 1.87 2.41 3.94 3.45 3.63 3.68 5.21 0.47 0.50 0.47 0.52 0.48 0.56 0.49 0.50 0.54 0.630.65 0.33 0.37 0.43 0.50 0.53 0.54 0.51 0.51 0.51 £ % 'A'' TOC 0.05 90.0 90.0 90.0 0.17 0.13 0.03 0.08 0.04 0.05 0.07 0.08 0.11 0.07 0.14 0.05 0.05 90.0 0.11 0.07 0.08 n.d. (, 10%) 1445 770 991 803 920 336 1169 562 726 476 671 896 928 2031 886 648 405 500 2061 471 0.70 1.38 1.46 0.87 0.58 1.59 0.33 0.97 1.21 1.49 1.32 1.221.64 (%) 1.05 0.81 n.d. 1.4 1.88 1.81 n.d. n.d. 3329.4 -3372.8 3084.0 -3086.0 3105.2 3108.0 3151.2 -3153.4 2542.0 -2563.0 3011.8 -3047.6 2520.0 2525.0 2603.0 2847.0 2887.0 3019.0 3035.0 3178.0 3289.2 3545.0 3694.0 1820.0 2010.0 2276.0 2545.0 2828.0 2944.0 3115.4 3155.0 3326.0 Depth 2437.0 (E) Hd2 Hd2 11d2 Hd2 H_d2 Hdl Hdl Hdl Hdl Hdl Hdl Hdl Hdl M2 Ξ M M M Ξ M $\bar{\Xi}$ Ξ Ξ M $\overline{\Sigma}$ Ξ Fm. E_2l^2 E_2l^3 E_2l^2 E_2l^3 $E_{2}l^{3}$ E,l' E3. E_2l^2 $E_{j}L_{j}$ E_{j} E_2l^3 $E_{j,l}$ $E_{2}I_{3}$ $E_{2}I_{3}$ Eil E,L E_2l^{-1} $E_{2}J^{3}$ E_2l^2 $E_2 l^3$ E_2L_3 E-1-E,1, $E_{2}I^{3}$ $E_{2}I$ $E_{j}[]_{j}$ Rock23 Rock34 Rock36 Rock29 Rock32 Rock33 Rock39 Rock31 Rock22 Sample Rock17 Rock28 Rock18 Rock 19 Rock20 Rock21 Rock35 Rock40 Rock37 Rock38 Rock07 Rock27 Oil Ōį Oil Ö Oii ž Oil

Note: A": bitumen A" in source rock; C_{29} 20S/(S + R): C_{29} sterane 20S/(20S + 20R); 22S/(S+R): C_{31} hopane 22S/(22S + 22R); MPI-1 - 1.5 ×(2-methylphenanthrene + 9-methylphenanthrene); TNR-2 = (1,3,7 + 2,3,6-) trimethylnaphthalene/(1,3,5- + 1,3,6- + 1,4,6-) trimethylnaphthalene; the definition of other geochemical parameters reference to Fig.3.

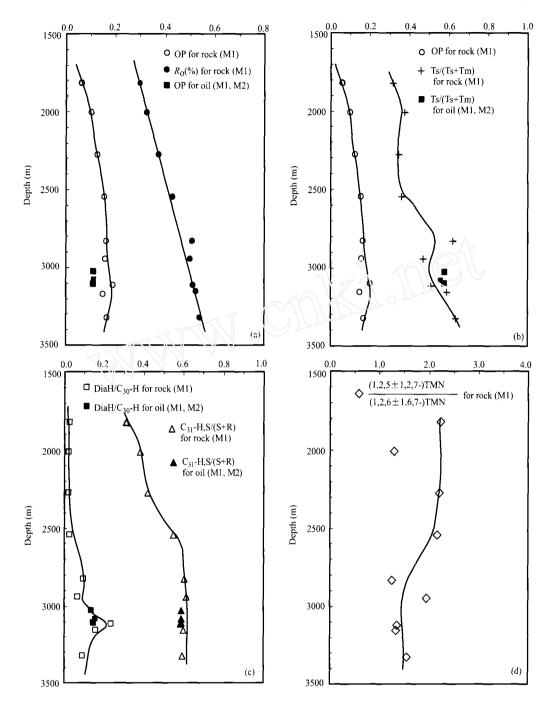


Fig. 3 (a) Depth-trend plots of OP and R_o (/%); (b) OP and Ts/(Ts+Tm); (c) diaH/C₃₀-H and C₃₁-H, S/(S+R); (d) (1,2,5-+1,2,7-)TMN /(1,2,6-+1,6,7)TMN of the source rocks in Well M1 and oils in Wells M1 and M2, the Fushan Depression.

Note: Ts/(Ts + Tm) = $18\alpha(H)$ -neohopane/($18\alpha(H)$ -neohopane + $17\alpha(H)$ -22,29,30-Trinorhopane); diaH/C₃₀-H = $17\alpha(H)$ -diahopane/($17\alpha(H)$ -diahopane + C₃₀-17 $\alpha(H)$ -hopane); (1,2,5- + 1,2,7-) TMN /(1,2,6- + 1,6,7-) TMN = (1,2,5- + 1,2,7-) trimethylnaphthalene / (1,2,6- + 1,6,7-) trimethylnaphthalene.

22S/(S+R) gets its equilibrium point at a depth of about 2600m (0.43, $R_o/\%$), which is apparently shallower than commonly accepted values of 0.60 ($R_o/\%$) (Peters et al., 2005).

Abundant diahopanes also occur in source rocks and oils from the Fushan Depression (Fig. 2). The $C_{30}17\alpha(H)$ -diahopane was identified by Moldowan et al. (1991). Volkman et al. (1983), Philp and Gilbert (1986) regard this compound as a possible terrigenous marker due to its

presence in coals and terrigenous oils. Peters et al. (2005) suggested that the C_{30} diahopane may be related to bacterial hopanoid precursors that have been undergone oxidation in the D-ring and rearrangement by clay-mediated acidic catalysis. C_{30} diahopane/ C_{30} hopane ratio has been developed to investigate the depositional environment for source rocks. Molecular mechanics calculations predict that the $17\alpha(H)$ -diahopane is more stable than $17\alpha(H)$ -hopane; thus, the C_{30} diahopane/ C_{30} hopane can be used as

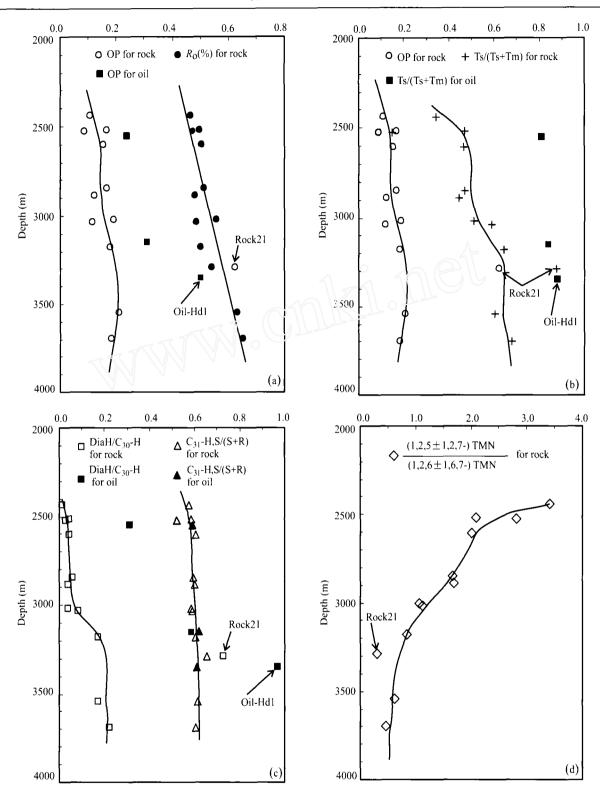


Fig. 4 (a) Depth-trend plots of OP and R_o (/%); (b) OP and Ts/(Ts + Tm); (c) diaH/C₃₀-H and C₃₁-H, S/(S + R); (d) (1,2,5- + 1,2,7-)TMN /(1,2,6- + 1,6,7) TMN of the source rocks and oils in Wells H1/Hd1/Hd2, the Fushan Depression. Note: The definition of geochemical parameters reference to Fig. 3.

maturity parameters (Moldowan et al., 1991). Fig. 3c illustrates the depth-trend of C_{30} diahopane/ C_{30} hopane. The curve is approximately similar to that of OP. The C_{30} diahopane/ C_{30} hopane ratio is very low at the depth shallower than 2600 m. It increases gradually when the burial depth is higher than that. It also gets a maximum of about 0.20 at the depth of ~3100 m, and then begins to decrease. It suggests that the generation of oleanane and

diahopane may be controlled by the same course of early diagenesis.

In Well M1, the OP turning point, which occurs at ~3100 m (Fig. 4a), corresponds to 0.55 (R_0 /%). The depth-trend of Ts/(Ts + Tm) is approximately as same as that of Well M1, except for Rock21 sample. There is no turning point in the curve of C_{31} hopane-22S/(S + R). The C_{30} diahopane/ C_{30} hopane ratio is very lower before the depth of about

3000m. It gets the maximum at about 3200 m, and then remains constant or increases slowly.

There is no consensus among geochemists on the petroleum-generating potential and the precise boundaries of corresponding oil-generation window (OGW) of terrigenous organic matter (Ekweozor and Telnæs, 1990). The hydrous pyrolysis experiment by Lewan and Williams (1987) indicated that oil generation from resinites is not likely to occur at low vitrinite reflectance values $(R_0<0.6\%)$. In the Tertiary of the Beaufort-Mackenzie basin, however, naphthenic oils and condensates have been generated from terrestrial derived organic matter at maturity of 0.4% to 0.6% (R_0) (Snowdon and Powell, 1982). Chen et al. (1999) thought that the main oil generation window is in ranges of 0.7% to 1.2% (R_0) in Jurassic coal of Northwest China. The commonly used threshold of oil-generation widow in Tertiary source rocks of eastern China lacustrine basins is 0.50% ($R_{\rm e}$). Thus, Snowdon and Powell (1982) pointed out that type III or terrestrial organic matter can generate oil, condensate, and gas at varying level of thermal maturation as a function of the content of resinite, liptinite, and vitrinite within the organic fraction.

The threshold depth of oil-generation window of Liushagang source rocks in the Weixinan and Haizhong Depressions of Beibuwan Basin is about 2400m, corresponding to the vitrinite reflectance of 0.5% (R_0) (Chen, 1982). However, the maceral composition variations in different depressions can cause to varying threshold. Vitrinite reflectance depends on changes of optical properties of vitrinite particles which are uninvolved in hydrocarbon generation. The OP value, however, is based on concentration changes of component which is actually involved in the oil generation process (Ekweozor and Telnæs, 1990). The depth corresponding to the OP turning point (threshold) has been interpreted to coincide with the diagenesis/catagenesis boundary for the stratigraphic column in Niger Delta (Ekweozor and Telnæs, 1990). Thus the oil-generation thresholds of Well M1 and Wells H1/Hd1/Hd2 determined by OP, equivalent to 0.53 and 0.55 $(R_0/\%)$, respectively may be more precisely than the vitrinite reflectance.

4.4 OP in oil-source correlation and source kitchen predicting

All corresponding parameters of oils from Well M1 and M2 are plotted in the Figs. 3a, b, c. Compared with oils from Wells H1/Hd1/Hd2, oils from Wells M1 and M2 have relatively lower OP values (0.11). The OP values are plotted in the range of source rock samples with burial depth within the oil window (Fig. 3a). The Ts/(Ts + Tm) ratios of oils from Wells M1 and M2 are about 0.58, which

is approximately equivalent to that of source rock at a depth of about 3300 m (Fig. 3b). The diahopane/hopane ratios are also plotted within the range of data of source rocks. All these evidence indicated that the oils from Wells M1 and M2 were derived from mudstone source rocks in situ.

All above parameters of the oils from Wells H1, Hd1 and Hd2 are distinctly different from those of source rock samples from Wells H1/Hd1/Hd2. For example, their OP values range from 0.24 to 0.50, which is two times higher than that of the corresponding source rocks. The Ts/(Ts + Tm), C₃₀diahopane/C₃₀hopane ratios are also much higher (Figs. 4a, b, c). It indicates that the oils discovered in these wells were not mainly sourced from the organic matter in Huachang Uplift. The pyrrolic nitrogen compounds, dibenzothiophene related geochemical parameters all suggest that the oil and condensates of Huachang Uplift are mainly charged from the Bailian Sag, which is located in the northeast of Huangchang Uplift (Li et al., 2007b). The maximum thickness of $E_2 l^3$, $E_2 l^2$ in Bailian Sag is up to 2300m on basis of seismic interpretation. On basis of maturity related molecular indices (e.g., Ts/(Ts + Tm), MPI-1 and TNR-2), the oils of H1/Hd1/Hd2 should be derived from the source rocks that have had undergone more maturity evolution. Their elevated OP values may be owing to the destruction of hopanes. Alberdi and López (2000) also pointed out that high maturity oils show a higher OP value than the original organic matter in the immature and low-maturity-level source rocks. The hydrocarbons discovered in the Fushan Depression are dominated by light oils, condensates and natural gas with high thermal maturity. According to the MPI1 and TNR-2, the maturity of oils from Huachang Uplift is estimated as 1.0–1.1 ($R_0/\%$) equivalent (Li et al., 2007b, c). We found that the OP value shows a strongly positive relationship to other maturity indices, e.g. MPI-1 and 2,4-/1,4-DMDBT (2,4-/1,4-dibenzothiophene), except for a few samples (will be discussed in details in other paper), which shows that the OP indeed increases with the increased maturity in late oil window. Because no wells have been drilled and no source rock samples available in depocenter of the Bailian Sag, the variations in lateral organic facies can not exclusively be ruled out.

4.5 The possible generation mechanism of oleananes in the Fushan Depression

Many researchers summarized the processes leading to the formation of saturated and aromatics oleanoids from 3-functionsed precursors (for review, see Murray et al., 1997). Three main processes including hydrogenation, progressive aromatization and skeletal alteration (loss, opening or cleavage of the *A* and *C* rings) are involved in the evolution of 3-functionsed precursors. For example,

1,2,7- and 1,2,5-trimethyl naphthalenes (TMN) are thought to be generated from the cleavage of *C* ring of oleanoids. Here we use the ratio of 1,2,7- plus 1,2,5-TMNs to 1,3,6-plus 1,3,7-TMNs to represent the relative abundance of cleavage of *C* ring to non-source specific naphthalenes (Figs. 3d and 4d). This ratio in Wells H1/Hd1/Hd2 is about 3.5 at the depth of 1820m. It decreases rapidly with the increasing depth above 3200m. The decrease may be resulted from a dilution effect, in which the initial concentration of 1,2,5- and 1,2,7-TMN is progressively decreased by 1,3,6-, and 1,3,7-TMNs generated by the cracking of kerogen.

This ratio gets a minimum of 0.5 at the lowermost sample of the studied stratigraphic column of wells H1/Hd1/Hd2. The turning point is at about 3100 m, which is approximately equivalent to the TOGW obtained by OP and C₃₀diahopane/C₃₀hopane. The sample of Rock21 has also an especially low value.

This downhole trend suggests that ring-C cleavage of oleanoids may not enhance with the increasing of maturity. Then the aromatization is likely to be the main process that competes with the hydrogenation of oleananes' precursors and leads to the decreasing of oleananes concentration.

5 Conclusions

The study of OP (Oleanane Parameter) for 21 core and cutting samples of mudstones from two profiles and five oil samples from five wells in the Fushan Depression, South China Sea was conducted in order to compare the depthtrend of OP and vitrinite reflectance, and other geochemical parameters. All these rock and oil samples contain relatively abundant oleananes.

The OP increases with the burial depth, and get to its maximum at a depth of 3000m in Well M1, and 3100m in Wells H1/Hd1/Hd2, which corresponds the $R_{\rm o}$ value of about 0.53% and 0.55%, respectively. Unlike $R_{\rm o}$ (%), OP can precisely indicate the top of oil generation widow (TOGW). The sample of Rock21 in Well Hd1 has abnormally high OP values, as well as Ts/(Ts + Tm) and C_{30} diahopane/ C_{30} hopane ratios. All geochemical indices suggest that it might be contaminated by the oil from the adjacent sandstone beds.

The OP values, Ts/(Ts + Tm), Diahopane/hopane ratios all indicate that the oils of Wells M1, and M2 were mainly sourced from the mudstone of E_2l in situ. All these indices of oils from Wells H1, Hd1 and Hd2 are apparently higher than those of rock samples in these wells, which suggests that the main source rocks for these oils do not locate in the Huachang Uplift.

It is concluded that the OP is a useful geochemical indices in the maturity assessment and oil-source

correlation in the Tertiary Fushan Depression.

Acknowledgements

The authors would like to thank Dr. Li Maowen of Geological Survey of Canada for his constructive comments and suggestions which significantly improved the quality of this paper. This work was financially supported by the Natural Science Foundation of China (Grant No. 40672093), CNPC Innovation Fund (07E1001), and the ESS-China Hydrocarbon Geosciences Collaboration Project under Natural Resources Canada's International Opportunities Program. We extend our thanks to South Oil Exploration and Development Company of PetroChina for assistance in data and sample collection.

Manuscript received June 18, 2007 accepted Jan. 21, 2008 edited by Zhang Xinyuan

References

- Alberdi, M., and López, L., 2000. Biomarker 18α(H)-oleanane: a geochemical tool to assess Venezuelan petroleum systems. *South American Earth Sciences*, 13: 751–759.
- Brooks, P.W., 1986a. Biological marker geochemistry of oils from the Beaufort-Mackenzie region, Arctic Canada. *Bulletin of Canadian Petroleum Geology*, 34: 490–505.
- Brooks, P.W., 1986b. Unusual biological marker geochemistry of oils and possible source rocks, offshore Beaufort-Mackenzie Delta, Canada. *Organic Geochemistry*, 10: 401–406.
- Chen Jianping, Huang Difan, Li Jinchao, Qin Yong and Zhu Xinshan, 1999. The petroleum generation model for organic matter from Jurassic coal measure, Northwest China. *Geochimica*, 28(4): 327–339 (in Chinese with English abstract)
- Chen Weihuang, 1982. The threshold maturity depth of source beds and the primary migration of the oil in the Beibu Gulf Basin. *Marine Geology Research*, 2(2): 21–26 (in Chinese with English abstract).
- Curiale, J.A., 1991. The petroleum geochemistry of Canadian Beaufort Tertiary "non-marine" oils. *Chemical Geology*, 93: 21–45.
- Ekweozor, C.M., and Udo, O.T., 1988. The Oleanane: Origin, maturation, and limit of occurrence in South Nigeria sedimentary basins. *Organic Geochemistry*, 13: 131–140.
- Ekweozor, C.M., and Telnæs, N., 1990. Oleanane parameter: Verification by quantitative study of the biomarker occurrence in sediments of the Niger Delta. In: Leythaeuser, D., and Rullkötter, J. (ed.), *Advances in Organic Geochemistry*, London: Pergamon Press, 16: 401–413.
- Fu, J.M., and Sheng, G.Y., 1989. Biological marker composition of typical source rocks and related oils of terrestrial origin in the People's Republic of China, review. *Applied Geochemistry*, 4: 13–22.
- Fowler, M.G., Gentsis, T., Goodarzi, F., and Foscolos, A.E., 1991. The petroleum potential of some Tertiary liginites from northern Greece as determined using pyrolysis and organic petrological techniques. *Organic Geochemistry*, 17: 805–826.

- Gong Zaisheng, 1997. The major oil and gas fields of China offshore. Beijing: Petroleum Industry Press, 199–222 (in Chinese).
- Grantham, P.J., Posthuma, J., and Baak, A., 1983. Triterpanes in a number of Far-Eastern crude oils. In: Bjorøy, M. et al. (ed.), Advances in Organic Geochemistry, 1981. Wiley, Chichester, 675–683.
- Hao, F., Li, S.T., Sun, Y.C., and, Zhang Q.M., 1998. Geology, compositional heterogeneities, and geochemical origin of the Yacheng gas field, Qiongdongnan Basin, South China Sea. Bulletin of American Association of Petroleum Geologists, 82 (7): 1372–1384.
- ten Haven, H.L., and Rullkötter, J., 1988. The diagenetic fate of taraxer-14-ene and oleanene isomers. *Geochimica et Cosmochimica Acta*, 52: 2543–2548.
- Killops, S.D., Woolhouse, A.D., Weston, R.J., and Cook, R.A., 1994. A geochemical appraisal of oil generation in the Taranaki Basin, New Zealand. American Association of Petroleum Geologists Bulletin, 78: 1560–1585.
- Killops, S.D., Raine, J.I., Woolhouse, A.D., and Weston, R.J., 1995. Chemostratigraphic evidence of higher-plant evolution in the Taranaki Basin, New Zealand. *Organic Geochemistry*, 23: 429-445.
- Lewan, M.D., and Williams, M.D., 1987. Evaluation of Petroleum Generation from resinites by hydrous pyrolysis. *American Association of Petroleum Geologists Bulletin*, 71: 207–214.
- Li, M.J., Wang, T.G., Liu, J., Zhang M.Z., Lu, H., Ma, Q.L., and Gao, L.H., 2007a. Occurrence and origin of carbon dioxide in the Fushan Depression, Beibuwan Basin, South China Sea. *Marine and Petroleum Geology*, Dio:10.1016/j. marpetgeo.2007.07.007.
- Li Meijun, Wang Tieguan, Liu Ju, Zhang Meizhu, Lu Hong, Ma Qinglin and Gao Lihui, 2007b. Oil charging orientation and accumulation characteristics of oil reservoirs in the Fushan Sag, Beibuwan Basin. *Petroleum geology and Experiment*, 29 (2): 172–176 (in Chinese with English abstract).
- Li Meijun, Wang Tieguan, Liu Ju, Zhang Meizhu, Lu Hong, Ma Qinglin, and Gao Lihui, 2007c. The genesis and source of the natural gas in the Fushan Depression of Hainan. *Natural Gas Geoscience*, 18(2): 260–265 (in Chinese with English abstract).
- Mello, M.R., Telnæs, N., Gaglianone, P.C., Chicarelli, M.I., Brassell, S.C., and Maxwell, J.R., 1988. Organic geochemical characterization of depositional palaeo-environments of source rocks and oils in Brazilian marginal basins. *Organic Geochemistry*, 13: 31–45.
- Murray, A.P., Sosrowidjojo, I.B., Alexander, R., Kagi, R., Norgate, C.M., and Summons, R.E., 1997. Oleananes in oils and sediments: Evidence of marine influence during early diagenesis. Geochemica et Cosmochimica Acta, 61(6): 1261–1276.
- Murray, A.P., Summons, R.E., Boreham, C.J., and Dowling, L. M., 1994. Biomarker and *n*-alkane isotope profiles for Tertiary

- oils: relationship to source rocks depositional setting. *Organic Geochemistry*, 22: 521–542.
- Moldowan, J.M., Fago, R.J., Carlson, R.M.K., Young, D.C., van Duyne, G., Glardy, J., Schoell, M., Pillinger, C.T., and Watt, D. S., 1991. Rearranged hopanes in sediments and petroleum. *Geochimica et Cosmochimica Acta*, 55: 3333–3353.
- Moldowan, J.M., Dahl, J., Huizinga, B.J., Fago, F.J., Hickey, L.J., Peakman, T.M., and Taylor, D.W., 1994. The molecular fossil record of oleanane and its relation to angiosperms. *Science*, 265: 768–771.
- Nytoft, H.P., Bojese-Koefoed, J.A., Christiansen, F.G., and Fowler, M.G., 2002. Oleanane or lupine? Reappraisal of the presence of oleanane in Cretaceous-Tertiary oils and sediments. *Organic Geochemistry*, 33: 1225–1240.
- Peters, K.E., Walters, C.C., and Moldowan, J.M., 2005. *The biomarker guide* (2nd edition). New York: Cambridge University Press.
- Philp, R.P., and Gilbert, T.D., 1986. Biomarker distributions in Australian oils predominantly derived from terrigenous source material. *Organic Geochemistry*, 10: 73–84.
- Qiu Zhongjian and Gong Zaisheng, 1999. Oil exploration in China (vol. 4), offshore. Beijing: Geological Publishing House and Petroleum Industry Publishing House.
- Riva, A., Salvatori, T., Cavaliere, R., Ricchiuto, T., and Novelli, L., 1986. Origin of oils in Po Basin, northern Italy. *Organic Geochemistry*, 10: 391–400.
- Rullkötter, J., Peakman, T.M., and ten Haven, H.L., 1994. Early diagenesis of terrigenous triterpanes and its implications for petroleum geochemistry. *Organic Geochemistry*, 21(3/4): 215–233
- Snowdon, L.R., and Powell, T.G., 1982. Immature oil and condensate modification of hydrocarbon generation model for terrestrial organic matter. *Bulletin of American Association of Petroleum Geologists*, 66: 775–778.
- Volkman, J.K., Alexander, R., Kagi, R.I., Noble, R.A., and Woodhouse, G.W., 1983. A geochemical reconstruction of oil generation in the Barrow Subbasin of Western Australia. *Geochemica et Cosmochimica Acta*, 47: 2091–2106.
- Waseda, A., and Nishita, H., 1998. Geochemical characteristics of terrigenous- and marine-sourced oils in Hokkaido, Japan. Organic Geochemistry, 28: 27–41.
- Whitehead, E.V., 1974. The structure of petroleum pentacyclanes. In: Tissot, B., Bienner, F. (ed.), Advances in Organic Geochemistry, Paris: Editions Technip, 225–243.
- Zhang, C.M., Li, S.T., Yang, J.M., Yang, S.K., and Wang, J.R., 2004. Petroleum migration and mixing in the Pearl River Mouth Basin, South China Sea. *Marine and Petroleum Geology*, 21: 215–224.
- Zhao Zongju, 2007. Exploration Potential of Marine Source Rocks Oil-Gas Reservoirs in China. *Acta Geologica Sinica* (English edition), 81(5): 779–797.