Geochemical Characteristics of Crude Oils from Zao-V Oil Measures in Shenjiapu Oilfield

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Abstract: The geochemical characteristics of crude oils from Zao-V oil measures in the Shenjiapu oilfield are systematically described in terms of the fractional composition of crude oils, GC characteristics of saturated hydrocarbon fraction of crude oils and the characteristics of their biomarkers. The depositional environment, type and evolution of the biological source are also discussed. All pieces of evidence such as low saturated hydrocarbon fraction, high resin and asphalt, high isoprenoid alkane, weak odd-carbon number predominance (CPI ranging from 1.23 to 1.29, OEP ranging from 1.14 to 1.16) and low sterane and terpane maturity parameters show these crude oils are immature oils. Low Pr/Ph ratios (0.66 – 0.88) and high gammacerance/C_{31} hopane ratios (0.59 – 0.86) indicate the source rocks were formed in a slightly saline to brackish reducing lake depositional environment. Gas chromatographic characteristics of the saturated hydrocarbon fraction and the predominance of C_{30} hopane in terpane series and C_{29} sterane in sterane series indicate the biological source of the crude oils is composed mainly of bacterial and algal organic matter, and some algae are perhaps the main contributor of organic matter to the source rocks.

Key words: crude oil; geochemical characteristics; biomarker; Zao-V oil measures; Shenjiapu oilfield

The Shenjiapu oilfield, located in the south of the Dagang oilfield, next to the Zaoyuan oilfield in the north and adjacent to the Wangguantun oilfield in the south, is a fault block reservoir complicated by two groups of NE- and NW-extending faults, which is divided into the Jia-11, Guan-128, Guan-135, Jia-1 and Guan-130 fault blocks from north-east to south-west. The strata plunge southeastwards, with a plunging angle of 10°. NE-extending faults are the main structural faults, characterized by a long extension and large fault throw, by which the deposition, oil migration & accumulation were apparently controlled. However, the NW-extending faults' fault throw is relatively small, which makes the structure more fractured. The main oil-bearing formations are Zao-Ⅳ and -Ⅴ oil measures of the first member of the Lower Tertiary Kongdian Formation. The Zao-Ⅴ oil measures are the target formation dealt with in the paper.

1 Samples and experimental

Crude oil samples were collected in five fault blocks respectively and detailed information about the samples is presented in Table 1. As a whole, the physical properties of crude oils are bad, char-

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acterized by "four highs", that is, high density, high viscosity, high resin & asphalt and high sulfur. The crude oil density ranges from 0.9010 to 0.9517 g/cm^3 on the ground, averaging 0.9314 g/cm^3. The crude oil viscosity ranges from 237.76 to 3173.16 mPa · s at 50℃, averaging 1297 mPa · s. The sulfur content ranges from 0.12% to 0.21%, averaging 0.16%. The freezing point ranges from 19 to 38℃, with an average of 30℃. The wax content ranges from 4.48% to 22.55%, averaging 12%.

Crude oil samples were first dissolved with petroleum ether to get rid of asphalt by way of precipitation, then the fractions were separated by using alumina/silica gel column tomography, the saturated hydrocarbon fraction, aromatic hydrocarbon fraction, non-hydrocarbon fraction were washed out by using n-hexane, CH_2Cl_2/n-hexane (v/v 2 : 1) and $CHCl_3$/acohol, respectively, and the saturated hydrocarbon fraction was finally analyzed by gas chromatography-mass spectrometry.

The apparatus used in gas chromatographic-mass spectrographic analysis of the saturated hydrocarbon fraction is an SSQ710-type gas chromatography-mass spectrometry system. Gas chromatography condition: DB-5 quartz capillary (30 m × 0.32 mm), carrier gas is helium gas, the temperature of gasification is 300℃; temperature programming: keeping 100℃ for one minute; raising the temperature from 100℃ to 220℃ at the rate of 4℃/min, raising temperature from 220℃ to 300℃ at the rate of 2℃/min, and keeping 300℃ for 20 minutes. Mass spectrometry condition: EI (70 eV) electron-bombardment, emission current 300μA, signal multiplication voltage 1000 V, scanning scope (m/z) from 50 to 600, and scanning time 1.8 sec.

2 Compositional characteristics of crude oil fractions

The saturated hydrocarbon fraction accounts for 33.85% to 36.66%, the aromatic hydrocarbon fraction, 13.06% to 18.28%; the resin & asphalt fraction, 41.27% to 48.74%; saturated hydrocarbon/aromatic hydrocarbon ratios, 1.89 to 2.63; and resin/asphalt ratios, 1.89% to 2.63% (Table 1). As a whole, crude oils from Zao-Ⅴ oil measures are characterized by low saturated hydrocarbon fraction, high aromatic hydrocarbon fraction, low saturated hydrocarbon/aromatic hydrocarbon ratio, high resin & asphalt, and high resin/asphalt ratio. All the above characteristics show that the maturity of Zao-Ⅴ oil measures is low.

Table 1. Fractional composition of crude oils from Zao-Ⅴ oil measures in the Shenjiapu oilfield

Fault block	Well No.	Depth (m)	St (%)	Ar (%)	St/Ar	Resin (%)	Asphalt (%)	Resin & asphalt (%)	Resin/asphalt
Jia-11	Jia 33 - 39	2089.8 - 2157.9	36.66	13.94	2.63	35.46	8.89	44.35	3.99
Guan-128	Jia 37 - 43	2114.6 - 2156.4	33.85	13.06	2.59	40.03	8.71	48.74	4.60
Guan-135	Jia 37 - 53	2161.3 - 2185.1	34.51	18.28	1.89	31.53	12.31	43.84	2.56
Jia-1	Jia 39 - 59	2069.5 - 2146.9	35.05	16.28	2.15	31.61	14.24	45.85	2.22
Guan-130	Jia 40 - 58	2131.8 - 2156.6	35.89	18.23	1.97	29.75	11.52	41.27	2.58

3 Gas chromatographic characteristics of the saturated hydrocarbon fraction

According to the distribution of n-alkanes and the peak shape of gas chromatogram, the five crude oil samples have basically consistent characteristics, which shows they came from the same source. As a whole, the characteristics of crude oils from Zao-V oil measures in the Shenjiapu oilfield are presented as follows (Fig. 1 and Table 2): (1) high isoprenoid alkane ($\leqslant C_{20}$); phytane usually gives the main peak of gas chromatogram; the contents of phytane and pristine are higher than those of the corresponding C_{17} n-alkane and C_{18} n-alkane in all crude oil samples; and pristane/n-alkane ratios and phytane/n-alkane ratios are all greater than unity. Moreover, phytane/n-alkane ratios are greater than two in some crude oil samples; (2) remarkable phytane predominance; pristane/phytane ratios are all less than unity; (3) n-alkanes are characterized by single-peak distribution; C_{17} or C_{20} n-alkane gives the main peak; high light hydrocarbon/heavy hydrocarbon ratios, C_{21}^{-}/C_{22}^{+}, 1.49 to 2.38, and $(C_{21}+C_{22})/(C_{28}+C_{29})$, 2.66 to 3.83; (4) weak odd-carbon number predominance; CPI ranges from 1.23 to 1.29; and OEP ranges from 1.14 to 1.16. All the above gas chromatographic characteristics show that crude oils from Zao-V oil measures probably resulted from the early-stage thermal evolution of homonemeae organic matter under reducing conditions.

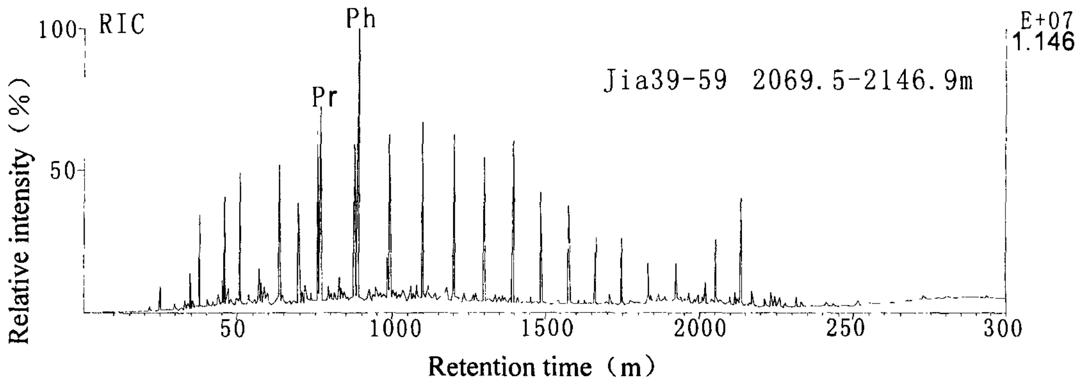

Fig. 1. Gas chromatogram of the saturated hydrocarbon fraction of crude oils from Zao-V oil measures in the Shenjiapu oilfield.

Table 2. Gas chromatographic parameters for the saturated hydrocarbon fraction of crude oils from Zao-V oil measures in the Shenjiapu oilfield

Fault block	Well No.	Pr/Ph	Pr/nC_{17}	Ph/nC_{18}	CPI	OEP	C_{21}^{-}/C_{22}^{+}	$(C_{21}+C_{22})/(C_{28}+C_{29})$
Jia-11	Jia 33 - 39	0.88	1.09	1.71	1.25	1.16	2.38	3.40
Guan-128	Jia 37 - 43	0.79	1.42	2.24	1.29	1.16	1.95	3.30
Guan-135	Jia 37 - 53	0.72	1.16	2.05	1.23	1.16	1.56	2.66
Jia-1	Jia 39 - 59	0.66	1.45	2.32	1.27	1.14	1.54	3.83
Guan-130	Jia 40 - 58	0.81	1.11	1.61	1.29	1.16	1.49	3.39

4 Gas chromatographic-mass spectrometric characteristics of saturated hydrocarbon fraction of crude oils

The results of gas chromatographic-mass spectrometric analysis for saturated hydrocarbon fraction show that crude oil samples from the five fault blocks are similar in steroid and terpenoid distribution, indicating that all the crude oils came from the same source rock, just consistent with the conclusion drawn from the analysis of gas chromatographic characteristics of the saturated hydrocarbon fraction.

Sterane series are the most important biomarkers of crude oils, which represent mainly the contribution of algal organic matter, and meanwhile offer the valuable information about crude oil maturity (Hou Dujie et al., 1999).

Full sterane series were found in all crude oil samples from Zao-V oil measures in the Shenjiapu oilfield, and the identification of sterane series is shown in Fig. 2. The characteristics of sterane series are described as follows: relatively low pragnane content; relatively high regular C_{27}, C_{28}, C_{29} sterane, among which C_{29} sterane content is highest and C_{27} sterane content is lowest; among the four isomers of C_{29} sterane, $C_{29}\alpha\alpha\alpha$ sterane (20R) content is highest, C_{29} sterane 20S/(20S + 20R) ranges from 0.27 to 0.29, C_{29} sterane $\beta\beta/(\beta\beta+\alpha\alpha)$ from 0.275 to 0.27; and pragnane and diasterane contents are relatively low (Fig. 2 and Table 3).

Terpane compounds are biomarkers distributed widely in all types of crude oil and source rock. Full terpane series were found in all crude oil samples from Zao-V oil measures in the Shenjiapu oilfield, and the identification of terpane series is shown in Fig. 3. Terpane series distribution is characterized by low tricyclic terpane and high pentacyclic triterpane contents: C_{20} tricyclic terpane is the main peak of tricyclic terpane, C_{23} tricyclic terpane content is low, C_{24} tetracyclic terpane content is high; C_{30} hopane content is too high and other triterpanes are low, long-chain pentacyclic triterpanes are of normal distribution; Ts content is low, Ts/Tm ratios range from 0.27 to 0.30, and C_{30} moretane content is high. In addition, relatively high gammacerane content was detected, gammacerane/C_{31} hopane ratios range from 0.59 to 0.86, gammacerane abundance is related to the salinity of depositional environment, for example, the source rocks and crude oils formed in highly saline depositional environment are rich in gammacerane. High gammacerane content may reflect a relatively reducing depositional environment and high-salinity water column. However, recent studies have shown that the high gammacerane content is probably related to water column stratification in the depositional environment (Sinninghe et al., 1995).

Table 3. Biomarker parameters for crude oil samples from Zao-V oil measures in the Shenjiapu oilfield

Biomarker parameter \ Well No.	Jia 33-39	Jia 37-43	Jia 37-53	Jia 39-59	Jia 40-58
20S/(20S+20R) $\alpha\alpha\alpha C_{29}$ sterane	0.292	0.289	0.289	0.290	0.274
$\beta\beta/(\beta\beta+\alpha\alpha)$ C_{29} sterane	0.269	0.267	0.265	0.259	0.254
22S/(22S+22R) C_{32} hopane	0.601	0.585	0.572	0.580	0.598
Ts/Tm	0.290	0.298	0.286	0.29	0.272
Gammacerane/C_{31} hopane	0.86	0.59	0.85	0.60	0.64
Tricyclic terpane/pentacyclic terpane	0.068	0.084	0.051	0.094	0.068
Pragnane/regular sterane	0.022	0.024	0.015	0.022	0.018
Sterane/terpane	0.167	0.195	0.173	0.208	0.198
C_{24} tetracyclic terpane/C_{26} tricyclic terpane	1.487	1.379	1.374	1.419	1.661

As viewed from sterane maturity parameters including C_{29} sterane 20S/(20S+20R) and C_{29} sterane $\beta\beta/(\beta\beta+\alpha\alpha)$, C_{29} sterane 20S/(20S+20R) ranges from 0.274 to 0.292 and C_{29} sterane $\beta\beta/(\beta\beta+\alpha\alpha)$ from 0.254 to 0.269 in all crude oil samples from Zao-V oil measures in the Shen-

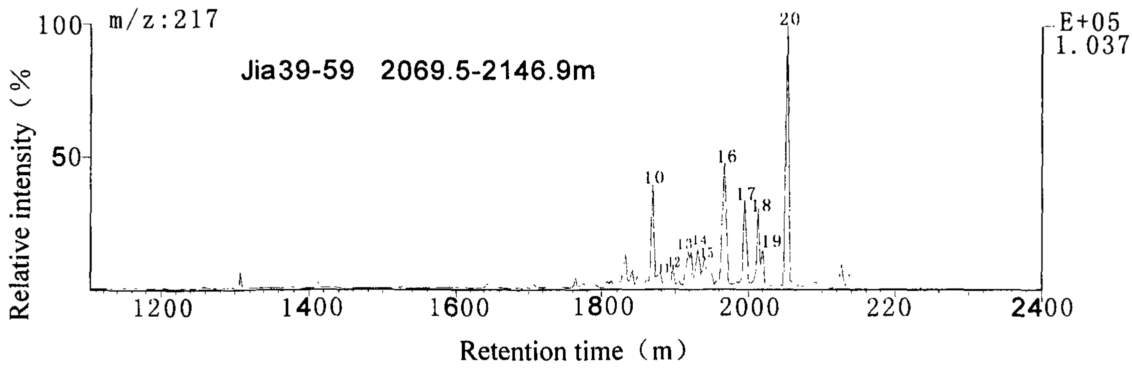

Fig. 2. Mass chromatogram (m/z = 217) of crude oils from Zao-V oil measures in the Shenjiapu oilfield. 1. Pragnane; 2. homosterane; 3 + 4. $C_{28}\beta\alpha$ diasterane (20S); 5 + 6. $C_{28}\beta\alpha$ diasterane (20R); 7. $C_{27}\alpha\alpha\alpha$ sterane (20S) + $C_{28}\alpha\beta$ diasterane (20S); 8. $C_{27}\alpha\beta\beta$ sterane (20R) + $C_{29}\beta\alpha$ diasterane (20S); 9. $C_{27}\alpha\beta\beta$ sterane (20S) + $C_{28}\alpha\beta$ diasterane (20R); 10. $C_{27}\alpha\alpha\alpha$ sterane (20R); 11. $C_{29}\beta\alpha$ diasterane (20R); 12. $C_{29}\alpha\beta$ diasterane (20S); 13. $C_{28}\alpha\alpha\alpha$ sterane (20S); 14. $C_{28}\alpha\beta\beta$ sterane (20R) + $C_{29}\alpha\beta$ sterane (20R); 15. $C_{28}\alpha\beta\beta$ sterane (20S); 16. $C_{28}\alpha\alpha\alpha$ sterane (20R); 17. $C_{29}\alpha\alpha\alpha$ sterane (20S); 18. $C_{29}\beta\beta\beta$ sterane (20R); 19. $C_{29}\alpha\beta\beta$ sterane (20S); 20. $C_{29}\alpha\alpha\alpha$ sterane (20R).

jiapu oilfield, far less than 0.4, indicating that all the crude oil samples belong to typical immature crude oils (Wang Tieguan et al., 1995). Low tricyclic terpane/pentacyclic terpane ratios, low pragnane/regular sterane ratios, low Ts/Tm ratios (Table 3), low diasterane contents and high C_{30} moretane contents show that the crude oil samples from Zao-V oil measures are immature, which is consistent with gas chromatographic characteristics of the saturated hydrocarbon fraction from crude oils.

Pristane/phytane ratios in crude oils or asphalts may indicate the depositional environment of source rocks (Hou Dujie et al., 1999). Pristane/phytane ratios in crude oils in the area studied are less than unity (0.66 to 0.88), and low pristane/phytane ratios and high gammacerane/C_{31} hopane ratios indicate that the source rocks were probably formed in a slightly saline to brackish lake reducing depositional environment. Hopane evolved from the precursor derived from bacterial cell wall (Ourisson et al., 1979) and high C_{30} hopane contents indicate that procaryote (bacteria) has made a certain contribution to organic matter in the source rocks. Sterane composition may reflect the composition of organic matter in the source rocks (Peters and Moldoman, 1993), and high C_{29} sterane contents usually were used as a symbol of high plant input (Czochanska et al., 1988). However, some algae contain abundant C_{29} sterol (Volkman et al., 1981). In combination with chromatographic characteristics of saturated hydrocarbon fraction from crude oils (mainly n-C_{17} alkane), it is considered that the biological source of Zao-V crude oils is composed predominantly of homonemeae organic matter, but some algae are probably the main contributors to their biological sources.

5 Conclusions

(1) Low saturated hydrocarbon contents, high resin & asphalt contents, high isoprenoid alkane contents, weak odd-carbon number predominance (CPI ranging from 1.23 to 1.29, OEP from 1.14

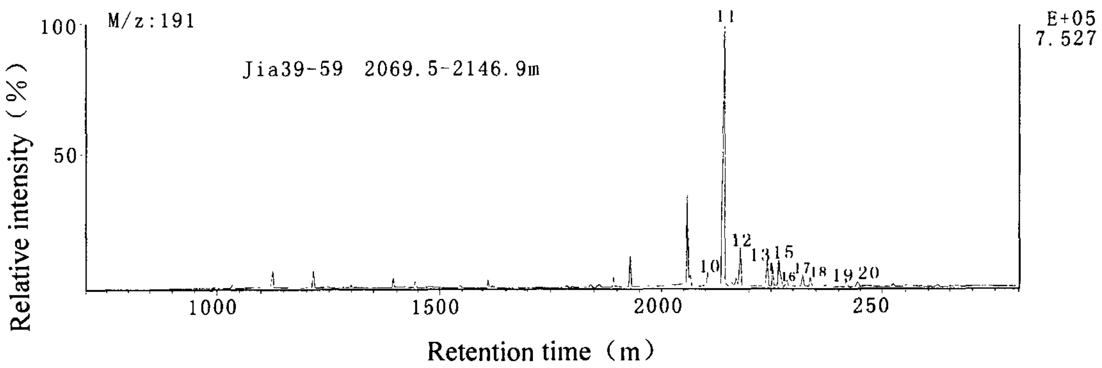

Fig. 3. Mass chromatogram (m/z = 191) of crude oils from Zao-V oil measures in the Shenjiapu oilfield. 1. C_{20} tricyclic terpane; 2. C_{21} tricyclic terpane; 3. C_{23} tricyclic terpane; 4. C_{24} tricyclic terpane; 5. C_{24} tetracyclic terpane; 6. Ts; 7. Tm; 8. C_{29} hopane; 9. C_{29}Ts; 10. C_{29} moretane; 11. C_{30} hopane; 12. C_{30} moretane; 15. gammacerane; 16. C_{31}(20R) moretane; 13, 17, 19. C_{31}, C_{32}, C_{33}(22S) hopanes; 14, 18, 20. C_{31}, C_{32}, C_{33}(22R) hopane.

to 1.16) and low sterane and terpane maturity parameters demonstrate that these crude oils are immature oils.

(2) Low Pr/Ph ratios (0.66 - 0.88) and high gammacerance/C_{31} hopane ratios (0.59 - 0.86) indicate that the source rocks were formed in a slightly saline to brackish lake reducing depositional environment.

(3) Gas chromatographic characteristics of saturated hydrocarbons and the predominance of C_{30} hopane in terpane series and C_{29} sterane in sterane series indicate that the biological source of the crude oils is composed mainly of bacterial and algal organic matter, and some algae are perhaps the main contributors of organic matter in the source rocks.

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