Chin.J.Geochem.(2011)30:093–098
DOI: 10.1007/s11631-011-0489-3

Geochemical characteristics of Ordovician crude oils in the northwest of the Tahe oil field, Tarim Basin

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Received July 20, 2009; accepted August 25, 2009

Abstract Forty-six crude oil samples were selected from the Ordovician in the northwestern part of the Tahe oilfield for detailed molecular geochemical and isotopic analysis, including group compositions, carbon- hydrogen isotopes and gas chromatograms of saturated hydrocarbons, as well as the characteristics of terpane, sterane and other biomarkers, indicating that crude oils are of the same origin from different districts in the Tahe oilfield and were derived from the same source kitchen (or oil source formation), i.e., mainly stemming from marine hydrocarbons. Detailed studies of oil physical properties of 25-honpane revealed that such oils have heavy or thick oil qualities due to biodegradation. Comprehensive assessment in terms of five maturity parameters shows that the oils from the Ordovician with R_o values varying from 0.80% to 1.59% are widely distributed in the northwest of the Tahe oilfield.

Key words Tahe oilfield; Ordovician; biomarker; heavy oil; maturity; biodegradation

1 Introduction

The Tarim Basin in Northwest China is a large composite basin. It has undergone several phases of structural deformation and may have undergone multiple periods of hydrocarbon generation, accumulation and migration. The resultant complexity of the Tarim Basin makes it more difficult to study petroleum geology (Zhang Shuichang et al., 2000). In the past long period, geochemical techniques have been used and some progress has been made in the study of migration-accumulation rules and reservoir-formatopm. Wang Tieguan (2004, 2008) discussed oil filling history of the Ordovician oil reservoirs in the major part of the Tahe oilfied. According to the distribution of double diamantine hydrocarbons in crude oils from the Tahe oilfield of the Tarim Basin Duan Yi (2007) got some information on oil and gas migration. However, there have long been controversies about the source. Gu Yi (2000) studied the forming mechanism of hydrocarbon pools in the Tahe oilfield, and he thought that the Cambrian-Lower Ordovician source rocks are the main source rocks. Ma Anlai et al. (2004) made oil-source correlation in the Lunnan and Tahe heavy oil fields. It is indicated that the oil came from the Middle and Upper Ordovician source rocks. Duan Yi (2009) also made the oil-source correlation of the Tahe oilfield. It is concluded that the crude oils are closely related to the Cambrian-Ordovician source rocks. Based on the results acquired by former researchers, this paper systematically analyzed the composition of biomarkers and carbon-hydrogen isotopic composition characteristics of Ordovician oils in the northwest of the Tahe oilfield. It is then concluded that the characteristics of molecular composition, organic phase and maturity provide clues to the forthcoming exploration and development of oil and gas.

2 Geological setting

The Tahe oilfield is situated in the southwest of the Akekule arch in the Shaya uplift, surrounded by the Caohu sag on the eastern side, the Halahatang sag on the western side and the Manjiaer depression on the southeastern side (Fig. 1). As the Tahe oil field is the largest oilfield found in Paleozoic marine carbonate rocks in China, crude oils have been recovered from the Ordovician carbonate rocks, also from the Carboniferous as well as Triassic sandstones, but Ordovician reservoirs

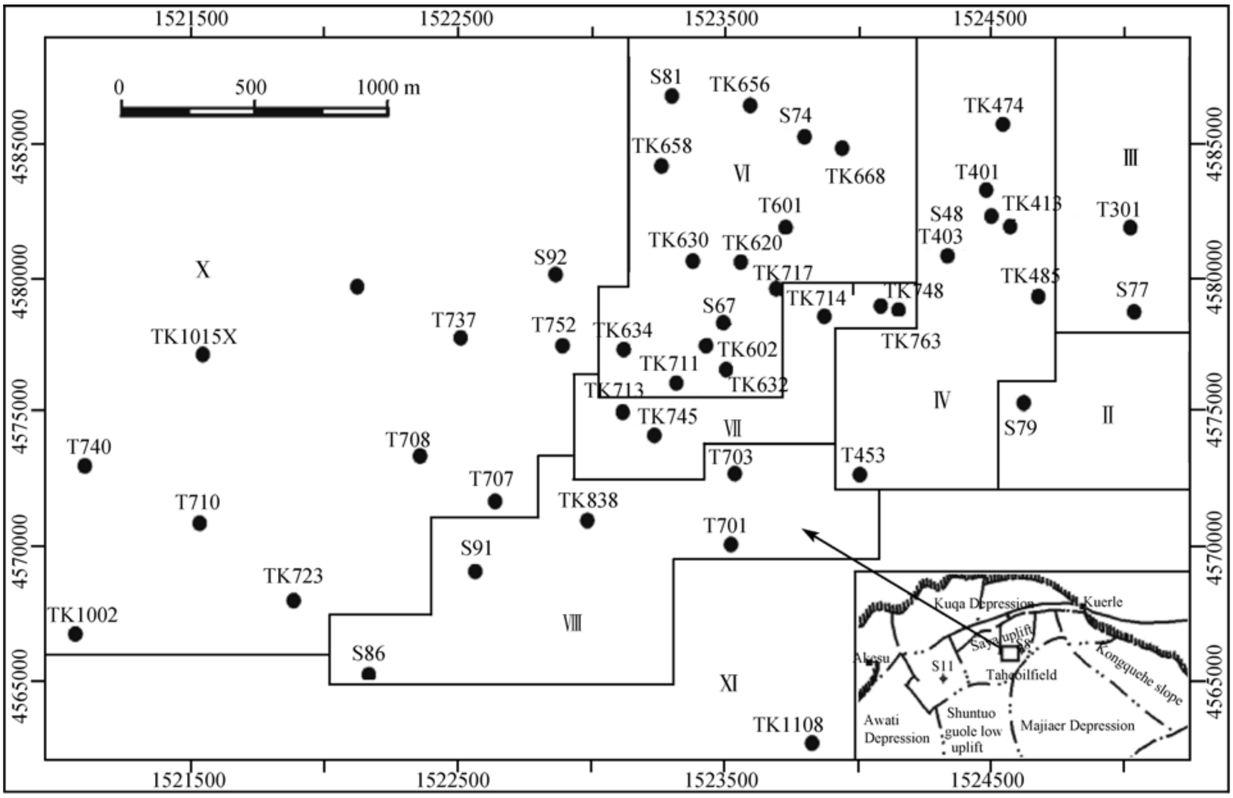

Fig. 1. The distribution of oil samples from the Ordovician reservoir in the northwest of the Tahe oilfield.

account for 91.5% of the total proved reservoirs in the Tahe oilfield (Kang Yuzhu, 2002; Zhang Kang, 2003).

3 Samples and experimental

Forty-six crude oil samples were collected from different districts in the Ordovician reservoir, northwest of the Tahe oilfield, as is shown in Fig. 1.

GC-MS analysis of the aliphatic and aromatic fractions has been performed on an HP 6890 N/5973 MSD coupled with a DB-5 fused silica capillary column (30 m×0.25 mm i.d.). Gas carrier was nitrogenous. The oven temperature programing was initiated at 100°C for 1minute, ramped up to 220°C at 4°C/min, then from 220–300°C at 2°C/min, and the temperature was maintained isothermally for 5 minutes for the aliphatic hydrocarbons. The temperature ramped from 80°C with 1 min initial isotherm to 300°C at 3°C/min, held at 300°C for 15 min for the aromatic fraction. The MS conditions are described as follows: electron impact (EI) ionization mode, electron energy 70 eV, and scanning range of 50–550 amu/s. The MSD operated in a multiple ion detection (MID) mode.

4 Results and discussion

4.1 The physical properties of crude oils

The Ordovician oils in the main northwestern part of the Tahe oilfield show the characteristics of heavy oils. Overall, these samples, high in density (0.86–1.03 g/cm^3), viscosity (>50 mm^2/s), sulfur content (0.72%– 3.46%), asphaltene content, but low in max content (4.55%–11.53%) and freezing point were likely affected by biodegradation.

4.2 Gross chemical composition

Most crude oils from the northwest of the Tahe Oilfield Group are widely variable in the contents of hydrocarbons, ranging from 15.48% to73.62%, and those of polar (NSO) fractions and asphaltene from 9.79%–53.33%. Saturate- to aromatics ratios range from 0.59 to 6.41, nonhydrocarbon to asphalt ratios from 0.27 to 28.5 in the major part of the Tahe oilfield, such as areas 4, 6, 7, 8 and 10. Most of the samples are high in asphaltene content, even up to 50% in part of oil at block 6. The density tends to decrease with the contents of NSO and asphaltene. So it also can reflected that the crude oils were subjected to strong biodegradation.

4.3 Gas chromatograms of saturated hydrocarbons

The chromatograms of the samples are almost similar and appear as being of the single-peak type, with the main peak carbons to be C_{13}-C_{17}. C_{21}^{-}/C_{22}^{+} ratios vary between 1.06–4.6, C_{21}+C_{22}/C_{28}+C_{29} ratios vary between 0.75–3.62, CPI and OEP indices are close to 1.0, demonstrating that the crude oils are already mature. As viewed from their distribution, the normal alkanes can be divided into two types: normal oils (Fig. 2a) and heavy oils (Fig. 2b). All the Ordovician crude oil samples show an intact *n*-alkane series and an evident base line 'bump'. Their coexistence in these oil samples can be interpreted as two oil filling processes occurring in the Ordovician oil reservoir of the Tahe oilfield, an early filled oil which had been severely biodegraded within the reservoir, and then a late filled non-biodegraded oil which was mixed into the same reservoir (Wang Tieguang et al., 2004; Ma Anlai et al., 2004). This is obvious in areas 4, 6, 8 and 10 in the northwest of the Tahe oilfield.

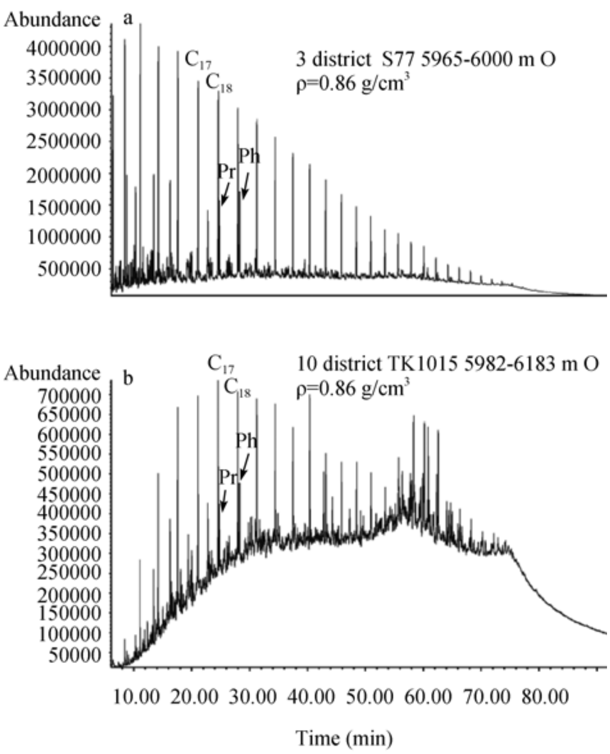

Fig. 2. Gas chromatograms of saturated hydrocarbon fractions of representative oils from the northwest of the Tahe oilfield.

The values of Pr/Ph, Ph/nC_{18} and Pr/nC_{17} can reflect the organic faces of the source rocks (Connan et al., 1980). Pr/Ph values are within the range of 0.5–1.1, mainly 0.7–0.9, indicating that the source rocks were deposited in a weakly deoxidizing environment (Li Hongbo et al., 2008). The three ratios are clustered into one group, showing similarity in organic faces (Fig. 3). However, the ratios of Ph/nC_{18} and Pr/nC_{17} show a positive correlative relationship with biodegradation. Obviously, the oils in areas 4, 6, 8 and 10 have suffered more serious biodegradation than those in area 11 (Fig. 4).

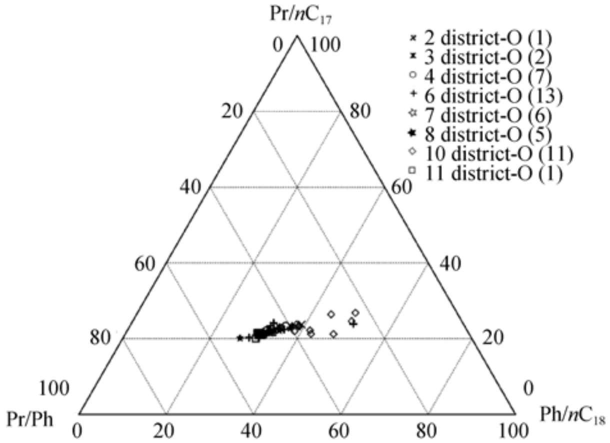

Fig. 3. Ternary plot showing the ratios of Pr/Ph, Pr/nC_{17} and Ph/nC_{18} in oil samples.

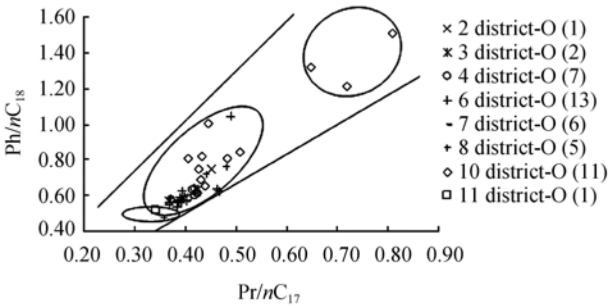

Fig. 4. Plot of Pr/nC_{17} and Ph/nC_{18} ratios for oils from the Ordovician reservoirs in the northwest of the Tahe oilfield.

4.4 Characteristics of sterane and terpane biomarkers

The terpane and sterane distribution patterns of the oils are similar (Fig. 5). Tricyclic terpanes are wildly variable in composition. It is generally believed that they have originated from algae or micro-organisms (Peters, 2000). As viewed from the distribution of the tricyclic terpanes in the Tahe oilfield there should be an entire series of homologous tricyclic terpanes in the C_{19}-C_{29}.

C_{23}-tiicyclic terpane is the main peak in tricyclic terpanes, with C_{24} or C_{21} being the second most dominant peak (Fig. 5a), which is different from those in continental oils marked by the highest peak at C_{19}. In addition to tricyclic terpanes, pentacyclic triterpanes are shown in the m/z 191 mass chromatograms of crude oils, Ts<Tm, and gammacerane, hopone and diahopane series are developed (Fig. 5a).

The presence of 25-norhopane in crude oils is commonly recognized as an indicator of severe biodegradation (Peters and Moldowan, 1993; Barry Bennett et al., 2006). As shown in Fig. 5b, 25-norhopane is detected on m/z 177 mass chromatograms in all the samples, including C_{26}, C_{28}-C_{34} 17α(H)21β(H) 25-norhopane and 17β(H), 21α(H) norhopane, mainly containing C_{29}25-norhopane (Fig. 5b). According to the relations between 25-norhopane/C_{30} hopane and 25-norhopane/ tricyclic terpanes, we can know the degree of biodegradation of the oil samples (Wang Chuangang et al., 2006). The result also shows that the oils from areas 4, 6, 7, 8 and10 have suffered server biodegradation.

Sterane series are the most important biomarkers of crude oils, which represent mainly the contribution of algal organic matter. Generally, C_{27} sterane is considered to have been derived from aquatic organisms and algae, whereas C_{29} sterane is believed to have been derived from terrestrial plant materials (Yin Wei et al., 2003;

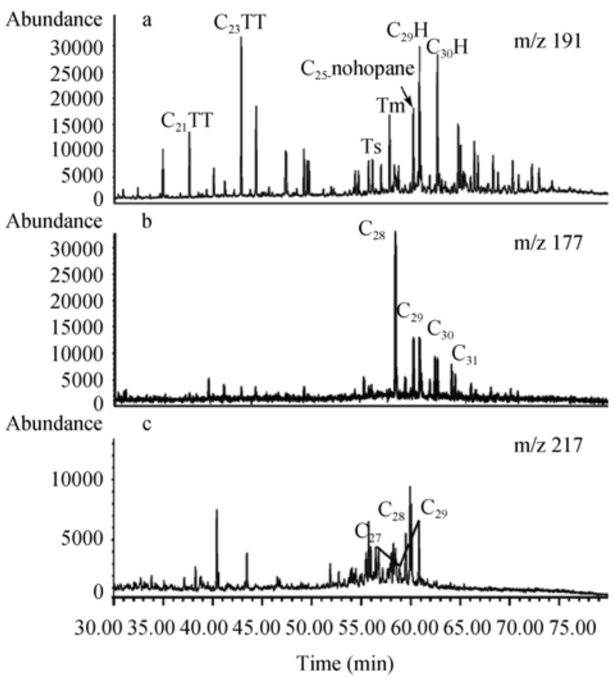

Fig. 5. Typical partial mass chromatograms of terpanes (m/z191), 25-nohopne (m/z177) and steranes (m/z 217) in the saturated hydrocarbon fractions of extracts from Ordovician crude oils in the northwest of the Tahe oilfield.

Li Zhiming et al., 2007). C_{29} regular sterane is predominant, C_{27} sterane ranks the second, and C_{28} sterane is relatively low, showing C_{29}>C_{27}>C_{28} in the distribution pattern (Fig. 5c). All the samples of different period show similar characteristics, mainly reflecting the input of aquatic organisms. The same results are also acquired by Nan Qinyun (2006), who discussed the homologue steranes from C_{27} to C_{29} and the characteristics of rearranged steranes.

4.5 Genetic grouping of the crude oils

The OM source was determined from the distributions of the saturated hydrocarbons (Tang Youjun et al., 2007). High abundance of C_{24} tetracyclic terpane can be indicative of a carbonate and evaporate depositional environment. Peters and Moldowan (1993) interpreted the high contents of C_{31}, C_{34} or C_{35} homohopanes as an indicator of a strongly reductive environment. Sinninghe Damsté et al. (1995) proposed that the gammacerane was an indicator of water column stratification. At present, gammacerane is commonly considered to be of tetrahymanol origin which occurs in saline waters. Different biomarker ratios were calculated in accordance with GC-MS, Pr/Ph values varying between 0.5 and 1.1, representing marine/reoxidizing depositional conditions. Similarly, the dibenzothiophene/phenan threne (DBT/P) ratio is <1, supporting a marine shale lithology. Very high hopane /sterane ratios (2.37–3.81) indicate a relatively high input of bacterial OM into the source rocks. Lower G/hopane (0.11–0.22) ratios suggest that the water is low in salinity. Regular steranes and C_{27}, C_{28} and C_{29} aββ isomers show similar distribution patterns in all the oils. Hopane, tricyclic terpane and sterane ratios, such as C_{21}/C_{23} (0.36–0.44), C_{29}/C_{30}-hopane (0.14–0.28), C_{29}Ts/(C_{29}-hopane+C_{29}Ts) (0.12–0.26), C_{24} tetracyclic terpane/C_{26} tricyclic terpanes (0.59–0.9), pregnane+ “ascending”-type homosterane/sterane (0.09–0.17) are also consistent with a source from marine shale. Study of the carbon isotopic composition of 20 crude oil samples from the northwest of the Tahe oilfield shows that the whole oils are isotopically light, with $\delta^{13}C_{PDB}$(‰) values ranging from −32.36‰ to −33.66‰, suggesting that source rocks for the Ordovician oils are basically similar in type from the marine rocks (Wang Darui, 2000). Hydrogen isotopic compositions of the twenty- seven oil samples from the Tahe oilfield range from −88.03‰ to −112.66‰, indicating the input of algae (Wang Darui, 2000; Wang Chuanggang, 2005). To sum up, the biomarker distributions of all the oils share similar organic geochemical characteristics. This is consistent with the results acquired by Zhan Shuichang et al. (2000) and Ma Anla et al. (2004).

4.6 Thermal maturity

A number of commonly accepted thermal maturity parameters have been used to determine the relative maturities of oils (Serferm and Moldowan, 1978). PI1, PI2, Ts/(Ts+Tm), 5α(H)-C_{29} steranes 20S/(20S+20R, C_{29}ββ/(ββ+αα) sterane ratios are within the range of 23.9–39.56%, 1.07–2.63, 0.12–0.28, 0.4–0.5, 0.54–0.58, respectively, belonging to mature to highly mature oils. MPI1 and MPI2 vary between 0.56–0.8 and 0.66–0.97, respectively. According to the calibration between MPI and vitrinite reflectance, the maturity of these oils is equivalent to R_o 0.74%–0.88%. The methyl double diamantane indicator (IMD)) varies between 0.29 and 0.51, equivalent to R_o 0.98%–1.59% (Duan Yi et al., 2007). Therefore, it can be concluded that oils in the northwest of the Tahe oilfield have similar thermal maturity, generally belonging to the mature to highly mature oils, with the lower limit of R_o to be 0.8%, and the upper limit to be 1.59 %.

5 Conclusions

(1) Detailed studies of oil physical properties, gross chemical composition, gas chromatograms of saturated hydrocarbons, high contents of 25-norhopanes revealed that oils from the Tahe oilfield have experienced early and late oil recharging periods and suffered serious biodegradation.

(2) On the basis of several organic geochemical characteristics including biomarker parameters, such as Pr/Ph, DBT/P, G/H, C_{21}/C_{23}, C_{29}/C_{30} hopane, C_{29}Ts/(C_{29}-hopane+C_{29}Ts), C_{24} tetracyclic terpane/C_{26} tricyclic terpanes, and stable carbon-hydrogen isotope data, it is shown that the oils have the same groups and were formed under marine/reduction depositional conditions.

(3) In terms of five maturity parameters, such as light hydrocarbons (P1 and P2), sterane maturity parameter, Ts/(Ts+Tm), methyl phenanthrene ratios and double adamantine index, the comprehensive evaluation of crude oils shows that oils from the Ordovician reservoir in the northwest of the Tahe oilfield are similar in thermal maturity, generally belonging to the mature to highly mature oils.

Acknowledgements This study was financially supported by Science Innovative Foundation of CNPC (Grant No.2008D-5006-01-10).

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