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Origins of Palaeozoic oils in the Tarim Basin: Evidence from sulfur isotopes and biomarkers

Chunfang Cai [a,*], Chunming Zhang [b], Liulu Cai [a], Guanhui Wu [c,1], Lei Jiang [a], Zhiming Xu [d], Kaikai Li [a], Anlai Ma [e], Lixin Chen [c]

[a] Key Lab of Petroleum Resources Research, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, PR China
[b] Department of Geochemistry, Yangtze University, Jingzhou, Hubei 434023, PR China
[c] Tarim Oilfield Company, PetroChina, Kuerle, Xinjiang 841000, PR China
[d] Southwest Petroleum University, Chengdu 610500, PR China
[e] Institute of Petroleum Exploration and Development, CENOPEC, Beijing 100083, PR China

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ABSTRACT

Crude oil, H_2S and pyrite samples from Palaeozoic formations in the Tarim Basin have been analyzed for $\delta^{34}S$ values together with oil samples for biomarkers, and fluid inclusions for chemical composition, to elucidate the origin of sulfur in the oil and to address potential applications in oil–source rock correlation. The results show that crude oil samples have sulfur contents from 0.02 to 2.47% and $\delta^{34}S$ values from +11.9 to +28.2‰. Non-degraded oils without associated H_2S gas have $\delta^{34}S$ values from +11.9 to +20.5‰, and are relatively rich in C_{28} ααα 20R sterane, aryl isoprenoids and/or gammacerane. The features are well-correlated with the Cambrian and Lower Ordovician source rocks with $\delta^{34}S$ values from +10.4 to +19.4‰. Non-degraded oils with associated H_2S gas have $\delta^{34}S$ values from +15.1 to +19.1‰, close to the H_2S (from +15.0 to +18.5‰), suggesting that the H_2S was incorporated into the oils, leading to the generation of 2-thiaadamantanes and likely alkyl-thiolanes in the oil with a $\delta^{34}S$ value of +18.5‰. Heavily biodegraded oils have the highest sulfur contents, and show $\delta^{34}S$ values from +20.0 to +28.2‰, significantly heavier than those of any of the potential source rocks (−15.3 to +19.4‰). Thus, it is likely that isotopically heavy sulfides have been incorporated into the biodegraded oils, resulting in $\delta^{34}S$ values of the oils becoming closer to Cambrian and Ordovician age seawater sulfates. The sulfides may have originated from thermochemical sulfate reduction (TSR), as evidenced by the occurrence of H_2S-rich fluid inclusions and late-stage and fracture-filling pyrite with $\delta^{34}S$ values mainly from +25 to +34‰ in the Palaeozoic reservoirs.

1. Introduction

Sulfur isotopic composition is widely used to distinguish between thermochemical sulfate reduction (TSR) and bacterial sulfate reduction (BSR) in nature. In the vast majority of petroleum-related sour gas settings, there is no significant sulfur isotopic fractionation between parent sulfate and reduced products (Krouse, 1977; Orr, 1977; Worden and Smalley, 1996; Cai et al., 2003; 2004b) despite the fact that during experimental simulation of TSR there is a 10–20‰ kinetic isotope fractionation (Harrison and Thode, 1957; Kiyosu and Krouse, 1990). This arises due to complete reduction of each batch of gypsum or anhydrite that dissolves and thus no preservation of kinetic isotopic effects (Machel et al., 1995; Worden et al., 2000).

Petroleum and bituminous tar resulting from back-reactions with TSR-derived H_2S have been proposed to have $\delta^{34}S$ values close to parent sulfates (Orr, 1974; Powell and MacQueen, 1984; Cai et al., 2001; 2003). Thus, in areas where TSR is active, petroleum sulfur may have two sources: one from the primary source rock, and the other from H_2S generated by TSR. It is possible to differentiate unaltered petroleum from TSR-altered petroleum based on the large difference in sulfur isotopic composition of the sources.

Unaltered oils have been shown to have secular change of $\delta^{34}S$ values relative to their source rock age seawater sulfates (e.g. Orr, 1974; Engel and Zumberge, 2007), and are enriched in ^{34}S up to 2‰ relative to their parent kerogen in the source rock (Orr, 1986; Claypool et al., 1980). It has been proposed that sulfur isotopes can be used as a tool for oil–source and oil–oil correlations (Krouse, 1977; Gaffney et al., 1980; Thode, 1981; Hirner et al., 1984; Orr, 1986; Premuzic et al., 1986; Robinson et al., 1991; Cai et al., 2007b). This proposal has been supported by closed-system dry and hydrous pyrolysis of immature kerogen (Idiz et al., 1990; Amrani et al., 2005).

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[*] Corresponding author. Fax: +86 10 62010846.
E-mail addresses: cai_cf@mail.iggcas.ac.cn, cai_cf@yahoo.com (C. Cai).
[1] Present address: Institute of Petroleum Exploration and Development, CNPC, Beijing 100083, PR China.

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In the Tarim Basin, it has been proposed that oils were derived from the Middle to Upper Ordovician source rocks (Hanson et al., 2000; Zhang et al., 2000). However, a limited distribution for the source rocks with TOC (total organic carbon) >0.5% and type II_2 and III-like kerogen (not oil prone) for higher TOC source rocks, do not match with huge petroleum resources found (Cai et al., 2009 and references therein). More recently, oil and fluid inclusion samples have been shown to have biomarker distributions characteristic of the Cambrian and Lower Ordovician ($\in$–O_1) source rocks (Sun et al., 2003; Xiao et al., 2005; Li et al., 2008; Pan and Liu, 2009).

Previous studies have shown that petroleum charge took place in three periods (Zhang et al., 2004; Xiao et al., 2005; Wang et al., 2007). The earliest charge occurred during the late Caledonian Orogeny, i.e., in the late Ordovician in the Tadong area (Wang et al., 2006), and from the late Silurian to the Devonian in the Central Tarim and Tabei areas (Wang et al., 2007; 2008). A great number of bitumen and heavy oils (including TD2 oil) in the Cambrian, Middle-Lower Ordovician and Silurian reservoirs are residual of the charge during this period (Lű et al., 2007; Wang et al., 2007). The second charge took place during the late Hercynian Orogeny at the end of the Permian (Xiao et al., 2005; Lű et al., 2007; Wang et al., 2007). Oils charged in this period may have been newly generated from the upper part of the $\in$–O_1 source rocks, or re-migrated from previously charged oil pools, which may have further emplaced into the Ordovician and Silurian reservoirs. As a result of subsequent uplift and exposure, part of the oils in the Silurian, Middle Ordovician and Cambrian reservoirs close to the Upper Devonian/Silurian and Carboniferous/Middle-Lower Ordovician unconformities were biodegraded (Xiao et al., 2005; Wang et al., 2007; Lű et al., 2007; Wang et al., 2008). The third charge took place likely during the late Yanshan to Himalayan Orogeny from the end of the Cretaceous to the Neogene (Zhang et al., 2000; Lű et al., 2007; Wang et al., 2008). Oils charged during this period may have been derived from the Upper Ordovician source rocks and/or previous oil pools, and were not biodegraded.

In our previous papers (Cai and Li, 2008; Cai et al., 2009), we showed significant differences in biomarkers and $\delta^{34}S$ values of kerogen after pyrite removal from the $\in$–O_1 and O_3 source rocks in the Tarim Basin. In this paper, we present $\delta^{34}S$ values of different sulfur species, including crude oil, H_2S gas and fracture-filling pyrite in the Tarim Basin. The objectives are to address the origin of sulfur in oils, to deduce unaltered oil $\delta^{34}S$ values, and to apply sulfur isotopes to oil–source rock correlation cross checked against new data on biomarkers of oils and chemical composition of fluid inclusions.

2. Experimental

2.1. Samples

Twenty oil samples were analyzed for sulfur isotopes. Thirteen of the 20 oil samples were analyzed for biomarkers. Seventeen crude oils were obtained from the Silurian, and Ordovician and Cambrian reservoirs in the Central Tarim, one Cambrian age oil from well TD2 in the Tadong area and two Ordovician age oils from the Tabei area (Figs. 1 and 2). The samples represent a wide range of petroleum types, including biodegraded oils, paraffinic–aromatic oils, and condensates. These oils have gravities from 0.8040 to 1.0217 g/cm^3, and sulfur contents from 0.02 to 2.47%.

Six H_2S samples in gas caps of oil pools and nine fracture-filling pyrite samples were collected from the Ordovician in the Central Tarim and Tabei areas, and analyzed for their sulfur isotope composition.

Sixteen limestone reservoir samples were collected from various formations of the Ordovician reservoirs in the Central Tarim and Tabei areas. Gaseous phase of multiphase aqueous inclusions in calcite cement and fracture-filling calcite from the 16 samples was measured for chemical composition.

2.2. Analytical methods

2.2.1. Sulfur isotopes measurement

Samples of oil (1 to 4 g) were combusted in a Parr bomb apparatus at ~25 atm oxygen to oxidize organically bound sulfur to sulfate. Dissolved sulfate was then precipitated as $BaSO_4$. $BaSO_4$ was directly decomposed to SO_2 by heating at 1700 °C in a quartz tube for isotopic analysis using the method of Bailey and Smith (1972). Isotopic determinations were carried out on a Thermo Finnigan Delta S mass spectrometer, calibrated by a series of IAEA standards. Results are presented as $\delta^{34}S$ relative to the Vienna Canyon Diablo Troilite (VCDT) standard. The reproducibility for $\delta^{34}S$ measurement is $\pm 0.3‰$.

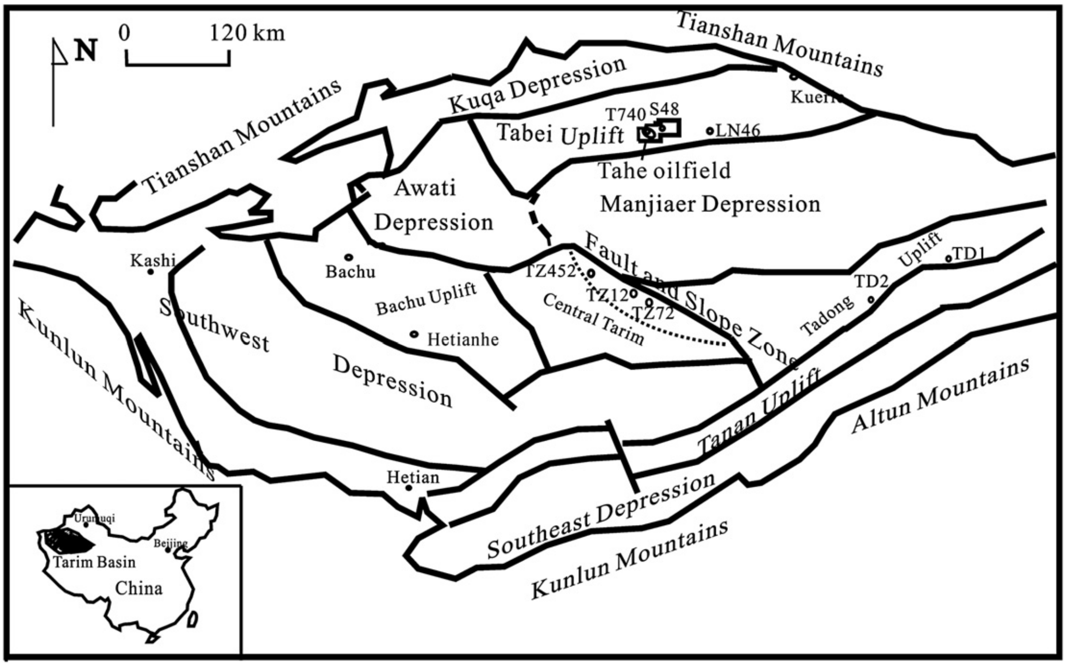

Fig. 1. Map of the Tarim Basin showing tectonic units and locations of sampling wells.

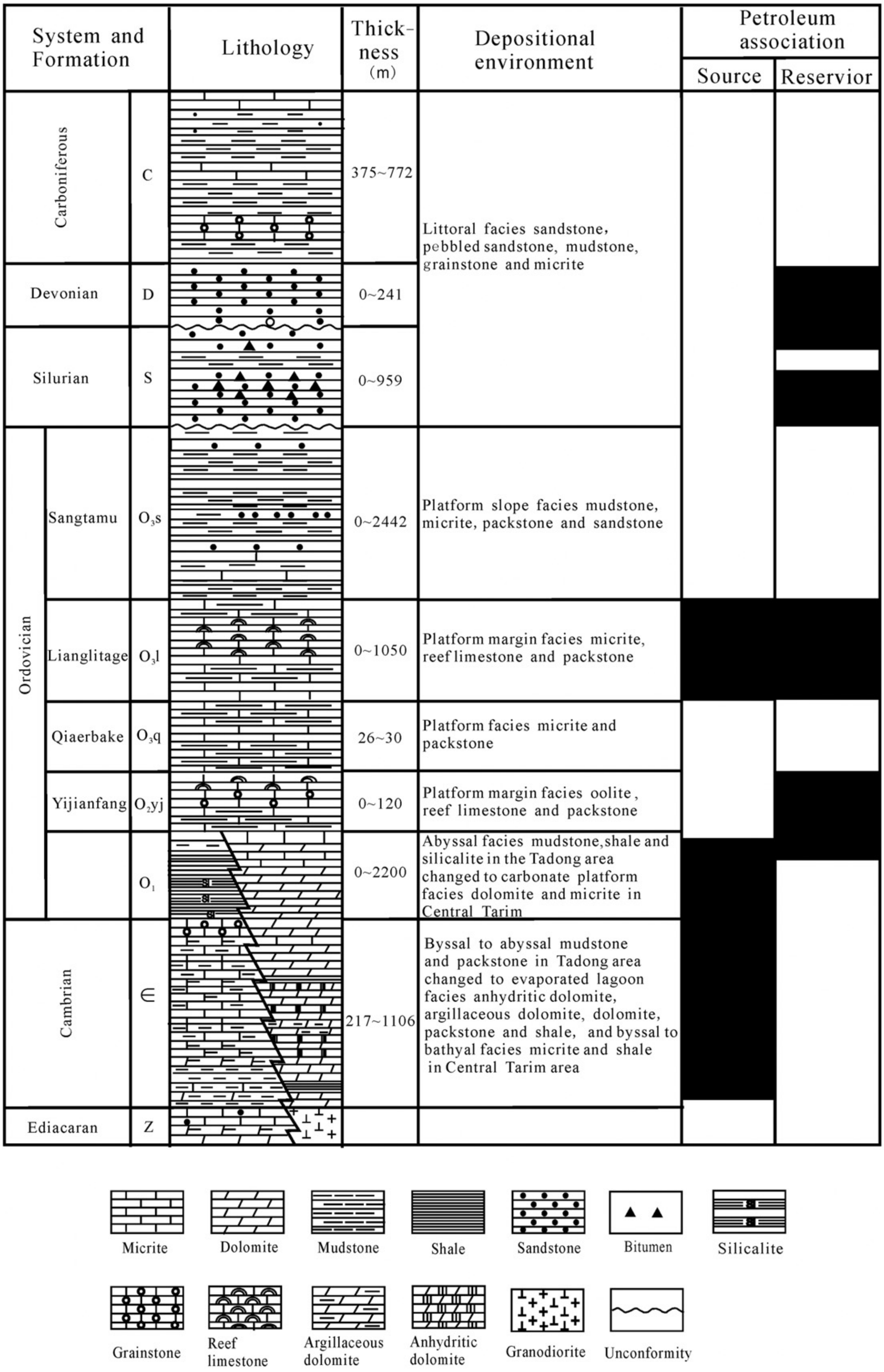

Fig. 2. Generalised stratigraphic column for the Tarim Basin showing complex petroleum systems. Basin-scale anhydrite beds occur in the Middle Cambrian while Lower Ordovician and Cambrian strata contain anhydrite in local areas.

2.2.2. Biological markers

After removal of the asphaltenes, oils were separated into saturates, aromatics and resins (NSO) by column chromatography using n-pentane, dichloromethane (DCM) and methanol as chromatographic solvents. The saturated and aromatic fractions were analyzed in both multiple ion detection (MID) and full scan modes using a Hewlett Packard 6890GC/5973MSD — mass spectrometer. The gas chromatograph (GC) was fitted with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm). The injection temperature was 300 °C and the oven was initially held at 50 °C for 1 min. The temperature was then increased from 50 °C to 310 °C at a rate of 3 °C/min, and then held at 310 °C for 18 min. Helium was used as a carrier gas (1.0 mL/min). Operating conditions were: ion source, 230 °C; emission current, 34.6 μA; quadrupole temperature, 150 °C and electron energy, 70 eV.

The aromatic hydrocarbons were tentatively identified in the first instance from the MID chromatograms using the ions characteristic of the particular class of compounds under investigation. Then, complete spectra of as many compounds as possible from the full scan mode were determined to confirm the preliminary identification made in the MID chromatograms.

Identification of *Chlorobiaceae* biomarkers and organic sulfur compounds was achieved through analysis of mass spectra, retention time, and comparison with literature data (Summons and Powell, 1987; Koopmans et al., 1996; Sinninghe Damsté et al., 1986; 1988; 1989a).

2.3. Chemistry of fluid inclusions

Sixteen doubly polished rock wafers from the 16 limestone samples, each approximately 200 μm thick, were observed for fluid inclusions. Fluid inclusions for Raman analysis generally have diameters from 15 to 40 μm and gas/liquid ratios of 5% to 10%. Raman microspectroscopic analysis was carried out using a J-Y company RAMNOR U1000 laser Raman probe. The exciting source was an argon laser with a wavelength of 514 nm and an output of 600 mW laser power at the source. Integration time was 10 s with ten accumulations for each spectral line. To diminish fluorescence, the location of intended analysis on calcite surface was heated with the laser beam for about 5 min. Molar proportions of the gaseous phase of multiphase aqueous inclusions were calculated using the relative Raman scattering cross-sections of 2.5 for CO_2, 7.5 for CH_4, 1.0 for N_2, 6.4 for H_2S, 3.46 for H_2O, 5.38 for SO_2 and 13.1 for C_2H_6 as suggested by Burke (2001), Pasteris et al. (1988) and Stephenson (1974).

3. Results

3.1. Oil biomarkers

3.1.1. Distributions of non-sulfur-containing compounds

GC and GC–MS data ($m/z = 85$) for thirteen oil samples (Table 1) show that Pr/Ph ratios are around 1.0 (from 0.57 to 1.13), and Pr/nC_{17} and Ph/nC_{18} ratios range from 0.16 to 0.48 and 0.19 to 0.89, respectively, with Ph/nC_{18} ratios greater than Pr/nC_{17}. T740-O_{1+2}, S48-O_{1+2}, TZ11-S and TZ30-S oils contain abundant alkanes with prominent baseline humps of unresolved complex mixtures (UCM) (Fig. 3).

For all the oils analyzed, maturity-related parameters, including CPI (Carbon Predominance Index), C_{29} ααα sterane 20S/(20S + 20R) and C_{32} homohopane 22S/(22S + 22R) ratios, show similar values. The CPI ranges from 1.00 to 1.18, C_{29} ααα sterane 20S/(20S + 20R) ratios range from 0.42 to 0.58, and C_{32} 22S/(22S + 22R) ratios from 0.56 to 0.61 (Table 1). These values are close to the respective equilibrium values. Ts/(Ts + Tm) ratios range from 0.26 to 0.68, and $C_{29}Ts/(C_{29}Ts + C_{29}H)$ ratios mainly from 0.13 to 0.31. The two parameters seem not controlled by maturity alone since they are significantly lower than the respective equilibrium values. Thus, these oils do not show significant differences in the distributions of the maturity-related biomarkers.

The oils analyzed show significant differences in biological precursor-related parameters. All the oils analyzed except TZ83-O_3, TZ83-O_1 and TZ62-S oils show that C_{29} ααα 20R sterane is the most abundant (Fig. 4g, h, i and j) with $C_{29}/(C_{27} + C_{28} + C_{29})$ ααα 20R sterane ratios from 37 to 56%. These oils contain a pseudo homologous series of aryl isoprenoids (Table 1, Fig. 5). The major components possess the

Table 1
Biomarker parameters of the oils from the Silurian to Cambrian reservoirs.

Sample no.	Depth (m)	Pr/ Ph	Pr/ nC_{17}	Ph/ nC_{18}	CPI	C_{27} ααα 20R%	C_{28} ααα 20R%	C_{29} ααα 20R%	Gm/ $C_{30}H$	$C_{24}Te/C_{26}TT$	$C_{23}TT/C_{30}H$	DinoSt	AIs	Ts/ (Ts + Tm)	$C_{29}H/C_{30}H$	C_{29} 20S/ (20S + 20R)	C_{32} 22S/ (22S + 22R)	$C_{29}Ts/(C_{29}Ts + C_{29}H)$	C_{29} DH/ $C_{30}H$	$C_{29}DH/C_{29}H$	DBT/ Phen	DBTs/ Phens
TD2-∈	4801	1.02	0.44	0.44	–	29	31	40	0.25	0.57	0.34	0.82	–	0.4	0.53	0.42	0.59	0.26	0.08	0.15	0.50	–
TZ83 -O_1	5666	0.93	0.16	0.19	1.00	tr	tr	tr	tr	tr	tr	–	tr	tr	0.64	tr	tr	tr	0.09	0.14	6.56	1.68
T740-O_{1+2}	6275	0.57	0.48	0.89	-	33.7	14.1	52.2	0.13	0.62	0.95	–	++	0.26	1.01	0.52	0.60	0.18	0.48	0.45	–	–
S48-O_{1+2}	5355	0.62	–	–	–	28	21	52	0.14	0.68	0.71	–	++	0.27	0.99	0.50	0.60	0.17	0.21	0.22	–	–
TZ83-O_3	5433	0.82	0.23	0.32	1.04	52.7	12.7	34.6	0.09	1.86	0.66	tr	×	0.68	0.58	0.46	0.57	0.50	tr	tr	0.70	0.17
TZ12-O_3	4652	1.0*	0.23	0.26	1.05	31.0	24.5	44.4	0.10	0.91	0.66	0.25	++	0.41	0.63	0.52	0.61	0.24	0.05	0.08	0.60	0.77
TZ10-S	4616	1.1*	0.26	0.27	1.03	26.6	23.2	50.2	0.16	0.94	0.58	tr	++	0.40	0.58	0.49	0.59	0.24	0.06	0.11	–	–
TZ168-O_3	4460	1.1*	0.18	0.19	1.07	21.2	21.5	57.3	0.15	0.83	1.60	tr	–	0.45	0.91	0.53	0.59	0.21	0.11	0.12	–	–
TZ30-O_3	4997	1.1*	0.22	0.24	1.02	22.7	28.0	49.3	0.26	0.51	0.03	tr	–	0.28	0.41	0.46	0.59	0.13	0.04	0.09	0.19	0.88
TZ30-S	4244	1.1*	0.2	0.21	1.03	31.9	23.1	45.1	0.17	0.54	2.28	tr	++	0.43	0.91	0.58	0.58	0.31	0.33	0.36	0.64	0.59
TZ11-S	4417	0.9*	0.2	0.36	1.13	31.7	12.7	55.6	0.57	0.74	1.57	0.10	++	0.57	1.02	0.58	0.56	0.15	0.47	0.46	0.51	0.84
TZ62-S	4052	0.98	0.37	0.39	1.18	29.2	33.7	37.1	0.21	0.64	0.92	–	×	0.35	0.64	0.48	–	0.26	0.11	0.17	0.12	0.34
TZ12-S	4394	0.93	0.27	0.37	1.05	31.1	20.0	48.9	0.06	0.78	0.29	0.15	++	0.39	0.58	0.55	0.59	–	0.05	0.09	0.26	0.32

Gm: Gammacerane, $C_{30}H$: C_{30} hopane; AI: Aryl isoprenoids; $C_{29}DH$: C_{29} 25-norhapane; $C_{29}H$: C_{29} hopane; TT: tricyclic terpane, Te: tetracyclic terpane; DinoSt: 4, 23, 24-trimethyl triaromatic dinosteroids/ (4, 23, 24-trimethyl triaromatic dinosteroids + 3-methyl-24-ethyl-triaromatic steroid).
++: very abundant, +: abundant, ×: absent or very low, –: no measurement; *: from GC data, others from $m/z = 85$.
DBT/Phen from 184/178; DBTs/Phens from (184 + 198 + 212 + 226)/(178 + 192 + 206 + 220).

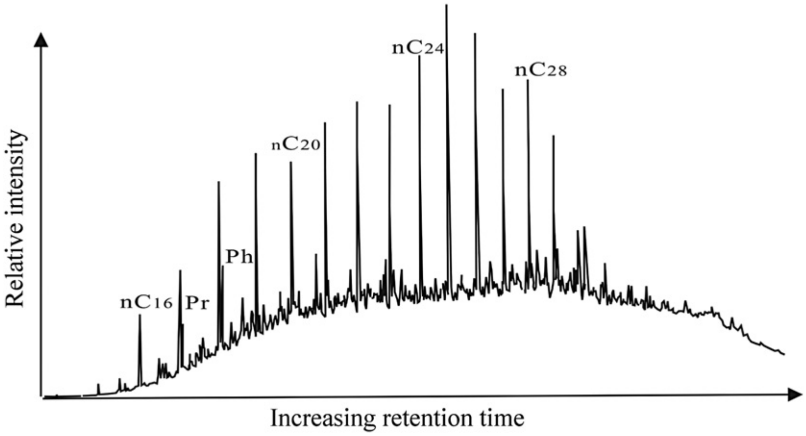

Fig. 3. GC data showing abundant *n*-alkanes and baseline bump (unresolved complex mixtures, UCM) in saturates of an oil from the Middle Ordovician (6275 m) in well T740.

2,3,6-trimethyl substituted pattern with a predominance of C_{13}–C_{23} homologues.

TD2-∈, TZ168-O_3, TZ30-O_3 and TZ62-S oils show C_{28}/C_{27} ααα 20R ratios higher than 1.0, gammacerance/C_{30} 17α, 21β hopane ratios greater than 0.15 and C_{24} tetracyclic terpane/C_{26} tricyclic terpanes ratios ≤ 0.8 (Table 1). The features are similar to the Cambrian and Lower Ordovician source rocks (Cai et al., 2009).

In contrast, TZ83-O_3 oil has significantly lower C_{28}/C_{27} ααα 20R ratio (0.24) and gammacerance/C_{30} 17α, 21β hopane ratio (0.09), higher C_{24} tetracyclic terpane/C_{26} tricyclic terpanes ratio (1.86) and lower triaromatic dinosteroids/(triaromatic dinosteroids + triaromatic steroid) ratio (DinoSt, <0.05) with no significant amounts of aryl isoprenoids (Table 1). These features are similar to TZ62-2-O_3 and TZ62-3-O_3 oils (Wang et al., 2007) and the Upper Ordovician source rocks (Cai et al., 2009 and references therein).

The oils (T740-O_{1+2}, S48-O_{1+2}, TZ11-S and TZ30-S oils) contain C_{28} to C_{34} 17α, 21β 25-norhopanes (Fig. 4d, e) with C_{29}DH/C_{30}H (C_{29} 17α, 21β 25-norhopane/C_{30} 17α, 21β hopane) ratios ranging from 0.21 to 0.46, and C_{29}DH/C_{29}H (C_{29}H = C_{29} 17α, 21β 30-norhopane) from 0.22 to 0.35. Thus, these oils are collectively classified as group I.

The other oils analyzed (group II) show no occurrence of UCM and contain small amounts of C_{28} and C_{29} 25-norhopanes with C_{29}DH/C_{30}H ratio < 0.11, C_{29}DH/C_{29}H < 0.15 and no significant amounts of C_{30} to C_{34} DH (Table 1, Fig. 4f). This group includes oils from TD2-∈, TZ12-S, TZ10-S, TZ62-S and TZ452-O_{1+2}, and all the other analyzed oils produced from the Upper Ordovician (Tables 1 and 2, Wang et al., 2007; Li et al., 2008).

3.1.2. Distributions of organic sulfur compounds

All the oils analyzed show that organic sulfur compounds (OSC) are dominated by DBTs, including dibenzothiophene (DBT), methyl-dibenzothiophenes (MDBT), dimethyl-dibenzothiophenes (DMDBT) and trimethyl-dibenzothiophenes (TMDBT) with small amounts of ethyl-dibenzothiophene (Fig. 6a, b). No thiophenes and benzothiophenes were detected in the oils. Among all the oils analyzed, the TZ83-O_1 oil contains the highest OSC content in aromatic fraction (41% of the total aromatic fraction), and has a DBT/phenanthrene ratio of 6.6 and a total DBTs/total phenanthrenes ratio of 1.7. The ratios are significantly higher than those of the other oils analyzed in this study (all < 0.9) (Table 1), the oils previously reported (DBT/phenanthrene ratios < 2.0) (Zhang and Huang, 2005), and the potential source rocks analyzed (Cai et al., 2009, not shown). Benzo[b]naphthothiophenes (BNTs: BNT + MBNT + DMBNT + TMBNT) were also detected with the highest content in the TZ83-O_1 oil. Interestingly, significant amounts of benzothienobenzothiophenes (BTBTs: BTBT + MBTBT + DMBTBT + TMBTBT), benzobisbenzothiophenes (BBBTs) and alkyl-thiolanes ($C_{10}H_{20}S$ to $C_{31}H_{62}S$) were detected not from the other oils and the source rocks analyzed, but only from the TZ83-O_1 oil (Fig. 7), from which 2-thiaadamantanes were previously detected by Jiang et al. (2008).

3.2. Crude oil sulfur contents and $\delta^{34}S$ values

Group I oils (T740-O_{1+2}, S48-O_{1+2}, TZ11-S and TZ30-S oils) have sulfur contents from 0.66 to 2.47%, densities from 0.9514 to 1.013 g/cm^3 and $\delta^{34}S$ values from +20.0 to +28.2‰ (n = 5, Table 2, Fig. 8). The oils were produced from the reservoirs which are directly covered by the Carboniferous or the Upper Devonian and close to the unconformities.

Group II oils have sulfur contents from 0.02 to 0.63%, densities from 0.804 to 1.022 g/cm^3 and $\delta^{34}S$ values from +11.9 to +20.5‰ (n = 17). The oils can be further divided into oils in association with H_2S (group II_1) and without H_2S (group II_2). Group II_1 oils, including TZ621-O_3, TZ62-O_3, TZ62-2-O_3, TZ62-3-O_3, TZ70C-O_3, TZ83-O_3 and TZ83-O_1 oils, have $\delta^{34}S$ values from +15.1 to +19.9‰ (n = 8). The associated H_2S has contents from 0.08% to 2.6% by volume in gas composition, and $\delta^{34}S$ values (from +15.0 to +18.5‰) close to those of the oils (Table 2).

Group II_2 oils (without H_2S) include TZ10-S, TZ62-S, TZ16-O_3, TZ452-O_{1+2}, TZ30-O_3, TZ12-O_3, TZ24-O_3, TZ168-O_3 and TD2-∈ oils. The oils have $\delta^{34}S$ values from +11.9 to +20.5‰ (n = 9). The values are close to those of the ∈–O_1 source rocks (from +10.4 to +19.4‰, n = 6), and are significantly different from those of the Upper Ordovician source rocks (from −15.3 to +6.8‰, n = 4) (Cai et al., 2009).

3.3. Occurrence of pyrite and H_2S and their $\delta^{34}S$ values

In Silurian sandstone reservoirs in Central Tarim, up to 600 ppm H_2S was detected in oilfield waters in well TZ12. Late-stage authigenic pyrite in wells TZ11 and TZ12 occupies up to 3% rock volume and shows $\delta^{34}S$ values mainly from +20.4 to +33.6‰ (Cai et al., 2001).

In the Ordovician, gases associated with oil pools have been measured to have up to 2.6% H_2S by volume in Central Tarim. The H_2S has $\delta^{34}S$ values from +15.1 to +18.5‰ (n = 5, Table 2). Abundant pyrite was found to occur in the Ordovician reservoirs or as fracture-fillings (Cai et al., 2008). Two fracture-filling pyrite samples were measured to have $\delta^{34}S$ values of +24.6‰ and +29.7‰ (Table 3).

In Tahe oilfield of Tabei area (Fig. 1), T740 Ordovician oil pool has H_2S concentrations up to 8.3% after acidification of the reservoir and a $\delta^{34}S_{H2S}$ value of +21.0‰ in this study. Similar values were reported in oil pools in the area around wells T751, T738 and T740 with H_2S up to 7.4% by volume and $\delta^{34}S_{H2S}$ values from +18 to +22‰ (Zhang et al., 2007). Seven fracture-filling pyrite samples were measured to have $\delta^{34}S$ values from +21.6‰ to +28.8‰ with an average of +25.2‰ (n = 7, Table 3).

Fluid inclusions were measured to have CO_2, N_2, alkane gas and H_2S components in calcite cements and fracture-fillings in the Ordovician

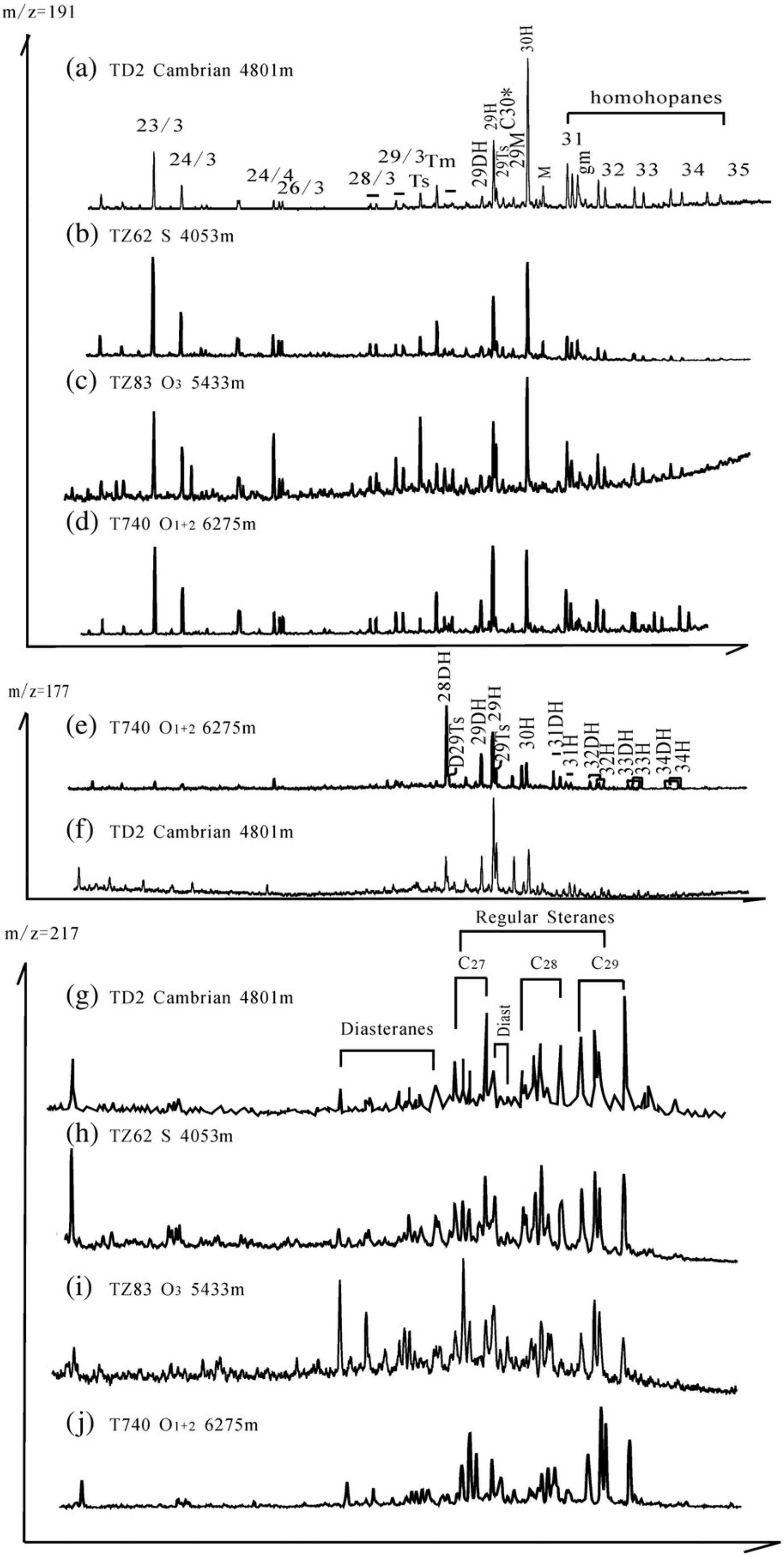

Fig. 4. Partial GC–MS fragmentograms (*m/z* = 191, 217 and 177) for oils from, (a, f, g) the Cambrian from well TD2; (b, h) the Silurian from TZ62; (c, i) the Upper Ordovician from TZ83; and (d, e, j) the Lower and Middle Ordovician from T740. Compounds identifications: H: 17α, 21β hopanes; M: C_{30} 17β, 21α moretane; DH: 25-norhopanes; C_{30}^{*}: C_{30} 17α, 21β diahopane; 29Ts: C_{29} 18α, 21β 30-norhopane; gm: gammacerane; 28/3: C_{28} tricyclic terpane; 29/3: C_{29} tricyclic terpane; etc; 24/4: C_{24} tetracyclic terpanes; Ts: 18α, 21β-22, 29, 30-trisnorhopane; Tm: 17α, 21β-22, 29, 30-trisnorhopane.

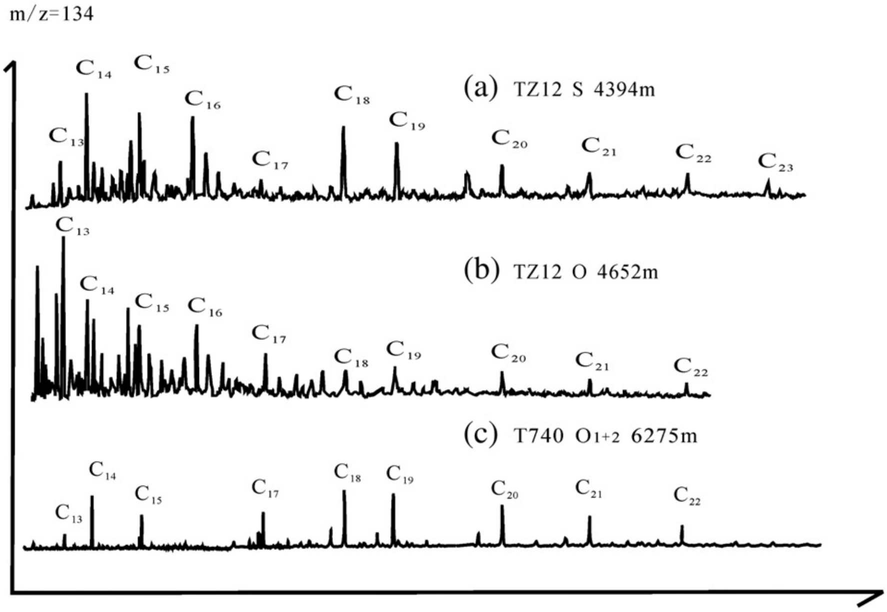

Fig. 5. GC–MS selected ion mass chromatograms (*m/z* 134) for oils from, a) the Silurian in well TZ12, b) the Upper Ordovician from TZ12, and c) the Lower Ordovician from T740.

reservoirs in the basin (Table 4). The H_2S molar percentages in gas phase composition range from 1.8 to 14.4 mol% with an average of 5.4 mol% ($n = 19$). The values are similar to those from a previous report which showed up to 22 mol% H_2S with an average of 5.2 mol% ($n = 16$) in gas phase of fluid inclusions in the Tahe oilfield (Qian, 2002). The H_2S concentrations in the fluid inclusions are significantly higher than those in the associated gas.

4. Discussion

The oils analyzed from the Tarim Basin may have complex origins, involving the two groups of potential source rocks, and possible post-generation alteration processes including biodegradation and the incorporation of inorganic sulfides. The sulfides may be originated from TSR or BSR, but unlikely from the mantle, based on $^3He/^4He$ ratios (Cai et al., 2001, 2002).

4.1. Oil biodegradation

The presence of 25-norhopanes in crude oils is commonly recognized as an indicator of severe biodegradation. 25-Norhopanes are commonly generated by bacterial removal of the methyl group at C-10 from the regular hopanes (Volkman et al., 1983). High ratios of $C_{29}DH/C_{30}H$ and $C_{29}DH/C_{29}H$ and occurrence of complete suite of bomologs (C_{28} to C_{34} 25-norhopanes) and unresolved complex compounds (UCMs) in Group I oils suggest that the oils were typically

Table 2
Density, sulfur content, $\delta^{13}C$ and $\delta^{34}S$ values of oils and associated H_2S from the Palaeozoic strata.

Area	Well	Formation	Depth[a] (m)	Oil group[b]	Oils				H_2S	
					Density[c]	Sul %	$\delta^{13}C$	$\delta^{34}S$	vol.%	$\delta^{34}S$
Central Tarim	TZ11	S	4417	I	0.9654	1.34	−32.5	21.4	Nil	–[d]
	TZ30	S	4252	I	0.9514	0.66	−31.9	20.0	Nil	–
	TZ10	S	4616	II_2	0.9086	0.63	−30.2	20.5	Nil	–
	TZ62	S	4053	II_2	0.9265	0.22	–	17.2	Nil	–
	TZ16	O_3	4252	II_2	0.8794	0.43	–	14.7	Nil	–
	TZ30	O_3	4997	II_2	0.8326	0.10	−31.6	18.4	Nil	–
	TZ12	O_3	4652	II_2	0.8198	0.14	−32.2	19.9	Nil	–
	TZ621	O_3	4933	II_1	0.8483	0.27	–	19.1	0.15	15.0
	TZ62	O_3	4729	II_1	0.8216	0.20	–	15.9	0.20	15.8
	TZ62-3	O_3	5118	II_1	0.8147	0.19	–	15.1	0.10	15.5
	TZ62-2	O_3	4932	II_1	0.8095	0.1	–	16.7	0.23	17.1
	TZ70C	O_3	4802	II_1	0.8040	0.19	–	15.3	0.80	–
	TZ83	O_3	5433	II_1	0.8307	0.1	–	17.5	0.10	–
	TZ242	O_3	4521.6	II_1	0.8122	0.18	–	–	0.03	18.5
	TZ24	O_3	4458.5	II_2	0.8224	0.023	–	11.9	Nil	–
	TZ168	O_3	4460	II_2	0.8653	0.02	−32.7	13.6	Nil	–
	TZ452	O_{1+2}	6466	II_2	0.8486	0.16	–	15.3	Nil	
	TZ83	O_1	5666	II_1	0.8237	0.38	–	18.5	2.61	–
Tahe oilfield	S48	O_{1+2}	5360.5	I	1.0130	2.47	−32.9	28.2	–	–
	T740	O_{1+2}	6275	I	0.9768	2.27	–	26.6	8.3[e]	21.0
Tadong	TD2	Cam	4801	II_2	1.0217	0.51	–	19.6	Nil	–

[a] Depth is set as the middle point between perforations in meters.
[b] See text for explanation.
[c] Density in g/cm^3.
[d] – no data available.
[e] After acidification of the reservoir.

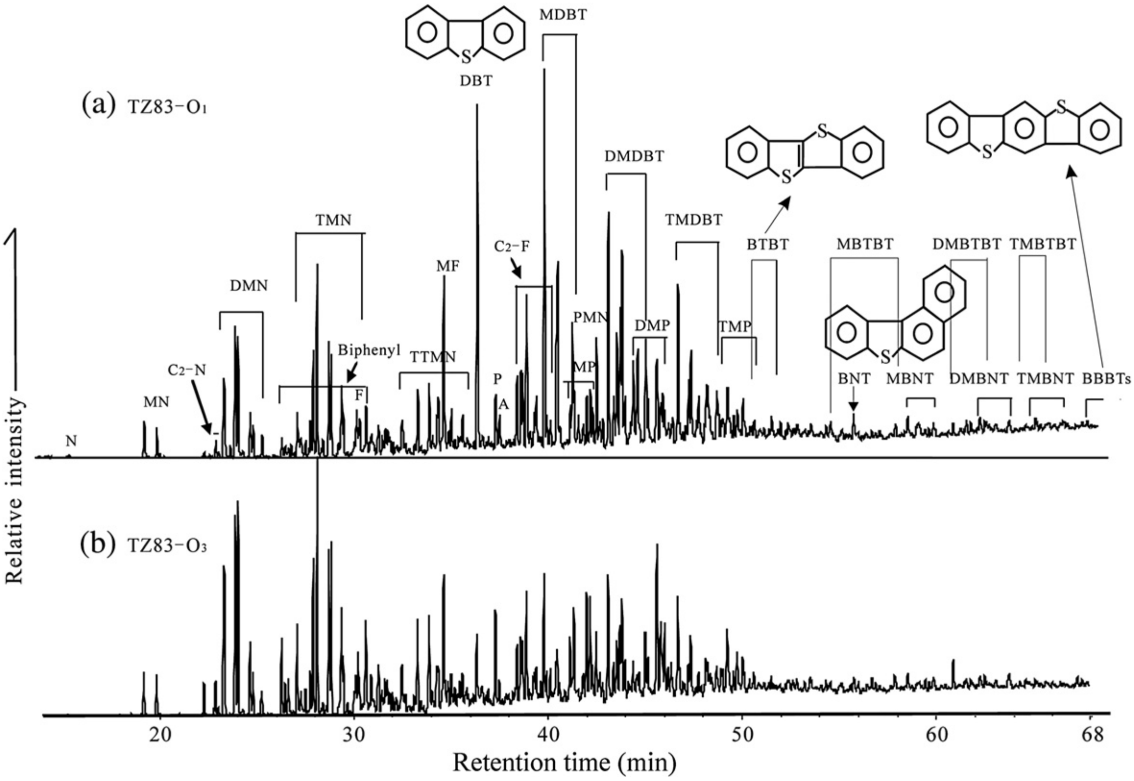

Fig. 6. Total ion chromatograms of aromatic fractions of oils showing significantly different distributions of organic sulfur compounds from, (a) TZ83-O_1 oil, and (b) TZ83-O_3 oil. Compounds identifications: N: naphthalene; F: fluorene; P: phenanthrene; A: anthrancene; DBT: dibenzothiophene; BTBT: benzothienobenzothiophene; BNT: benzonaphthothiophene; BBBTs: benzobisbenzothiophenes; PMN: 4,4,8,8,9-pentamethyldecanhydronaphthalene; M: methyl-; DM: dimethyl-; TM: trimethyl-; C_2: ethyl-.

biodegraded (Moldowan and McCaffrey, 1995; Bennett et al., 2006; Cai et al., 2007a).

Because the general sequence of biodegradation of biomarkers is *n*-alkanes followed by isoprenoids, steranes, hopanes/diasteranes and aromatic steroids, abundant *n*-alkanes in the studied oils may have been a result of a later input of fresh oil, after biodegradation. Thus, group I oils may represent a mixture of a later fresh oil and an earlier, heavily biodegraded oil (Wang et al., 2008).

That group I oils were biodegraded is supported by their occurrence. The oils were produced from reservoirs close to the Carboniferous/Middle and Lower Ordovician (C/O_{1+2}) or Upper Devonian/Silurian unconformities. The reservoirs may have been favourable for ancient freshwater with bacteria to flow through, leading to biodegradation of the oils. Similar case has been reported in the reservoirs close to the C/O_1 unconformity in the Hetianhe gasfield, southwest to the Central Tarim by Cai et al. (2002), who proposed that ^{12}C-rich light hydrocarbon gases were preferentially depleted by bacteria introduced into the reservoir by an influx of meteoric water by way of an inversion-related unconformity.

However, small amounts of 25-norhopanes found in group II oils are unlikely to result from biodegradation. In contrast, they may have been derived from source rocks. The reasons include the following aspects: 1) group II oils have $C_{29}DH/C_{30}H$ and $C_{29}DH/C_{29}H$ ratios within the UK background reference level of 25-norhopanes concentrations in source rocks ($C_{29}DH/C_{30}H < 0.12$ and $C_{29}DH/C_{29}H < 0.15$; Blanc and Connan, 1992); 2) $C_{29}DH$ was detected as free hydrocarbons in the TD2 Cambrian source rock in the Tarim Basin [Fig. 7a in Cai et al. (2009)], similar to previous case studies reported from other basins (Noble et al., 1985; Blanc and Connan, 1992); 3) occurrence of only C_{29} 25-norhopane and C_{28} 25-norhopane in the group II oils rather than the complete suite of bomologs (C_{28} to C_{34} 25-norhopanes), which are typically found in biodegraded oils from the Tarim Basin (group I oils) and other basins (Moldowan and McCaffrey, 1995; Bennett et al., 2006).

Geological evidence supports that the group II oils were not likely biodegraded, as is typified by the TD2-∈ oil. TD2 oil reservoirs were rapidly buried down to more than 6000 m (up to 210 °C) after oil charge during the late Ordovician, and thus were very likely to have been sterilized. Wilhelms et al. (2001) proposed that sterilization of petroleum reservoirs occurred at temperatures higher than around 80–90 °C during deep burial, killing the organisms needed for oil biodegradation to occur after the basin uplift. Thus, it is reasonable to consider that the TD2-∈ oil was not biodegraded although the reservoirs were subsequently uplifted to depths of about 2200 m (~75 °C) (Wang et al., 2006).

4.2. Oil–source rock correlation based on biomarkers

Palaeozoic oils in the Tarim Basin were considered to have been derived from the Middle to Upper Ordovician source rock using presumably age diagnostic biomarkers including 24-isopropylcholestanes, dinosteranes (4,23,24-tri-methylcholestanes), triaromatic dinosteroids, and 24-norcholestanes (Hanson et al., 2000; Zhang et al., 2000). However, these biomarkers have been found to have high contents in Upper Ordovician source rocks from Keping outcrop (Ma et al., 2006), indicating that they may not be age-specific.

It has been generally accepted that the ∈–O_1 source rocks have higher percentages of C_{28} ααα 20R sterane among C_{27} to C_{29} ααα 20R steranes, higher gammacerane/C_{30} 17α, 21β hopane ratios, significantly more abundant aryl isoprenoids and higher DinoSt ratio than the O_3 source rocks (Sun et al., 2003; Zhang et al., 2004; Xiao et al., 2005; Ma et al., 2006; Wang et al., 2007; Gong et al., 2007; Li et al., 2008; Pan and Liu, 2009; Cai et al., 2009). Oils from TD2-∈ and TZ62-S in this study, and TZ16-O_3, TZ452-O_{1+2}, TZ62-O_3, TZ70C-O_3 and TZ24-O_3 (Xiao et al., 2005; Wang et al., 2007; Li et al., 2008) have most of the biomarker distributions (except DinoSt ratio) similar to those of the ∈–O_1 source rocks (Table 1), and thus were most likely derived

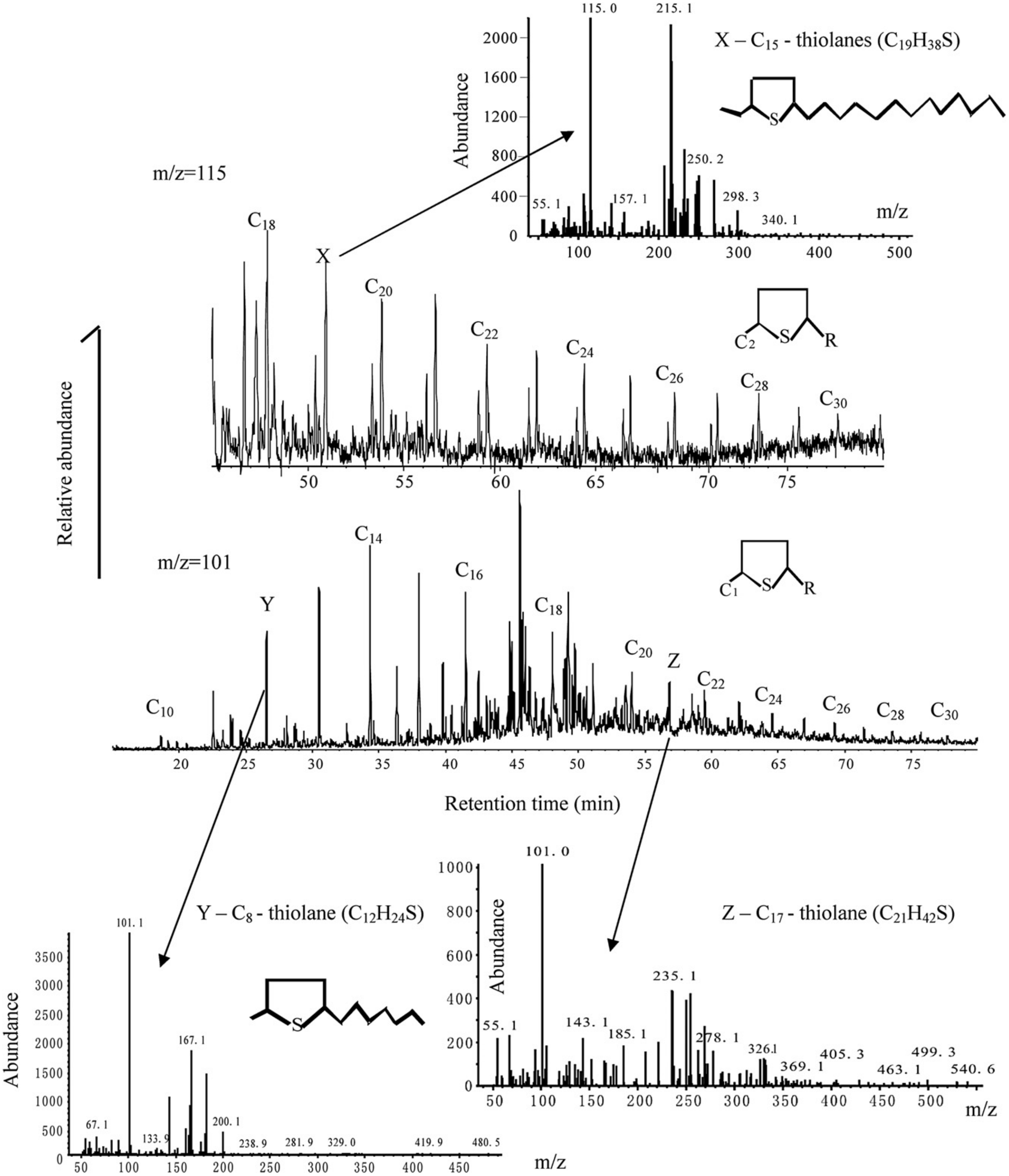

Fig. 7. Partial GC–MS fragmentograms ($m/z = 101$, 115) showing abundant long chained alkyl-thiolanes in the TZ83-O$_1$ oil with mass spectra of peaks X, Y and Z for identification. The spectra are not entirely those of the pure compounds.

from the source rocks. This suggestion is supported by the distribution of biomarkers extracted from fluid inclusions and absorbed hydrocarbons from the Upper Ordovician carbonate rocks in the Central Tarim (Pan and Liu, 2009).

Not all of the biomarker distributions of the oils are wholly matched with the ∈–O$_1$ source rocks and typical oils generated from them (TD2-∈ and TZ62-S oils). Possible reasons include, 1) mixtures of oils derived from the ∈–O$_1$ source rocks with different organic facies, 2) the ∈–O$_1$ source rocks — derived mature oil contaminated with small amount of the O$_3$ source rocks — derived immature oil, or 3) mixtures of oils derived from the ∈–O$_1$ with the O$_3$ mature source rocks.

In general, a mature oil has much lower contents of biomarkers than an immature oil. Thus, if a mature oil was contaminated by an immature oil, the resulting oil is expected to have the biomarker distributions very similar to those of the immature oil. Thus, the oils with part of the biomarker distributions not matched with the ∈–O$_1$

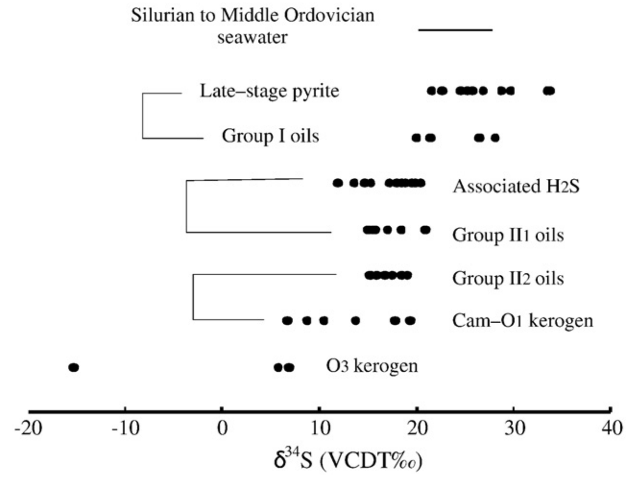

Fig. 8. Diagram showing $\delta^{34}S$ values of different oil groups, their potential source rock kerogens, associated H_2S, late-stage pyrite and Silurian to Middle Ordovician age seawater with possible genetic links shown for comparison. Note: group I: heavily biodegraded oils; group II_1: non-degraded oils with associated H_2S gas; and group II_2: non-degraded oils without associated H_2S gas.

source rocks may be considered to have been contaminated by the O_3 source rocks — derived immature oil (hypothesis 2), although the other two possibilities cannot be ruled out.

Different from the above oils, oils from TZ83-O_3 in this study, TZ62-2-O_3 and TZ62-3-O_3 (Wang et al., 2007) have the biomarker distributions similar to the Upper Ordovician source rocks (Cai et al., 2009 and references therein), and thus these oils are genetically correlated with the Upper Ordovician.

The TZ83-O_1 oil has low contents of steranes and terpenoids and a high wax content (24%), and thus it is unlikely to determine the source rock for this oil.

4.3. Oil–source rock correlation based on sulfur isotopes

Experimental simulations under open-system conditions suggest that the oil and its source rock kerogen may have significant isotopic discrimination (Amrani et al., 2005). However, peak oil generation from a rapidly buried source rock is likely under semi-closed to closed systems, before and after episodic petroleum expulsion (Cai et al., 2009), resulting in small differences in $\delta^{34}S$ values of residual mature kerogen, H_2S and oil (<2‰) (Thode, 1981; Orr, 1986; Amrani et al., 2005). For example, in the Tarim Basin, TD2-∈ oil was generated from the Cambrian source rock with a buried rate of ~110 m/Ma or a heating rate of ~3.56 °C/Ma (Wang et al., 2006), and has a $\delta^{34}S$ value (+19.6‰) very close to that of its source rock kerogen (+19.4‰). Thus, $\delta^{34}S$ values can be utilized for oil–source rock correlation in such a rapidly buried basin.

In the case of the Tarim Basin, group II_2 oils (non-degraded and no associated H_2S) have $\delta^{34}S$ values very close to the ∈–O_1 source rocks, which was rapidly buried immediately after deposition in the whole basin (Cai et al., 2009). This evidence indicates that sulfur in the oils may have been mainly derived from the ∈–O_1 source rocks. Although a small percentage of isotopically heavy sulfur may have directly been inherited from biomass, relatively heavy and narrow $\delta^{34}S$ values of the group II_2 oils may well suggest a relatively limited sulfate supply during the deposition or the early diagenesis of the source rocks (Orr, 1986). Interestingly, our data also indicate that most of the oils with relatively heavy organic sulfur contain abundant aryl isoprenoids, molecular indicators for photic zone anoxia (Koopmans et al., 1996), and abundant gammacerane, a biomarker indicating a stratified water body (Sinninghe Damsté et al., 1995) and thus an indirect marker of euxinia (Meyer and Kump, 2008). A similar case with isotopically heavy organic sulfur was reported from a euxinic basin across the Frasnian–Famennian boundary (Joachimski et al., 2001). These features are different from those reported by Engel and Zumberge (2007), in which oils derived from source rocks deposited under photic zone anoxia have very light sulfur isotopic composition.

Table 3
$\delta^{34}S$ values of fracture-filling pyrite in carbonate reservoirs.

Area	Well	Strata	Depth (m)	$\delta^{34}S$‰
Central Tarim	TZ161	O_3	4509.56	+24.6
	TZ12	O_3	5080	+29.7
Tahe oilfield, Tabei area	S86	O_3	5683.56	+28.8
	S86	O_3	5684.16	+25.3
	T759	O_2	5835.5	+22.6
	T759	O_2	5837	+25.2
	T705	O_2	5765.58	+21.6
	T705	O_2	5760.74	+25.8
	T705	O_2	5761.28	+26.9

Table 4
Chemistry of fluid inclusions from calcite cements and fracture-filling calcite.

Areas	Well	Strata	Occurrence	Gas phase inclusions (mol%)						
				CO_2	H_2S	SO_2	CH_4	C_2^+	N_2	H_2O
Central Tarim	TZ621	O_3l	Cement	42.8	3.8	tr	3.8	21.0	tr	28.7
	TZ621	O_3l	Cement	tr	6.0	tr	3.6	29.2	25.8	35.4
	TZ621	O_3l	Cement	22.3	4.6	tr	3.8	30.5	tr	38.7
	TZ621	O_3l	Cement	tr	6.1	tr	tr	12.8	51.3	29.9
	TZ72	O_3l	Cement	15.1	5.0	tr	7.8	15.6	32.0	24.4
	TZ72	O_3l	Cement	27.6	5.4	tr	4.4	28.6	tr	34.1
	TZ72	O_3l	Vein	37.0	3.1	tr	3.3	19.1	tr	37.5
	TZ823	O_3l	Vein	13.3	3.3	tr	tr	10.7	29.6	43.2
	TZ823	O_3l	Cement	tr	2.8	tr	42.5	16.5	19.6	18.6
	TZ823	O_3l	Cement	35.3	7.5	tr	3.7	36.7	tr	16.7
	TZ823	O_3l	Vein	17.7	2.6	tr	2.3	9.8	34.4	33.2
Tahe oilfield	S110	O_3l	Vein	tr	6.3	tr	4.9	60.7	tr	28.0
	T904	O_3q	Vein	tr	14.4	tr	8.7	33.0	tr	43.9
	T904	O_3q	Vein	22.8	3.3	tr	tr	7.8	47.4	18.7
	S94	O_2yj	Vug	30.6	5.1	13.4	5.0	13.1	tr	32.7
	T904	O_2yj	Vein	8.4	1.8	tr	3.2	17.4	41.6	27.6
	S79	$O_{1+2}y$	Vein	30.4	6.9	tr	5.4	3.9	36.9	16.5
	S79	$O_{1+2}y$	Vein	tr	11.1	tr	10.0	46.7	tr	32.2
	S83	$O_{1+2}y$	Vein	19.7	3.2	tr	5.1	17.7	14.8	39.4

Note: tr represents trace; – is no measurement.

It is generally accepted that H_2S and pyrite generated from photic zone anoxia have light $\delta^{34}S$ values (Meyer and Kump, 2008). This is because, 1) the euxinic water columns where bacterial sulfate reduction (BSR) takes place are an open system and thus there exists a significant isotopic fractionation with the product sulfide being depleted in $\delta^{34}S$ values up to 30‰ relative to its parent sulfate; 2) recycling of H_2S by green and purple sulfur bacteria results in isotopically light sulfate (Zerkle et al., 2009 and references therein). This sulfate in turn may be reduced to even lighter H_2S by subsequent bacterial sulfate reduction. Thus, resulting pyrite and organic sulfur are expected to have light sulfur isotopes.

However, relatively limited sulfate supply may occur in pore water of shallow burial fine sediments which more closely represent closed systems (Meyer and Kump, 2008). Intense sulfate reduction fuelled by high organic carbon, may have resulted in the conversion of most of the sulfates to sulfides and the subsequent assimilation into the kerogen. Consequently, pyrite and kerogen in the rock record tend to be isotopically heavy as a result of environmental Rayleigh distillation. Thus, relatively heavy reduced sulfur (pyrite and organic sulfur) from euxinia reflects intense sulfate reduction in basins with initially low sulfate concentrations (Meyer and Kump, 2008), most likely under relatively closed early-diagenetic conditions.

Thus, the $\delta^{34}S$ values and the biomarker distributions of the group II_2 oils in the Tarim Basin consistently reflect that their source rocks were deposited under a euxinic and likely stratified environment with a limited sulfate supply during early diagenesis. That is, the oils were genetically correlated with the ∈–O_1 source rocks, but not with the O_3 source rocks (Cai et al., 2009). However, it is likely for the group II_2 oils to have mixed with small proportions of the O_3 source rocks — derived oils. This is because sulfur contents of the ∈–O_1 source rocks are significantly higher than those of the O_3 source rocks (Cai et al., 2009).

The group I and II_1 oils have been altered by biodegradation or incorporation of TSR- or BSR-derived inorganic sulfur (next sections), thus $\delta^{34}S$ values cannot directly be used for oil–source rock and/or oil–oil correlations.

4.4. Effect of biodegradation on oil sulfur isotopes

Increasing documents suggest that organic sulfur compounds (OSC) are biodegradable by aerobic and anaerobic bacteria (Fedorak, 1990; Annwerler et al., 2001). Biodegradation may involve the oxidation of sulfur atoms or only oxidation of carbon atoms to organic acids (Kropp and Fedorak, 1998).

The oxidation of sulfur atoms is associated with a kinetic effect with the S-isotopically light OSC being preferentially removed by biodegradation, leading to an increase in $\delta^{34}S$ values of the residual oils. Microbes prefer low molecular weight OSC, mainly residing in aromatic fractions, thus the aromatics is expected to have a significant increase in $\delta^{34}S$ values after the biodegradation of OSC. In contrast, large molecular weight OSC in resins and asphaltenes tend to retain the $\delta^{34}S$ values characteristic of the unaltered oils. However, 1) the differences in $\delta^{34}S$ values of different fractions are very limited compared with large variations in whole oil $\delta^{34}S$ values for biodegraded oils with different aromatics/(resins + asphaltenes) ratios, and 2) resins and asphaltenes showed the same variations in $\delta^{34}S$ values and sulfur contents as the whole corresponding oils with increasing biodegradation (Thode, 1981; Méhay et al., 2009), ruling out the possibility that the heavy sulfur in heavily biodegraded oils was derived from biodegradation alone. In the case of the Tarim Basin, the differences in $\delta^{34}S$ values between S-isotopically heaviest biodegraded oils (group I) and non-degraded oils (group II_2) may be up to 8‰, thus the biodegraded oils must have sulfur derived from the incorporation of or exchange with isotopically distinct sulfides.

4.5. Incorporation of BSR- or TSR-derived sulfides into biodegraded oils

Labile compounds generated by biodegradation of petroleum, particularly functionalised compounds, are considered to be suitable precursors to facilitate the incorporation of reduced S generated by sulfate reduction (BSR) into oils (Cai et al., 2005; Méhay et al., 2009 and references therein). In general, H_2S of BSR origin is isotopically lighter than the pre-biodegraded oils, and thus heavily biodegraded oils after the incorporation of or exchange with the H_2S show lighter $\delta^{34}S$ values (Manowitz et al., 1990; Cai et al., 2005; Méhay et al., 2009). In contrast, Thode (1981) proposed that isotopically heavy sulfur in biodegraded oils have resulted from the BSR-derived H_2S, who, however, provided no supportive $\delta^{34}S$ values of such kind of H_2S.

In the case of the Tarim Basin, biodegraded oils (Group I) have $\delta^{34}S$ values (up to + 28.2‰) significantly heavier than those of pre-biodegraded oils (< + 20.5‰), inferred from the analyzed source rocks and non-degraded oils (Cai et al., 2009; Table 2). This line of evidence suggests that at least part (if not all) of the incorporated or exchanged H_2S should have $\delta^{34}S$ values heavier than + 28‰. Two lines of evidence supports that the incorporated or exchanged H_2S is unlikely to be biogenic: 1) if the H_2S was generated during late diagenesis, the temperatures that these reservoirs have experienced are too high for BSR (Cai et al., 2001; 2008), 2) If the H_2S was generated by BSR in the Silurian to the Middle Ordovician reservoirs during further shallow burial after the reservoirs were uplifted and eroded, the H_2S is expected to have $\delta^{34}S$ values significantly lighter than those of its parent sulfates (Silurian to Middle Ordovician age seawater, from + 20 to + 28‰, Claypool et al., 1980). This is because sulfate may have been supplied by meteoric water along the overlying unconformities (Cai et al., 2002), and thus was not very limited. Thus, the incorporated or exchanged H_2S is most likely to have been derived from TSR (Cai et al., 2001; 2003; Amrani et al., 2006).

The TSR-H_2S inferred from the late-stage authigenic pyrite and fracture-filling pyrite should have $\delta^{34}S$ values up to + 29.7‰ in the Ordovician in this study (Table 3), and up to + 33.6‰ in the Silurian (Cai et al., 2001). The H_2S may have been generated by TSR in the Cambrian and Lower Ordovician anhydrite-bearing carbonate rocks, and was likely up-migrated to the Middle Ordovician to Silurian reservoirs (Cai et al., 2001). Occurrence of TSR-H_2S is supported by abundant H_2S in the fluid inclusions in calcite cement and fracture-fillings (Section 3.3) with homogenization temperatures >120 °C (Qian, 2002; Cai et al., 2008). Significantly higher H_2S concentrations in the gaseous phase of the fluid inclusions than in the associated gas may well indicate that the oil pools had high H_2S concentrations and H_2S may have been precipitated as late-stage and fracture-filling pyrite, and/or incorporated into the heavily biodegraded oils. Reactive sulfate for the TSR was very likely to be derived from the dissolution of the anhydrite in the ∈–O_1 strata, and thus TSR rate was controlled by rate of anhydrite dissolution (Bildstein et al., 2001). Consequently, almost all of the dissolved sulfate may have been reduced to sulfide, resulting in the product sulfide having $\delta^{34}S$ values close to their parent sulfate, as proposed by Machel et al. (1995) and Worden et al. (2000). Late diagenetic pyrite occurs along beds in the Silurian sandstone or as fracture-fillings in the Ordovician, and these different occurrences of pyrite have similar $\delta^{34}S$ values, supporting that the H_2S was derived from deeper strata rather than generated in situ.

The $\delta^{34}S$ values (mainly + 25 to + 34‰) of the TSR-H_2S are heavier than or close to those of the biodegraded oils (+ 20 to + 28‰), supporting that the H_2S was incorporated into the biodegraded oils. Organo-sulfur fractions newly generated from the incorporation of TSR-H_2S into labile compounds of biodegraded oils would, in general, adopt the heavy sulfur of the original anhydrite as transmitted by the TSR-H_2S, leading to heavily biodegraded oils becoming sulfur-isotopically heavier. The $\delta^{34}S$ values of the whole biodegraded oils after the incorporation of the TSR-H_2S depend on residual organic sulfur/incorporated sulfur ratio, initial organic sulfur $\delta^{34}S$ value and incorporated sulfur $\delta^{34}S$ value. Thus, it is not unexpected for the biodegraded oils to have the range of $\delta^{34}S$ values.

Alternatively, group I oils may not have been biodegraded but resulted from the selective destruction of petroleum hydrocarbons by TSR. Petroleum altered by TSR has been demonstrated to have similar characteristics to biodegradation (e.g., loss of saturates, increase in aromatics, increase in UCM) (Sassen, 1988; Manzano et al., 1997).The fact that 25-norhopanes are present in the non-degraded oils examined in this study, makes it possible that the 25-norhopanes in the group I oils were originated from the kerogen, and that the process of TSR has enriched their concentration as well as producing the apparent degradation effects. This explanation does not invoke biodegradation and TSR in the same reservoirs. However, the proposal may not be consistent with complex geological background in the Tarim Basin with several times of uplifts and erosion and thus unconformities (Cai et al., 2008; 2009), lots of work needs to be done.

4.6. Incorporation of TSR-derived H_2S into non-degraded oils

Non-degraded oils with associated H_2S (group II_1 oils) have $\delta^{34}S$ values (from + 15.1 to + 19.1‰) close to those of the H_2S (from + 15.0 to + 18.5‰). The similarity of $\delta^{34}S$ values of the oils and the H_2S may result from three possibilities: 1) the H_2S and the oils were all sourced from decomposition of kerogen; 2) the H_2S was derived from cracking of the oils; and 3) the H_2S was generated by TSR and incorporated into or exchanged with the oils.

It is hard to rule out any one of the possibilities. However, it is more likely for the H_2S to have a TSR origin. The H_2S was associated with barite with $\delta^{34}S$ values from +42 to +46‰; and the barite was replaced by calcite in reservoirs; thus, the H_2S is considered to have been generated through reactions of limited hydrocarbons with excessive dissolved sulfate, which may have been up-migrated from the Cambrian and Lower Ordovician evaporite-bearing strata (Cai et al., 2008 and references therein). A significant sulfur isotope fractionation during thermochemical reduction of dissolved sulfate has been well demonstrated by TSR experiments using Na_2SO_4 solution as reactive sulfate (Harrison and Thode, 1957; Kiyosu and Krouse, 1990) and some case studies from native sulfur vein and MVT sulfides ores (Alonso-Azcarate et al., 2001; Basuki et al., 2008). Thus, the H_2S in studied area may have been generated in two periods. One generation (likely earlier) of H_2S was migrated from the Cambrian and Lower Ordovician into the Silurian and Ordovician reservoirs, and shows heavier $\delta^{34}S$ values than the other generation (likely later) of H_2S generated by TSR in situ. However, there exists a possibility that TSR took place in only one period, and the H_2S associated with the non-degraded oils was a mixture of the isotopically heavier TSR-H_2S with early-diagenetic BSR-derived lighter H_2S. However, in the Central Tarim, the oils associated with the H_2S were not biodegraded, indicating that the reservoirs after oil charge may not have been favourable for microorganisms to grow on. Thus it is less likely for a significant amount of H_2S to have been generated by BSR in the reservoirs.

The H_2S with the highest content (2.6% by volume) in gas composition in the Central Tarim is associated with the TZ83-O_1 oil containing significant amounts of 2-thiaadamantanes (Jiang et al., 2008) and alkyl-thiolanes in this study.

Significant amounts of 2-thiaadamantanes have only been found in the active TSR areas (Hanin et al., 2002; Wei et al., 2007), and were generated by reactions of non-sulfur-containing diamondoids with H_2S or elemental sulfur in laboratory (Wei et al., 2007). Besides thiaadamantanes, abnormally high thiol contents have been observed in TSR-altered oils, condensates and natural gas (Orr, 1974; Cai et al., 2003), and may have been generated by back-reactions of TSR-H_2S with hydrocarbons containing double bonds, most likely generated during high temperature hydrous pyrolysis of *n*-alkanes (Cai et al., 2003). OSC including thiols rather than elemental sulfur have been proposed to initiate hydrocarbon oxidation during TSR (Zhang et al., 2008). Unfortunately, no thiols were measured in this study.

It is very likely for other OSC besides thiols and thiaadamantanes to have been generated from the TSR-H_2S incorporation. However, these OSC may be difficult to be distinguished from kerogen cracking derivatives (Cai et al., 2003). In this study, alkyl-thiolanes were most likely to result from the incorporation of TSR-H_2S, and part of DBTs may have a similar origin. This proposal is supported by three lines of evidence: 1) of aromatic fraction, DBTs and other OSC concentrations detected in the TZ83-O_1 oil (41%) are significantly higher than those in the other oils and the source rocks analyzed in the basin (7% to 21%); 2) importantly, significant amounts of BTBTs, benzobisbenzothiophenes and alkyl-thiolanes ($C_{10}H_{20}S$–$C_{31}H_{62}S$) were detected only in the TZ83-O_1 oil, not in the other oils and the source rocks analyzed in this and previous studies (cf. Li et al., 2005); and 3) H_2S with the highest concentration is associated with the TZ83-O_1 oil.

Alkyl-thiolanes were reported from immature oils sourced from hypersaline lacustrine and marine high sulfur organic matter (Sheng et al., 1986; Sinninghe Damsté et al., 1986;1989a; Cai et al., 2004a). Sheng et al. (1986) suggested that alkanes might react with H_2S or elemental sulfur to generate alkyl-thiolanes. Thiolane compounds are thermally unstable and are thought to undergo dehydrogenation to generate thiophenes (Sinninghe Damsté et al., 1989b). Thermal and thermocatalytic studies have established that nonthiophenic sulfur (aliphatic as in thiols, acyclic and cyclic sulfides) evolves to produce H_2S much more easily than thiophenic sulfur (Orr and Sinninghe Damsté, 1990). Interestingly, the TZ83-O_1 oil contains less thermally stable thiolanes and very stable DBTs, BNTs and BTBTs but lacks thiophenes and benzothiophenes with thermal stabilities ranging between thiolanes and DBTs. To our knowledge, no such oil has been reported in previous publications. Coexistence of H_2S (2.6%), thiolanes and DBTs but no thiophenes and benzothiophenes in the TZ83-O_1 oil pool, may suggest that thiolanes, like thiols (Cai et al., 2003), were very likely to have been newly generated by the TSR-H_2S incorporation into labile compounds, which were likely generated during relatively high temperatures (this oil experienced heating up to 142 °C based on rebuilding of burial history, Cai et al., 2001). This supports the possibility that thiolanes can be generated by TSR-related reactions, as initially proposed by Orr (1974).

Kelemen et al. (2008) suggested that solid bitumens altered by TSR show an increase in aromatic carbon and sulfur/nitrogen atomic ratio. Significantly higher OSC contents and highly aromatic compounds in the aromatic fraction of the TZ83-O_1 oil are most likely to have resulted from the alteration by TSR.

5. Conclusions

Crude oils may have complex sulfur sources in the Tarim Basin. Non-degraded oils without associated H_2S may have been derived from the $\in$–O_1 source rocks, and show characteristics of the source rocks (heavier $\delta^{34}S$ values, abundant aryl isoprenoids, high gammacerane/C_{30} 17α, 21β hopane and/or relatively high C_{28} ααα 20R sterane). Non-degraded oils with associated H_2S may have been derived from the Upper Ordovician, and the Cambrian and Lower Ordovician source rocks, based on biomarker distributions, and may have sulfur contributed from TSR-derived inorganic sulfur. The incorporation of the TSR-H_2S into the oils may have led to similar $\delta^{34}S$ values of the oils and the associated H_2S, and to the generation of 2-thiaadamantanes and alkyl-thiolanes. To our knowledge, this is the first report that an oil contains significant amounts of thermally labile alkyl-thiolanes and thermally stable dibenzothiophene, methyl-, ethyl-, dimethyl- and trimethyl-dibenzothiophenes but no detectable thiophenes and benzothiophenes with stabilities between them. Heavily biodegraded oils may have incorporated TSR-derived ^{34}S-rich sulfides, resulting in oil $\delta^{34}S$ values becoming closer to Cambrian and Ordovician age seawater sulfates. Thus, $\delta^{34}S$ values can be used as a tool for correlation of source rocks with those non-degraded oils without associated H_2S.

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