Origin of the unusually high dibenzothiophene concentrations in Lower Ordovician oils from the Tazhong Uplift, Tarim Basin, China

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Abstract: The origin of the unusually high dibenzothiophene (DBT) concentrations in Lower Ordovician oils from the Tazhong Uplift, Tarim Basin was studied by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The most abundant sulfur compounds in the oils are S₁ species with double-bond equivalent (DBE) values of 1–19 and 11–48 carbon atoms. The range of the number of carbon atoms in the sulfur compounds detected by the FT-ICR MS (S₁ species with DBE=9) is about ten times larger than that for sulfur compounds detected by GC/MS (DBTs). This suggests that FT-ICR MS is a much better approach than GC/MS for characterization of DBTs in crude oils. The abundance of S₁ species with DBE=1–8 decreased with increasing thermal maturity, while the abundance of S₁ species with DBE=9 (primarily DBTs) increased. Therefore, thermal maturity is an important factor in the formation of oils with high DBT concentrations. Unusually high abundances of S₁ species with low DBE values (1–8), which include sulfide, thiophene and benzothiophene, were observed in several oils, especially the TZ83 (O₁) oil with high or very high thermal maturity. Thermochemical sulfate reduction (TSR) was thought to be the reason for the high abundance of these low DBE compounds in deep reservoirs, and thermochemical sulfate reduction could affect the distribution and composition of DBTs in the oils. According to the results of FT-ICR MS analysis, there are no signs that TSR is occurring or has occurred recently for most of the Lower Ordovician oils.

Key words: Tazhong Uplift, crude oil, FT-ICR MS, sulfide compounds, maturity, TSR

1 Introduction

Organosulfur compounds are important heteroatomic species in crude oils that can be used to provide information about the paleoenvironment (Hughes et al, 1989; Lin et al, 1988), migration (Wang et al, 2005), and thermal maturity (Ho et al, 1974; Radke et al, 1982) of the oil. Usually, most of the most common sulfur compounds in oils are C₀–C₃-dibenzothiophenes (C₁₂–C₁₅), except for in less mature oils, which contain the low thermal stability compounds of thiophene and benzothiophene (Sheng et al, 1986). Samples are typically analyzed by gas chromatography (GC/MS). However, Fourier transform ion cyclotron resonance mass

spectrometry (FT-ICR MS) has the ability to detect a much wider range of sulfur compounds, up to C-50, than GC/MS (Li et al, 2011b). In recent years, FT-ICR MS has been used to investigate the sulfur compounds present in petroleum products (Purcell et al, 2007; Müller et al, 2005; Panda et al, 2007; Shi et al, 2010a, b; Liu et al, 2010a, b; Liu et al, 2011), and the results could be used to solve some complex problems in petroleum geology. For example, the origin of the unusually high concentrations of dibenzothiophenes (DBTs) in oils from the Lower Ordovician in the Tazhong Uplift, Tarim Basin (Li et al, 2009; 2010a; 2011a, b;). Although several factors influence the concentrations of these compounds, the key factor and mechanism of action have not been clarified. In this study, FT-ICR MS and GC/MS were used to characterize the DBTs in Tazhong marine oils. The concentration of these compounds in the Lower Ordovician oils was evaluated.

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2 Petroleum geological background

The Tazhong Uplift is located in the middle of the Tarim Basin, which is an inherited palaeohigh with oil/gas generating areas that have excellent hydrocarbon migration and accumulation conditions. The uplift originally started to take shape at the end of the early Ordovician, and was characterized by block faulting with an extensive unconformity that developed between the Upper and Lower Ordovician formations. By the end of the late Ordovician, the Tazhong uplift featured fold movements, which were followed by the formation of a large composite anticline. From the end of the Caledonian to the early Hercynian, the uplift underwent a period of tectonic adjustment and reconstruction, and then a period of stability with a slight fluctuation after the Hercynian. The multiphase tectonic activities have given the Tazhong Uplift a vertical structure of multiple layers with north-south zoning and latitudinal blocking, resulting in a complex tectonic framework containing several hydrocarbon bearing intervals (Zhou et al, 2010; Pang et al, 2010; Lü et al, 2009).

From 2006 to 2010, forty-three wells were drilled in the Lower Ordovician Yingshan Formation. Twenty-seven of these wells are highly productive for industrial oil and gas, and the productive area of the Lower Ordovician is up to 1866 km². The Yingshan Formation is a potential petroleum province that developed on a large karst ramp region. It is a huge quasi-layered reservoir with proven oil and gas stocks of up to 1.62 x10⁶ ton. Most of the oils are condensate with a small amount of normal oil. The physical properties of the Lower Ordovician oil appear to be controlled by faults connecting gas sources, and large discrepancies were observed in both the east and west of the X-shaped shear faults.

3 Sample and experiment

Ten low Ordovician oils and eight middle-upper Ordovician as well as one Silurian oils from the Tazhong Uplift in the Tarim Basin were selected for the whole oil gas chromatography, saturated and aromatic hydrocarbons GC-MS, and FT-ICR MS analysis. Three marine oils from the Yingmaili Tectonic Belt in the Tabei Uplift were also selected for a correlative study (Li et al, 2010b).

3.1 Gas chromatography-flame ionization detection (GC-FID) and GC-MS

GC-FID of whole oil samples was performed on a Carlo Erba 160 GC fitted with a PONA column (60 m, 0.25 mm i.d., 0.32 µm film thickness). The GC oven was initially set at 35 °C for 10 min, and then programmed to 300 °C at 4 °C/min, holding time for 40 min at 300 °C. GC-MS of saturated and aromatic hydrocarbons of the crude oils were carried out on a Agilent 6890 GC coupled to a 5973 mass selective detector. The GC column is a HP-1 fused silica column (30 m, 0.25 mm i.d., 0.25 µm film thickness). For saturate GC analysis, the GC oven was initially set at 50 °C for 2 min, programmed to 100 °C at 2 °C/min and then to 310 °C at 3 °C/min, with a final hold time of 15 min. For aromatic hydrocarbons GC

analysis, the GC oven was initially set at 60 °C, programmed to 150 °C at 8 °C/min and then to 320 °C at 4 °C/min, with a final hold time of 10 min. The mass spectrometer was operated in selected ion monitoring mode, targeting the molecular ions and characteristic fragment ions of selected aromatic hydrocarbons. Peak identifications and quantitative methods are reported in Jiang et al (2001).

3.2 Methylation of sulfur compounds and sample preparation

Sulfur compounds were converted to methylsulfonium salt polar derivatives for ESI (electrospray ionization) FT-ICR MS analysis. The method was successfully implemented by J. T. Anderson's group (Müller et al, 2005) and reported in some recent publications (Liu et al, 2010a, b, 2011; Müller et al, 2005; Panda et al, 2007; Purcell et al, 2007; Shi et al, 2010a). Briefly, a 100 mg oil sample was diluted with 2 ml dichloromethane (CH₂Cl₂). A total of fifty microlitres methyl iodide was added to the sample solution. The mixture in a beaker was immersed in an ultrasonic bath at room temperature for 5 min. While mixing, a solution of 20 mg/ml silver tetrafluoroborate and 2 ml 1, 2-dichloroethane was added. A yellowish brown precipitate formed immediately. The reaction mixture in the beaker remained in the ultrasonic bath for an additional 5 min to allow the reaction to continue. Then the reaction mixture solution was stored in the dark for 48 h. A mixture consisting of methyl sulfonium salts, silver iodide, silver tetrafluoroborate and unreacted oil was obtained after nitrogen was used to remove the 1, 2-dichloroethane and the dichloromethane from the solution. Five milliliters of toluene was used to remove the un-reacted oil and obtain the methyl sulfonium salts.

Methylsulfonium salts (10 mg) were diluted with 1 ml dichloromethane. Five microliters of the methylsulfonium salt solution was further diluted with 1 ml toluene/methanol/dichloromethane (3:3:4 vol/vol/vol) solution. Glassware was used to handle and transfer the solvent, except for the stainless steel pistons used in the 100 µl Hamilton syringes.

3.3 FT-ICR MS Analysis

Mass spectrometry analysis was carried out by a Bruker Apex ultra FT-ICR mass spectrometer equipped with a 9.4 T superconducting magnet. The methylsulfonium salt solution was infused via the Apollo II electrospray source at 180 µl h⁻¹ by using a syringe pump. The operation conditions for positive ion formation were -2.5 kV emitter voltage, -3.0 kV capillary column introduced voltage, and 320 V capillary column end voltage. Ions accumulated for 0.01 s in a hexapole with 2.4 V direct current and 300 Vp-p radio-frequency (RF) amplitude. The optimized mass for Q1 was 250 Da. Hexapole collision pool were operated at 5 MHz and 400 Vp-p RF amplitude, in which ions accumulated for 0.5 s. The transfer time was set to 1.2 ms to transfer the ions to an ICR cell by electrostatic focusing of transfer optics. The ICR mass spectrometer was operated at 11.75 db attenuation, 200-800 Da mass range, and 4 M acquired data size, and time-domain data sets of 256 acquisitions were co-added.

4 Results and discussion

4.1 Conventional geochemical characteristics of the Lower Ordovician oils

The Tazhong Lower Ordovician oils are typically of marine origin. They are mostly light oils with density and viscosity ranges of 0.77–0.83 g/cm³ and 1.09–4.92 mm²/s, respectively (Table 1). The oils are characterized by moderate-to-high wax contents (5.75–23.44 %), while their sulfur concentration is relatively low (0.05–0.40 %) (Table 1). The exception is the oil from Well TZ4-7-38 (O₁), which

has a relatively high sulfur content (up to 1.56 %) (Table 1). The gases associated with the Lower Ordovician oil generally have a high abundance of H₂S. For example, the H₂S concentrations in the oils from wells TZ4-7-38, ZG6, 7, 8, and 10 are 2.59 %, 9 %, 4.381 %, 3.67 %, and 10 %, respectively (Table 1). The Lower Ordovician oil also has a relatively high mercaptan content (3.2 and 173.9 µg/mL), which is much higher than that of the Middle-Upper Ordovician oils. For example, in wells ZG16, ZG17 and ZG19, the mercaptan concentrations are 2.4, 4.8 and 1.6 µg/mL. Mercaptan has low thermal stability, and relatively high concentrations of this compound in the oils may suggest a complex chemical

Table 1 Physical properties of Lower Ordovician oils

Well	Strata	Depth m	Density (20°C) g/cm ³	Viscosity (50°C) mm ² /s	Pour point °C	Wax %	Sulfur %	Resin %	Bitumen %	H ₂ S* %	Mercaptan µg/ml
TZ4-7-38	O _{1p}	3936.43-3985.5	0.99	2667.60	12.8	6.18	1.56	15.18	10.00	2.59	u.d
TZ721	O ₁	5355.5-5505	0.83	4.12	31.0	17.45	0.27	0.10	0.13	-	u.d
TZ83	O ₁	5666.1-5681	0.82	4.92	41.5	23.44	0.37	-	-	2.03	u.d
ZG10	O _{1y}	6198-6309.8	0.77	1.09	-6.0	9.26	0.34	0.07	0.00	10	44.9
ZG 11	O _{1y}	6165-6631.1	0.79	1.47	-14.0	5.75	0.40	0.00	0.00	-	16.0
ZG 111	O _{1y}	6008-6250	0.78	1.28	-14.0	10.20	0.02	0.00	0.00	-	35.3
ZG 13	O _{1y}	6458-6550.36	0.80	1.89	-28.0	5.10	0.15	1.73	0.09	-	3.2
ZG 21	O ₁	5753-5874.16	0.78	1.36	-10.0	8.55	0.07	0.00	0.00	-	63.7
ZG 22	O _{1y}	5605-5736.66	0.82	2.52	-6.0	7.90	0.14	0.00	0.00	-	57.7
ZG 23	O _{1y}	5898-5946	0.79	1.53	2.0	9.80	0.18	1.16	0.07	-	43.3
ZG 43	O _{1y}	4980.08-5334.09	0.80	1.68	-6.0	8.00	0.18	0.45	0.05	-	173.9
ZG 501	O _{1y}	6515.5-6294.1	0.79	1.59	-14.0	6.10	0.05	1.12	0.03	-	54.5
ZG 6	O ₁	5934.5-6172.73	0.78	1.36	-8.0	9.38	0.12	0.20	0.12	9	138.8
ZG 7	O _{1y}	5865-5882	0.80	1.83	2.0	6.93	0.13	0.00	0.00	4.38	140.5
ZG 8	O ₁	5893-6145.58	0.77	1.21	-8.0	7.30	0.17	0.00	0.00	3.67	60.1

Notes: * Percentage of the H₂S in the associated gases of the oils; “-” means no detection; “u.d” means undetectable.

reaction system in the Lower Ordovician interval.

The concentration range for saturated hydrocarbons in the Lower Ordovician oil is 73.1–95.8 %, which is much higher than those of the aromatics (2.09–19.4 %) and resin+asphaltene (generally <5 %) (Li et al, 2011a). Paraffin hydrocarbons are the predominant fraction in the Lower Ordovician oils, and the contents of biomarkers for thermal cracking are minimal (Li et al, 2011a). Consequently, the biomarkers could not be used as thermal maturity indicators. These results suggest that the Lower Ordovician oil has a high or very high thermal maturity compared with the Middle-Upper Ordovician oil (Li et al, 2010a; 2010c).

The unusually high concentration of DBTs in the Lower Ordovician oil is a particularly important distinguishing factor (Li et al, 2011a, b). Among the aromatics identified in the

Fig.1 The absolute and relative abundance of DBTs in the oils and aromatics respectively

oils, the DBT volume fractions in the oils from wells TZ83, ZG5-1, TZ721, ZG6 and ZG111 are 55.2 %, 52.3 %, 41.4 %, 43.1 % and 43.4 % respectively. These volume fractions are much higher than those in the Middle-Upper Ordovician oils with the same burial depth (Fig. 1b). For some of the oil samples (e.g., Z83, 55.17 %; ZG5-1, 52.33 %), DBTs are the most abundant species in the aromatics fraction. Some of the oils, such as those from wells ZG6, 7 and 8, have a relatively high absolute concentration of DBTs (Fig. 1a). Oils with high DBT concentrations have been discovered at many oil fields worldwide; especially in those where the oil has been altered by thermochemical sulfate reduction (TSR). Kelemen et al (2008) reported that the reservoir of the Mississippian Madison limestone and Devonian Nisku Formation, which underwent TSR, was particularly enriched in aromatic carbons and almost all of the organosulfur was in an aromatic form. In the Nisku Formation of the Albert Brazeau river region, Manzano et al (1997) found that the ratios of saturated HCs/aromatics decreased and the aromatic sulfur contents increased as TSR increased. Wells have not been drilled into the deep intervals of the Tazhong Uplift, and the reason for the unusually high concentrations of DBTs in these oils needs to be determined through multiple geochemical tests and a comprehensive geochemical and geological investigation.

4.2 Characteristics of the high resolution mass spectra for the Lower Ordovician oils

The elemental compositions of the sulfur species detected in the Lower Ordovician oils of the Tazhong Uplift by FT-ICR MS are $N_1O_1S_1$, $N_1O_2S_1$, N_1S_1 , O_1S_1 , O_2S_1 , S_1 and S_2 . O_1S_2 , O_3S_1 and S_3 species were only detected in Well TZ83 (Fig. 2; Table 1, 2). Among the sulfur species, S_1 is the most abundant (77–95.18 %) and then O_1S_1 (average 12 %).

Fig. 2 Relative abundance of the different sulfur species in the Tazhong Lower Ordovician oils

The DBE values of the S_1 species are plotted with the number of carbon atoms (x-axis) and the relative abundance (intensity) of each species in Fig. 3. The number of carbon atoms includes all carbon atoms in the original oil samples plus one extra carbon atom from methylation of the sulfur compound. For the S_1 species, the range of the DBE values is about 1–19 and that for the number of carbon atoms is 12–41. Most of the S_1 species in the Lower Ordovician oils are congregated in Block I in Fig. 3, and the S_1 species with DBE=9 are the most abundant. The Lower Ordovician

Table 2 Basic information about sulfur compounds detected in the oils analyzed

Elemental compositions of sulfur species	Compound name	DBE value	Carbon number
S_1	sulfur ether	0	C_{11} - C_{40}
	(Thiophane)	1	C_8 - C_{46}
	-	2	C_{11} - C_{45}
	Thiophene	3	C_9 - C_{45}
	-	4	C_{12} - C_{43}
	-	5	C_{11} - C_{43}
	Benzothiophene	6	C_9 - C_{44}
	-	7	C_9 - C_{43}
	-	8	C_{14} - C_{43}
	Dibenzothiophenes	9	C_{10} - C_{47}
	-	10-11	C_{12} - C_{44}
	-	12	C_{14} - C_{44}
	-	13	C_{14} - C_{41}
	-	14	C_{16} - C_{44}
	-	15	C_{18} - C_{42}
	-	16	C_{19} - C_{41}
	-	17	C_{20} - C_{41}
	-	18	C_{23} - C_{40}
	-	19	C_{25} - C_{40}
O_1S_1	-	0-14	C_8 - C_{40} *
O_1S_2	-	4-9	C_7 - C_{29} *
O_2S_1	-	1-10	C_{11} - C_{37} *
O_3S_1	-	2-7	C_5 - C_{28} *
S_2	-	8-10	C_{13} - C_{46} *
S_3	-	7	C_{23} - C_{48}

Notes*: Carbon number varying with the DBE value;

“-”:unrecognizable at present

oils from wells ZG5-2 and TZ83 are very different to the other oils. A number of the S_1 species, such as those from the YM2-4 and YM206 wells in the Yingmaili Tectonic Belt and those from the TZ12 wells in the Tazhong Uplift (Figs. 3 i, j) (Li et al, 2011b), are located in Block II and Block IV (Fig. 3), which indicates these oils have relatively low thermal maturity. The S_1 species with DBE=1, 3, 6, and 9 represent sulfur ether, thiophene, benzothiophene and DBT series, respectively, and other compounds with similar DBE values. For example, the S_1 species with DBE=9 corresponds to a DBT core with alkyl side chains and/or dibenzohomologs of two cyclic-ring sulfides (Shi et al, 2010a). Most

Fig. 3 Plots of DBE versus the carbon number for the S_1 class species in methylated Tarim oils from the positive-ion ESI FT-ICR MS. The largest dot corresponds to the most abundant monosulfur species in the sample.

of the S_1 species in the Lower Ordovician oils have $DBE > 8$, which indicates they have relatively high thermal maturity. Low thermal maturity cannot contribute to the differences observed for the TZ83 and ZG5-2 oils, because these oils have high or very high thermal maturity as indicated by their lack of biomarkers, such as steranes and terpanes, which were depleted by thermal cracking.

Fig. 4 shows the relative abundance of the S_1 species with different DBE values. Compounds with $DBE=9$ are the most abundant species in the Lower Ordovician oils (Figs. 4a, b), with an exception of the oil from Well TZ83 (O_1) (Fig. 4f). For the $DBE=9$ S_1 species, their concentrations increased as

the thermal maturity increased (Fig. 4), and most of these species are DBTs (Li et al, 2011b; Shi et al, 2010a). The relative abundance of the $DBE=9$ S_1 species in the oils from Well TZ12 (S_1 , O_3), which have the lowest thermal maturity among the oils studied (Li et al, 2010a), is 11.45–13.07 % (Fig. 4e). By comparison, the relative abundances of the $DBE=9$ S_1 species in the Lower Ordovician oil from wells ZG501, ZG11 and ZG13 range from 22.48–28.39 % (Figs. 4a and b). These oils have a relatively high thermal maturity. These results show that the relative abundance of the $DBE=9$ S_1 species can vary largely among oils with different thermal maturity levels, in a similar manner to the DBTs abundance in the oils

(Fig. 1b). This suggests that the aromatic sulfurs detected in the oils by GC/MS and FT-ICR MS are related to the oils' origins. Earlier investigations have shown that the thermal maturity of the oils decreases in the order of Fig. 4a>b>c>d>e (Li et al, 2010a, b; 2011a, b). The relative distributions of the S_1 species in the oils are very different (Fig. 4). The relative abundances of the S_1 species with DBE=1–8 decreased with increasing thermal maturity, while the relative abundance increased with increasing thermal maturity for the S_1 species with DBE=9 (Figs. 4a, b, c, d, and e). This does not mean that the S_1 species with low and high DBE values converge

towards an intermediate value (i.e., DBE=9), which would not be consistent with basic thermal and chemical kinetics for thermal cracking or condensation of macromolecules in crude oils. The dissolution capability of the highly condensed species may be crucial (Shi et al, 2010a), and the low solubility of the high DBE species may result in relative enrichment of DBE=9 compounds. The curves for the oils from TZ83 (O_3 , O_1) and TZ821 are different to the other oils, which suggests that there are other factors controlling the compositions of these oils (Li et al, 2011b).

Fig. 4 Relative distribution of the S_1 species with varying DBE values of oils in the Tazhong Uplift

4.3 Formation mechanisms of the oils (O_1) with unusually high DBT concentrations in the Tazhong Uplift

4.3.1 Effects of thermal maturity on the aromatic sulfur compounds in the oils

The absolute and relative abundances of DBTs in the aromatic compounds in the Lower Ordovician oils are positively correlated to the ratios of saturated HCs/aromatics, 1,3,7-/(1,3,7+1,2,5)-methyl naphthalene (TMNr) and 1,3,6,7-/(1,3,6,7+1,2,5,6+1,2,3,5)-methyl naphthalene (TeMNr). These ratios can be used as thermal maturity or maturity-related indicators for the oils (Li et al, 2010a). The factors controlling the variation in the abundance of DBTs in the oils with the thermal maturity are not clear. The relative and absolute abundances of DBTs are positively correlated with DBE_9/DBE_{1-17} in this study (Figs. 5a, b), which indicates that there is a close link between the DBTs and S_1 species with DBE=9. The range of the number of carbon atoms for the

DBTs detected by FT-ICR MS is nearly ten times that for the DBTs detected by GC/MS. Therefore, the DBTs detected by FT-ICR MS are more representative and comprehensive than those detected by GC/MS. Consequently, FT-ICR MS may be a better approach to investigate the thermal evolution of DBTs in crude oils.

The relative distribution of the S_1 species in the oils changed with the thermal maturity (Fig. 4). The ratios of the sum of the S_1 species with the DBE=1–8 to those with DBE=9 (DBE_{1-8}/DBE_9) and of the sum of the S_1 species with the DBE=9 to those with DBE=1–17 (DBE_9/DBE_{1-17}) can be plotted against the maturity indicators (saturated HCs/aromatics, TMNr and TeMNr) and used to evaluate the effect of thermal maturity on the sulfur compounds. A negative relationship was observed between DBE_{1-8}/DBE_9 and the thermal maturity indicators (Figs. 6a, b, and c), whereas a positive relationship was observed between DBE_9/DBE_{1-17} and the thermal maturity indicators (Figs. 6 d, e and f), which

Fig. 5 Relationship of absolute and relative abundance of DBTs in aromatics analyzed by GC/MS and DBE₉/DBE₁₋₁₇ ratios of the S₁ species by FT-ICR MS for the oils studied

Fig. 6 Cross plots of FT-ICR MS parameters of DBE₁₋₈/DBE₉ and DBE₉/DBE₁₋₁₇ with GC/MS parameters of hydrocarbons

indicates relative enrichment of the S₁ species DBE=9. Both DBE₁₋₈/DBE₉ and DBE₉/DBE₁₋₁₇ of the S₁ species could be used as thermal maturity parameters. Particularly, because

most of the S₁ species with DBE=9 value are actually DBTs, the enrichment of these species in the oils with increasing thermal maturity explains why the majority of the Lower

Ordovician oils in the Tazhong Uplift have unusually high DBT concentrations. Thermal maturity is obviously important in the formation of these oils. There is no obvious enrichment of the S_1 species with $DBE > 9$ in the oils with high thermal maturity, and this may be related to the low solubility of species with high DBE values (Shi et al, 2010a). These species may arise from solid phases such as asphaltene and/or pyrobitumen in the reservoir rocks. The enrichment of the S_1 species with $DBE = 9$ in the oils with a relatively high thermal maturity is a static survey, and the mechanisms for this remain uncertain.

In addition to the aromaticity (DBE) of the S_1 species, the thermal maturity also affects the length of the alkyl side chains of the compounds. Positive relationships were observed between the ratio of C_{10} – C_{19} homologs to C_{20} – C_{50} homologs of the S_1 species with $DBE = 9$ ($C_{10-19}/C_{20-50}DBE_9$) and the ratios of saturated HCs/aromatics, TMNr, and TeMNr (Fig. 7). These results indicate that the long side chains break into shorter ones with increasing thermal maturity, which is very common for hydrocarbons in saturated and aromatic fractions of crude oils.

Thermal maturity appears to be a critical factor in the formation of oils with high DBT concentrations and high or very high thermal maturity in the Lower Ordovician in the Tazhong Uplift. The results that support this include the enrichment of S_1 species with $DBE = 9$ with increasing thermal maturity, the apparent link between DBTs in the aromatics and S_1 species with $DBE = 9$ in all the oils, and the larger range of the sulfur compounds detected by FT-ICR MS than GC/MS (suggesting that the results from FT-ICE MS are much more representative). The relative abundance of dibenzothiophenes with maturity should be complex, which may be controlled by the thermal stability of various hydrocarbons and non-hydrocarbons.

4.3.2 Effects of TSR on the aromatic sulfur compounds

S_1 species with low DBE values (i.e., 1–6) were detected in several of the oils, including TZ83 (O_1 , O_3) and TZ821 (O_3) (Figs. 3h, 4f, 6a, 6b, and 6c). Species with $DBE = 1, 3$, and 6 are primarily sulfur ethers, thiophenes and benzothiophenes, respectively, with relatively low thermal maturity (Shi et al, 2010a). These compounds are usually present in less mature oils. However, this is not consistent with the fact that TZ83 (O_1 , O_3) and TZ821 (O_3) have high or very high thermal maturity, and the distribution pattern of the S_1 species in TZ83 (O_1) is different to the oils with relatively low maturity (i.e. YM206) (Figs. 3h, i, and j). Secondary alteration of the oil within the reservoir is the only possible cause for this inconsistency. Furthermore, relatively high H_2S concentrations were detected in the gases associated with TZ83 (O_1) (Table 1). Many earlier case studies of oilfields and laboratory investigations have shown that TSR can produce high levels of H_2S (Ho et al, 1974; Sassen R and Moore, 1988; Chakhmakchev et al, 1995; Cai et al, 2004; Hu et al, 2010). Some TSR products were also detected by GC/MS in TZ83 (O_1) oil (Jiang et al, 2007), including thiophenes with long side chains and thio-diamantane, which is produced from hydrocarbons by incorporation of inorganic sulfur during TSR (Jiang et al, 2007). All of these factors suggest that TSR probably led to the coexistence of sulfur compounds with a

Fig. 7 Cross plots of $C_{10-19}/C_{20-50}DBE_9$ with GC/MS parameters

wide range of thermal stabilities in the oils. Further studies are required to clarify if the TSR occurs in situ.

The abnormalities observed with the oils from Well TZ83 (O_3) and Well TZ821 (O_3) (Fig. 4f; Figs. 6a, b, and c) can be related to those in the TZ83 (O_1) oil. The TZ83 (O_3) and TZ83 (O_1) oils are from different intervals of the same well. Source-connecting faults near Well TZ83 were recognized as one of the most important predominant vertical migration pathways (Xiang et al, 2009). As a result, some of the hydrocarbons in the Upper Ordovician might have migrated from the Lower Ordovician of Well TZ83. Similarly, the TZ821 (O_3) and TZ83 (O_1) wells are located near each other and these oils could have mixed through lateral migration (Li et al, 2010a).

Theoretically, thiophenes and benzothiophenes with relatively low thermal stability would transform into compounds with relatively high thermal stability (i.e., DBTs) during thermal evolution. The absolute and relative abundances of the DBTs are not largely different between

the TZ83 (O₁) oil and the other oils (Fig. 1b). Considerable amounts of low DBE species, such as sulfur ethers and thiophenes, in the TZ83 (O₁) oil are probably the product of recent or current TSR, and these have not yet been transformed into their counterparts with relatively high thermal stability. Whether or not the other Lower Ordovician oils without sulfur ethers and thiophenes contain some TSR altered oils could not be determined at present. Also, it could be determined if TSR occurred at intervals deeper than the Lower Ordovician. The only TSR evidence that has been discovered so far includes the high H₂S content in the Lower Ordovician oil and associated gas, which is possibly a result of hydrocarbon migration and mixing, and the high mercaptan content, which is possibly a product of oil thermal cracking.

There are multiple factors controlling the composition and distribution of the aromatic sulfur compounds in crude oils, including the paleoenvironment of the source rocks, organic source input, thermal maturity, water-washing, and TSR (Li et al, 2011a, b). In our previous studies, we found that only source rocks with a relatively low organic richness, such as limestones, argillaceous limestone, marlstone and calcareous mudstone, were detected in rock extracts with a relatively high abundance of DBTs (unpublished data). Compared with the oil and gas prone mudstone and shale with relatively high organic richness in the Tarim Basin, the rocks with relatively low organic richness are unlikely to be the main source rocks of the Lower Ordovician oils. Particularly, the Lower Ordovician oils contained a relatively high abundance of DBTs, and they reportedly have a close affinity to the overlying Middle-Upper Ordovician oils (Li et al, 2011a). This suggests that different types of source rocks are unlikely to be the main factor leading to the differentiation of the Upper and Lower Ordovician oils. Water-washing and biodegradation may affect the sulfur compounds present in the oils. However, the temperature of the reservoir below the 5000 m of the Lower Ordovician in the Tazhong Uplift is not suitable for microorganisms, and the impact of biodegradation on the oils can be excluded. In summary, the thermal maturity and TSR, are suggested to be crucial factors for the formation of the oils with unusually high DBT concentrations in the Lower Ordovician of the Tazhong Uplift.

5 Conclusions

Compared with conventional GC/MS analysis, FT-ICR MS can be used to detect large sulfur compounds. This method was used to study the formation mechanism of oils with unusually high DBT concentrations from the Lower Ordovician interval in the Tazhong Uplift.

The GC/MS results for the absolute and relative abundance of DBTs in the Lower Ordovician oils correlated with the DBE=9 S₁ species, which are primarily DBTs, detected by FT-ICR MS. The range for the number of carbon atoms in the compounds detected by FT-ICR-MS (C₁₁–C₄₈) was ten times larger than that for GC-MS (C₁₂–C₁₅). Therefore, FT-ICR MS provides a more comprehensive and representative analysis of the DBTs than GC/MS.

The different S₁ species showed large differences in their relative abundance as the thermal maturity of the oil

increased. The relative abundance of the S₁ species with DBE=1–8 decreased as the thermal maturity increased, while the relative abundance of the S₁ species with DBE=9 increased with increasing thermal maturity. Because of thermal cracking, the S₁ species with relatively short side alkyl chains became more predominant over their homologs with long side alkyl chains as the thermal maturity increased. In conclusion, thermal maturity is a crucial factor in the formation of oils with unusually high DBTs concentrations in the Lower Ordovician of the Tazhong Uplift.

Large amounts of sulfur ether, thiophene, and benzothiophenes with low DBE values and low thermal stability were detected in a few of the Ordovician oils, and they could be produced by TSR. TSR could affect the concentrations of DBTs in the oils. The FT-ICR MS results showed no obvious signs of recent or current TSR for most of the Lower Ordovician oils. However, TSR could be occurring or have recently occurred in deeper intervals.

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