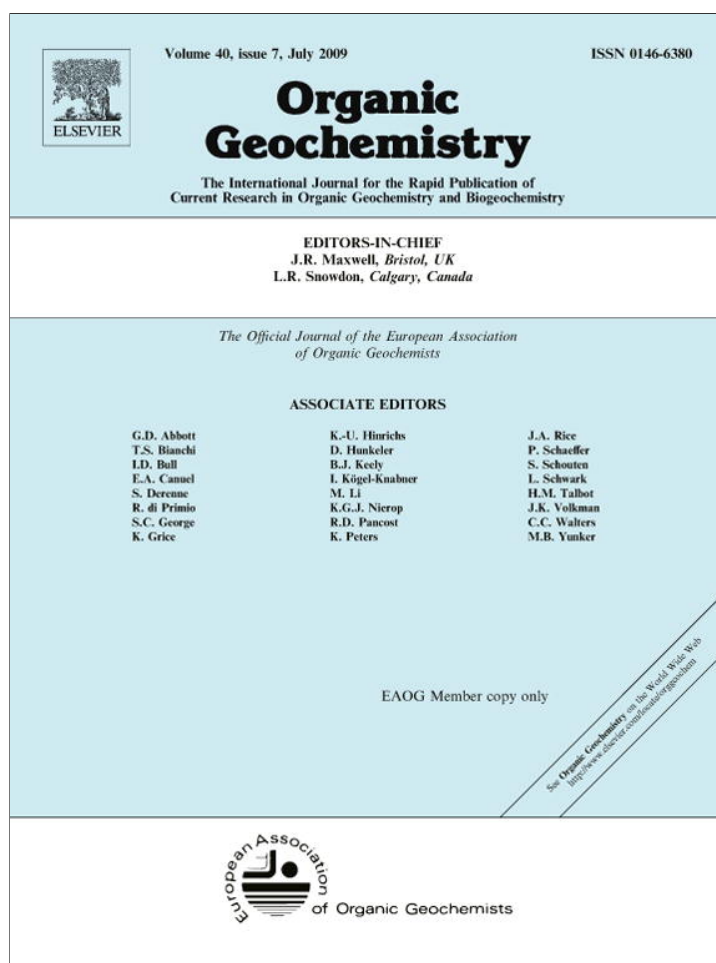


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Distinguishing Cambrian from Upper Ordovician source rocks: Evidence from sulfur isotopes and biomarkers in the Tarim Basin

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ABSTRACT

The reported source rocks for the abundant petroleum in the Tarim Basin, China range from Cambrian to Lower Ordovician and/or Upper Ordovician in age. However, the difference between the two groups of source rocks is not well characterized. In this study, pyrite was removed from eleven mature to over mature kerogen samples from source rocks using the method of CrCl₂ reduction and grinding. The kerogen and coexisting pyrite samples were then analyzed for $\delta^{34}\text{S}$ values. Results show that the kerogen samples from the Cambrian have $\delta^{34}\text{S}$ values between +10.4‰ and +19.4‰. The values are significantly higher than those from the Lower Ordovician kerogen ($\delta^{34}\text{S}$ of between +6.7‰ and +8.7‰), which in turn are generally higher than from the Upper Ordovician kerogen samples ($\delta^{34}\text{S}$ of between –15.3 and +6.8‰). The associated pyrite shows a similar trend but with much lower $\delta^{34}\text{S}$ values. This stratigraphically controlled sulfur isotope variation parallels the evolving contemporary marine sulfate and dated oil $\delta^{34}\text{S}$ values from other basins, suggesting that seawater sulfate and source rock age have an important influence on kerogen and pyrite $\delta^{34}\text{S}$ values. The relatively high $\delta^{34}\text{S}$ values in the Cambrian to Lower Ordovician source rocks are associated with abundant aryl isoprenoids, gammacerane and C₃₅ homohopanes in the extractable organic matter, indicating that these source rocks were deposited in a bottom water euxinic environment with water stratification. Compared with the Upper Ordovician, the Cambrian to Lower Ordovician source rocks show abundance in C₂₈ 20R sterane, C₂₃ tricyclic terpanes, 4,23,24-trimethyl triaromatic dinosteroids and depletion in C₂₄ tetracyclic terpane, C₂₉ hopane. Thus, $\delta^{34}\text{S}$ values and biomarkers of source rock organic matter can be used for distinguishing the Cambrian and Upper Ordovician source rocks in the Tarim Basin.

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1. Introduction

Huge petroleum resources have been found reservoir in the Cambrian, Ordovician, Carboniferous and Triassic in the Central Tarim and Tabei uplifts in the Tarim Basin, China. However, debate is ongoing about the source of the oils. Potential source rocks for the petroleum include the Cambrian to Lower Ordovician and the Upper Ordovician (Zhang et al., 2000a; Sun et al., 2003; Gong et al., 2007). Biomarkers in the crude oils have been well characterized; for example, aryl isoprenoids were detected in aromatic and asphaltene fractions in all the oils analyzed in this area (Sun et al., 2003; Jia et al., 2007). However, aryl isoprenoids have seldom been reported in the source rocks (Jia, 2004).

It has been proposed that sulfur isotopes can be used as a tool for oil–source and oil–oil correlations (Thode, 1981; Orr, 1986; Premuzic et al., 1986; Cai et al., 2007). Oils have been found to be enriched in ³⁴S up to 2‰ relative to their parent kerogen in the source rock (Orr, 1986). This proposal has been supported by closed system, dry and hydrous pyrolysis of immature kerogen (Idiz et al., 1990; Amrani et al., 2005).

However, few kerogen $\delta^{34}\text{S}$ values have been reported. One of the reasons is that it is difficult to remove contaminant pyrite from kerogen. Much of the pyrite in kerogen occurs as framboids (collections of tiny pyrite crystals in a cluster) and single crystals (<50 μm). Pyrite is dispersed in the kerogen and is commonly coated with organic matter; these coatings effectively hinder removal of pyrite using chemical reagents (Amrani et al., 2005).

Many methods, including LiAlH₄, 6 N HNO₃ and 2.4 N HNO₃ solutions, have been used to attempt to remove pyrite from kerogen (Dinur et al., 1980; Thode, 1981; Orr, 1986). After these treat-

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ments kerogen has been reported to have variable $\delta^{34}\text{S}$ values from some studies but relatively homogeneous values from other studies. For example, Maastrichtian bituminous chalk samples from the Horon Basin, the Zefa-Efé Basin and the Nebi-Musa Basin, in the Dead Sea region of the Middle East, have been shown to have $\delta^{34}\text{S}_{\text{kerogen}}$ values of -8.0‰ , -10.2 to -10.7‰ , and $+1.2$ to $+8.3\text{‰}$, respectively. Some $\delta^{34}\text{S}_{\text{kerogen}}$ values from the Nebi-Musa Basin are close to those of oils in this area with an average of $+1.6 \pm 1.2\text{‰}$ (Aizenshtat and Amrani, 2004b). The $\delta^{34}\text{S}_{\text{kerogen}}$ value of Mississippian Lower Bakken shale from the center of the Williston Basin is $+3.5\text{‰}$, being close to those of unaltered oils from the Bakken with an average of $+2.8 \pm 0.8\text{‰}$, and is concluded to have been the source of oil in the basin (Thode, 1981).

A more effective method for separating pyrite from kerogen was developed by Acholla and Orr (1993), who used an acidic aqueous solution of CrCl_2 as the reducing agent to remove pyrite without causing significant alteration of the organic matter. However, no kerogen sulfur isotope measurements after the treatment have been reported.

A similar but simplified method was used by Joachimski et al. (2001), in which pyrite was removed using an acidic aqueous solution of CrCl_2 on whole rock powder. The residue was presumably pyrite free, and was directly burned using an Eschka[®] (Merck 3162) to transform organically bound sulfur to BaSO_4 , on which $\delta^{34}\text{S}$ values were measured. However, no data were presented to show that pyrite was completely removed from the samples.

In this paper, we have collected samples of all potential source rocks in the Tarim Basin and adopted the method of Acholla and Orr (1993) to remove inorganic sulfur from kerogen which have then been analysed for $\delta^{34}\text{S}$. The objectives of the study are to distinguish the Cambrian to Lower Ordovician source rock and the Upper Ordovician source rock based on $\delta^{34}\text{S}$ values cross checked against new biomarker data, and to discuss possible factors that control the differences in kerogen $\delta^{34}\text{S}$ values. In a subsequent paper, we will report $\delta^{34}\text{S}$ values of oils from the Tarim Basin and discuss oil-source rock correlation.

2. Geological setting

The Tarim basin, located in the northwest of China (Fig. 1a), has been shown to have good prospects for petroleum exploration. Recently, more than five billion barrels of oil equivalent (proven and controlled reserves; Jiaotong, 2005; Xinhuanet, 2005) have been found in the Ordovician carbonate rocks in the Central Tarim and Tabei uplifts (Fig. 1a).

2.1. Stratigraphy and structure

A description of the geological settings of the Tarim Basin has been published previously (Cai et al., 2001, 2008). In brief, Ediacaran (Upper Neoproterozoic) beach to shallow marine facies sediments lie on Archean and Proterozoic crystalline basement. The overlying Cambrian and Ordovician strata are composed of platform facies limestone and dolomite, slope facies limestone and marlstone, and basinal facies mudstone, shale and marlstone. The Silurian to Carboniferous sequence consists of marine sandstone and mudstone. Permian strata are composed of lacustrine sediment and volcanic rock. Continuing the emergence of the sediments, Mesozoic and Cenozoic units are represented by non-marine fluvial sandstone and mudstone.

Several orogenies led to 18 recognized unconformities in the basin (Fig. 1b and c). Basin scale unconformities include Ediacaran/Pre-Ediacaran, Silurian/Pre-Silurian, Carboniferous/Pre-Carboniferous, Triassic–Upper Permian/Pre- (Triassic–Upper Permian), Cretaceous/Pre-Cretaceous and Eocene/Pre-Eocene

contacts (Jia, 1997; Wang, 2006). The Middle and Upper Ordovician in the eastern Central Tarim and Tabei areas were completely removed by erosion during the late Caledonian Orogeny at the end of Ordovician. No Devonian or Silurian strata remain in the majority of the Tabei area as a result of the early Hercynian Orogeny at the end of the Devonian. The late Yanshanian Orogeny, during the Neogene, resulted in either no sedimentation or complete removal of the Cretaceous in the Southwest Depression, eastern Central Tarim. These orogenies, and resulting fracturing and tilting, have been linked to large scale fluid cross formational flow in the Tarim Basin (Cai et al., 2008).

In the central Tarim, early Paleozoic strata form a wide anticline and the late Paleozoic occurs as a nose shaped structure which dips towards the west whereas Mesozoic and Cenozoic strata dip very gently (Xiao et al., 2000a; Cai et al., 2001). Thus, the Central Tarim became a palaeo-uplift at the end of the Ordovician (Jia, 1997). A few large thrust faults in the east–west direction have developed, dividing the Central Tarim area. Fault No.1 was active during the Caledonian Orogeny at the end of the Ordovician and cut Ordovician, Cambrian and late Neoproterozoic (Ediacaran) strata and pre-Ediacaran basement (Fig. 1b). This fault was reactivated during subsequent orogenies. Faults and fractures in the uplift are considered to be important conduits for upward migration of oil and gas from the Cambrian and Ordovician source rocks (e.g. Cai et al., 2001).

The Tabei area became a single large scale uplift (YM – Lunnan Uplift, Fig. 1) at the end of the early Ordovician due to the late Caledonian orogeny (Jia, 1997; Zhang, 2000). It was then separated into the discrete Xinhe, Lunnan and Kuerle paleo-uplifts from the west to the east. The Lunnan area was transformed into a large scale nose uplift during the Devonian when it was affected by the early Hercynian orogeny. The Lunnan and Sangtamu fault-horst belt was formed as a result of east–west faulting during the late Hercynian orogeny at the end of the early Permian. Thrusting in the south of the basin was significantly greater than in the north as a result of different structural stresses. Thus, the basement subcrop surface dips toward the north and formed the present day uplifted structure during the Cenozoic period (Lü et al., 2004). Up to the present day, many oil and condensate fields, including the Tahe and YM oilfields, have been discovered in the Tabei area, with petroleum coming out of Ordovician, Carboniferous, Triassic and Jurassic reservoirs.

2.2. Source rocks

Reported source rocks for the petroleum in the basin show significant differences in depositional environment and TOC (Table 1).

2.2.1. Cambrian and Lower Ordovician source rocks

The Cambrian abyssal to bathyal facies mudstone, carbonaceous shale and marlstone are found around the Manjiaer depression and the Eastern Tarim and Keping uplifts (Fig. 2). The source rocks have total organic carbon (TOC) values generally from 1.2–3.3 wt%, but reach a maximum of 7.6 wt%. Strata with TOC >1.0 wt% occupy 60–70% of the sequence and the net source rock thickness ranges from 120–415 m (Zhang et al., 2000a).

The other source rock is the Cambrian evaporitic lagoon facies, composed of anhydritic dolomite and argillaceous dolomite. This source rock occurs in the Central Tarim and Bachu Uplift. In the Central Tarim area, this source rock was encountered in wells Z4 and TC1 with TOC from 0.16–0.85 wt% (average of 0.6 wt%) and a thickness up to 265 m (Jia, 2006). In the Bachu Uplift, this source rock was encountered in wells He4 and F1 with TOC ranging from 0.5–2.4 wt% and a thickness of 173 m and 195 m, respectively. The $\delta^{13}\text{C}$ values for the He4 evaporite source rock range from -29.4 to -31.8‰ (Cai et al., 2002).

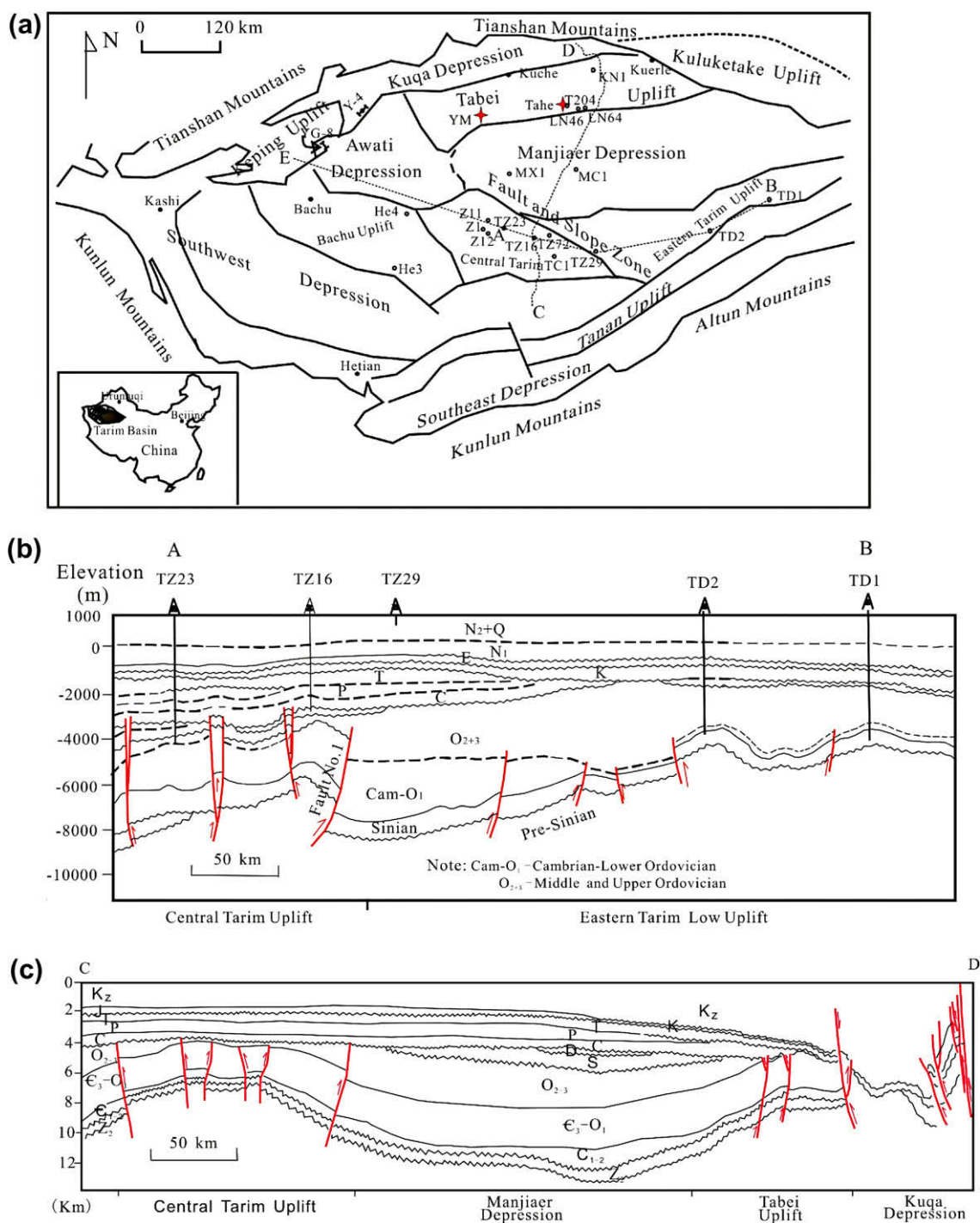


Fig. 1. (a) Map of the Tarim Basin showing tectonic units, locations of sampled wells and outcrops and cross sections AB, CD and EB; (b) west-east cross section AB; and (c) south-north cross section CD.

The O₁₋₂ Heituo Formation bathyal sediments, which are composed of under compensated basin facies carbonaceous, siliceous mudstone and graptolite or radiolarian shale, was encountered in wells TD1 and TD2 in the Eastern Tarim Uplift with TOC values from 0.84–2.7 wt% (average of 1.9 wt%). The Heituo Formation has a thickness of 48 m in well TD1 and 63 m in well TD2. In the Queerquekeshan outcrop in the Kuluketake Uplift in the east of the basin (Fig. 1a), this carbonaceous and siliceous shale is 12 m thick with TOC from 0.6–2.1 wt% ($n = 3$; Jia, 2006). It is expected

that this candidate source rock extends laterally over the whole Manjiaer Depression.

Based on maceral analyses of polished thin sections of the source rocks, organic matter is mainly composed of striated algal residue, suggesting type I-II₁ kerogen for the Cambrian and Lower Ordovician source rocks (Xiao et al., 2000b; Wang et al., 2003; Jia, 2006). The source rock samples analysed for TOC have VRE (vitrinite reflectance equivalent), which is measured on reflectance values of marine vitrinite-like macerals and bitumen; Xiao et al.,

Table 1
Characteristics of organic matter from the Cambrian to Ordovician strata^a.

	Formation	Organic facies	Lithology	TOC (wt%) ^b	Thickness (m)	VRE (%)	Kerogen type	Distribution	$\delta^{34}\text{S}$ (‰) ^c
Middle to Upper Ordovician	Lianglitage formation (O ₃)	Marginal platform slope facies lime-mud mound	Marlstone and argillaceous limestone	0.21–1.99/0.93 0.2–0.85/0.43 Mainly 0.49–0.84, up to 3.3	33 m Up to 12.5 m 20–80 m for TOC >0.5%	0.81–1.3	Mainly type I; some II ₂ to III	Limited to Well He3 in Bachu Tabei Central Tarim	+5.8 –15.3 +3.8 to +6.8
	Saergan Formation (O _{2–3})	Marginal shelf to basin facies	Black mudstone and shale	0.56–2.86/1.56	10–30 m	1.1–1.3		Limited to Keping and Awati	+6.8
Cambrian to Lower Ordovician	Heituao formation (O _{1–2})	Bathyal starved basin facies	Carbonaceous, siliceous mudstone and graptolite or radiolarian shale	0.6–2.67/1.8	12–63 m	1.5–2.3	I–II ₁	Eastern Tarim, Kuluketake and Manjiaer	+6.7 to +8.7
	Cambrian	Evaporated lagoon facies Byssal to bathyal facies	Anhydritic dolomite and argillaceous dolomite Mudstone, carbonaceous shale and marlstone	0.16–0.85/0.6 (Z4) 0.5–2.43%/0.8 Mainly 1.2–3.3, up to 7.6	80 (TC1)–265 m (Z4) 173–195 m 120–415 m			Central Tarim Bachu Uplift Manjiaer, Eastern Tarim and Keping	+10.4 +13.8 to +19.4

^a See text for data source.
^b TOC is expressed as range/average.
^c See Table 2 for detail.

2000b; Wang et al., 2003) from 1.5–2.3% (Table 1) and thus are over mature, showing low H/C atomic ratios mainly from 0.2–0.8 and amounts of extractable organic matter mainly from 120–220 ppm (Wang et al., 2005; Ma et al., 2006; Jia, 2006). The pre-maturation TOC values presumably would have been significantly higher.

2.2.2. Upper Ordovician source rocks

The Middle and Upper Ordovician source rocks include the Saergan and Lianglitage formations. The Saergan Formation marginal shelf to basin facies black mudstone and shale has a thickness from 10–30 m, and reported TOC values from 0.56–2.86 wt% with an average of 1.56 wt% in the Keping Uplift (Zhang et al., 2000b).

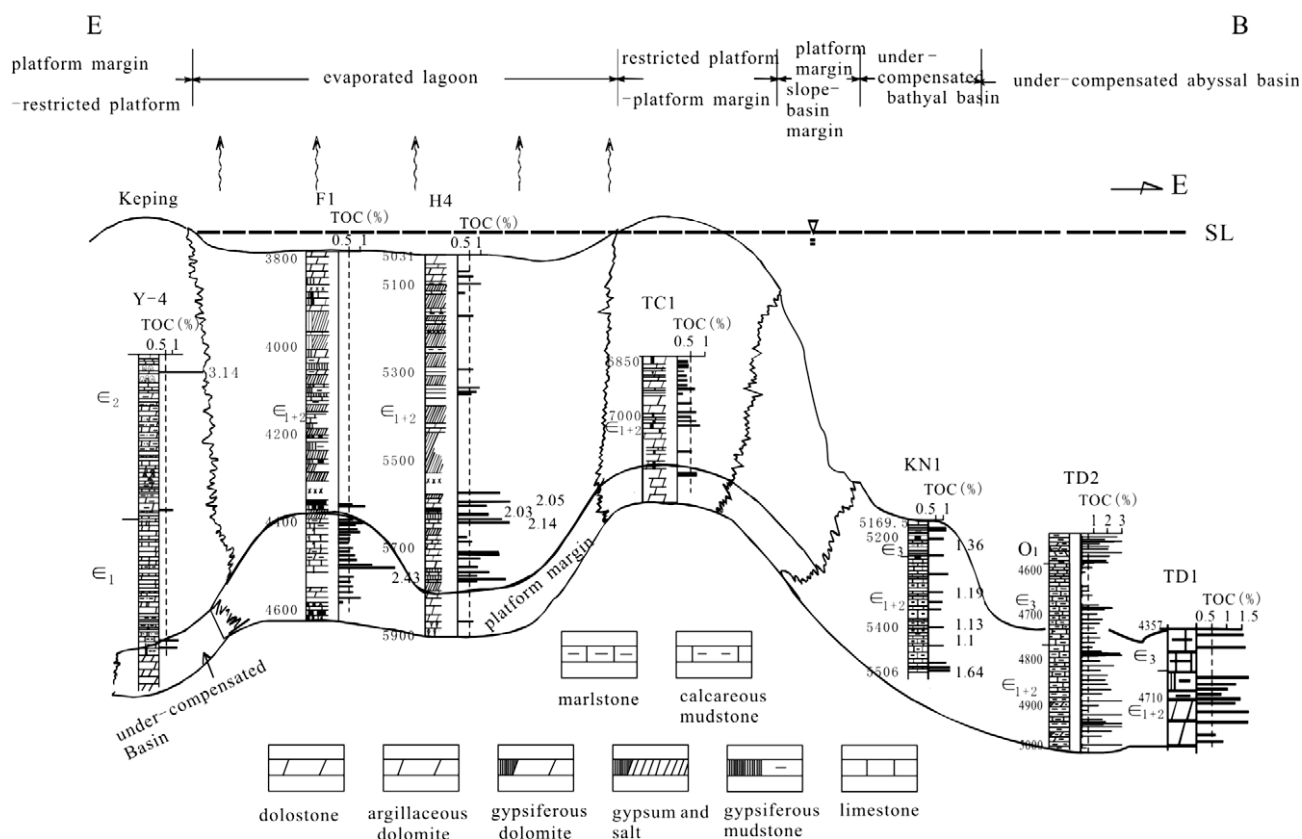


Fig. 2. Variation of sedimentary facies and TOC of the Cambrian and Lower Ordovician source rocks in the cross section EB.

However, the sample analysed in the present study has a TOC value of 4.4 wt%. The extractable organic matter ranges from 470–4090 ppm with an average of 1188 ppm. A similar source rock is likely to occur in the Awati depression, based on organic facies analysis, but not in the Central Tarim, Bachu and Tabei areas (Gao et al., 2006).

The O₃ Lianglitage Formation source rock is found in the Central Tarim, Bachu and Tabei areas. In the Central Tarim, this source rock is a marginal platform to slope facies, lime mud mound marlstone and argillaceous limestone with TOC values mostly from 0.49% to 0.84 wt%. A few samples show TOC values higher than 1.0%, with a maximum value of 3.3 wt% in well Z11 (Wang et al., 2005). Extractable organic matter ranges from 100–1395 ppm (Zhang et al., 2000b). The cumulative thickness for TOC > 0.5 wt% ranges from 20–80 m in 13 wells in the northern slope and the crest of the Central Tarim (Jia, 2006). Similar rocks were encountered in the well LN46 in the Tabei Uplift, and in wells He3 and He4. The Upper Ordovician source rock in well He3 is 33 m thick and has TOC from 0.21–1.99 wt% with an average of 0.93 wt% in the Bachu Uplift. In the Tabei area, the Upper Ordovician source rock has a thickness up to 12.5 m, TOC values from 0.2–0.85 wt% with a mean of 0.43 wt% (Zhang et al., 2000b). These source rocks seem to undergo lateral facies (and commensurate TOC) changes on a small scale. For example, Upper Ordovician rocks, equivalent to the source rock units, have TOC values less than 0.4 wt% in wells such as Z1, Z4, Z11 and Z12 in the Central Tarim (Jia, 2006); and less than 0.11 wt% in well LN64 in the Tabei area (Wang et al., 2005). It was concluded that the distribution of the O₃ source rock with TOC > 0.5 wt% in the Tabei and neighbouring areas is very limited and presumably spatially heterogeneous (Wang et al., 2005). Sediments with high TOC values have been found in palaeo-depressions between mounds, or as banded occurrences. Thus, the thickness and TOC for the source rock varies significantly both vertically and laterally.

The O₃ source rocks have VRE mainly from 0.81–1.3% (Zhang et al., 2000b; Wang et al., 2003, 2005; Jia, 2006). The source rocks contain type I and type II₂–III like kerogen (Zhao et al., 2000; Wang et al., 2005; Gao et al., 2006). Source rocks with high TOC tend to contain type III like kerogen (Zhao et al., 2000; Wang et al., 2005). Macerals in the type III like kerogen are composed of 64–93% vitrinite-like maceral, 1–34% amorphous maceral, 1–15% liptinite and 0–7% inertinite (Zhao et al., 2000). Unlike typical type III kerogen from higher plants, the vitrinite group macerals were derived from benthic brown algae or macro algae, acritarchs, cryptospores and arthropods (Zhang et al., 2000b; Zhao et al., 2000). ¹³C NMR data show that the type III like kerogen is mainly composed of aromatic and short chained aliphatic carbon, and thus is not oil prone (Zhao et al., 2000).

The Upper Ordovician type I source rocks are composed of 88–99% amorphous macerals and less than 10% vitrinite and inertinite macerals with organisms mainly derived from pelagic algae, and are oil prone. TOC for the source rocks is generally less than 1.0%.

2.3. Burial and thermal history

The burial and geothermal histories of different tectonic units of the Tarim Basin have been reported previously (Xiao et al., 2000a; Cai et al., 2001, 2002; Wang et al., 2006; Gong et al., 2007). For comparison, the histories of wells with high TOC source rocks from the different tectonic units have been collated here (Fig. 3).

Fig. 3 shows that the Cambrian to Lower Ordovician source rocks in wells TZ29, MX1, TC1 and TD2 were rapidly buried to >4000 m as a result of subsidence during the Cambrian to Ordovician. The temperature increased rapidly to 130–150 °C with a resulting vitrinite reflectance (*R*_o) increase to 1.1–1.5%. Peak oil generation took place during the late Ordovician (440–450 Ma) in the Eastern Tarim Basin

(Wang et al., 2006), and from the end of the Silurian to the Permian in the Central Tarim Uplift (e.g. Yang et al., 2004; Xiao et al., 2005) and Manjiaer Depression (Xiao et al., 2000a).

The Upper Ordovician (O₃) source rocks in wells TC1 and LN46 (Fig. 3) and TZ12 (Cai et al., 2001) became marginally mature as a result of subsidence during the Permian. It was concluded that oil generation for the Upper Ordovician source reached a peak during the Tertiary (Zhang et al., 2000a). The Upper Ordovician (O₃) source rock in well He3 was significantly uplifted during the late Silurian to the Devonian and during the period from the late Permian to the Eocene. The source rock first became mature as the result of subsidence during the early Permian, and oil generation was considered to have reached a peak during the Himalayan Orogeny (Neogene).

It can be concluded that the Cambrian to Lower Ordovician source rocks show more rapid sedimentation and burial than the Middle to Upper Ordovician source rocks. This inevitably led to more rapid organic matter maturation and petroleum generation.

3. Experimental

3.1. Samples

Eleven source rock samples include two from outcrops in the Keping and Akesu areas, and nine from well cuttings in the Bachu, Central Tarim, Tabei and Eastern Tarim uplifts (Fig. 1). The 11 samples represent potential source rocks, most of which have been widely used for the purpose of oil-source rock correlation in the Cambrian and Ordovician successions of the basin (Zhang et al., 2000a,b; Ma et al., 2004, 2006; Jia, 2004). All 11 samples were analysed for sulfur isotopes. Eight of the 11 samples were analysed by GC–MS. Two other samples were collected from a high TOC interval (TOC from 0.99–3.54%) at depths from 5335–5358.4 m in well Z11 (Wang et al., 2005) for GC–MS analysis.

Nine oils were collected from the basin, and analysed for their $\delta^{34}\text{S}$ values. These oils were not associated with H₂S and non-degraded, based on biomarker distributions (Cai et al., 2007).

3.2. Analytical methods

3.2.1. Kerogen separation and $\delta^{34}\text{S}$ measurement

Fresh rock samples, after having their potentially weathered surfaces removed, were finely ground and extracted with dichloromethane (CH₂Cl₂) to remove soluble bitumen and elemental sulfur. Next, these samples were treated with hot 6 N HCl, a mixture of 6 N HCl and 40% HF, and then 6 N HCl, to dissolve minerals. After dilution by distilled water and centrifugation, the remaining kerogen was separated from the residue (precipitate) using heavy liquids (KBr + ZnBr) with densities of 2.0–2.1 g/cm³. Subsequently, pyrite was further removed from the kerogen using a method similar to that reported by Acholla and Orr (1993); a mixture of hot 6 N HCl and CrCl₂ were added to the kerogen under nitrogen with gas flow carrying the H₂S to a trap where it was recovered as Ag₂S. Excess acids and acid soluble salts were removed from the residual kerogen by water washing (Acholla and Orr, 1993). About 2 h later, the residual kerogen was collected, and reground to expose new pyrite surfaces, and the whole procedure was repeated. After the two treatments, the residual kerogen was further analyzed using X-ray diffraction (XRD) to determine whether pyrite was below the detection limits ($\leq 0.5\%$ depending on conditions). If not (for example if the amount of the treated kerogen and/or contents of pyrite in the kerogen is too high), more treatments were employed. For comparison, the conventional, straightforward and single step 6 N HCl treatment of kerogen was also carried out in this study.

Two samples after the treatment were analysed for elemental composition using a Leco 932 instrument.

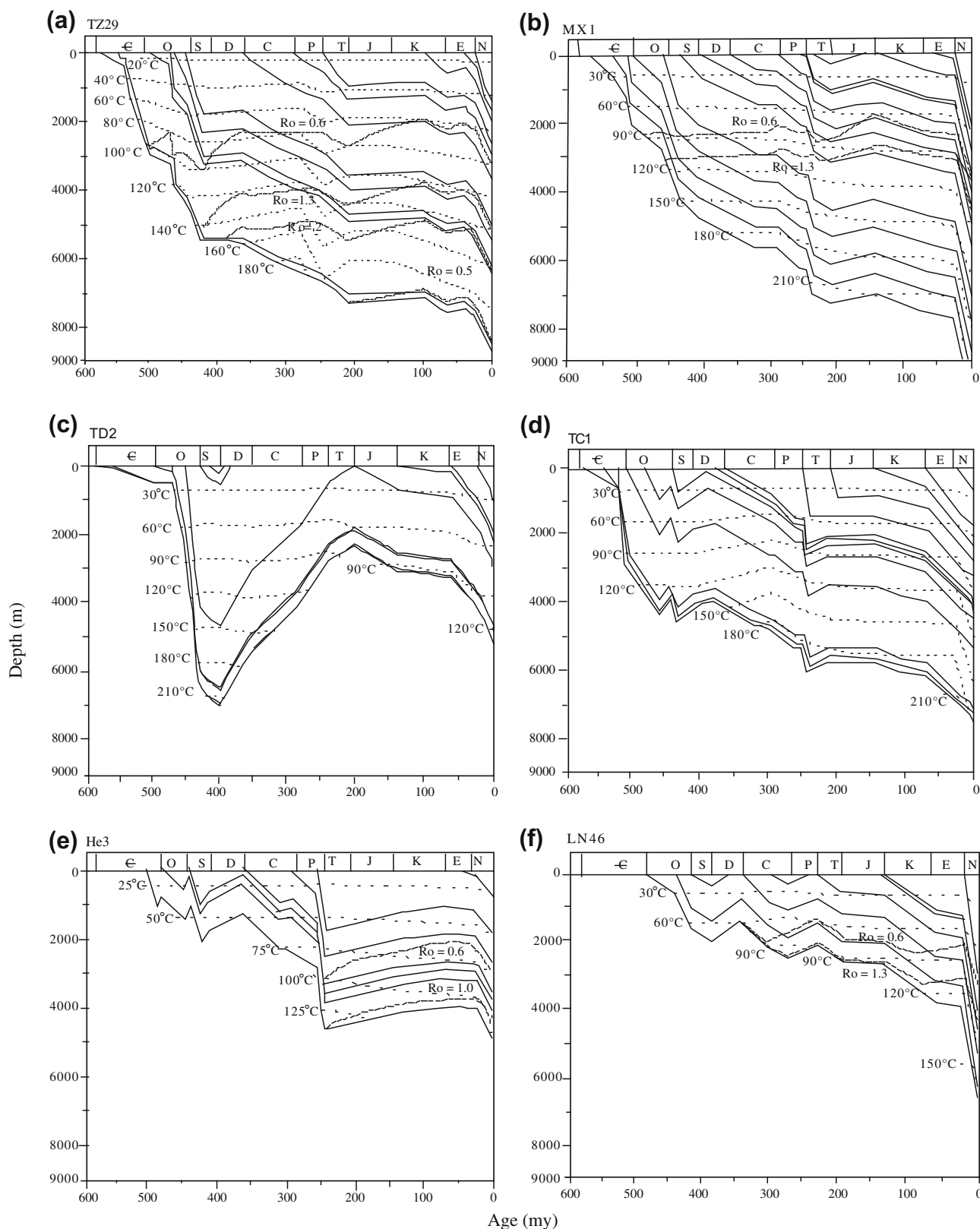


Fig. 3. Burial histories of wells TZ29, MX1, TD2, TC1, He3 and LN46 from different tectonic units showing the Cambrian and Lower Ordovician sediments were rapidly buried to >4000 m while the Upper Ordovician was uplifted soon after the deposition.

A known weight (between 350 and 900 mg) of kerogen, with pyrite less than the XRD detection limit, was combusted in a Parr bomb apparatus at ~25 atm oxygen to oxidize organically bound sulfide to sulfate. Dissolved sulfate was then precipitated as BaSO₄

and weighed to give total residual kerogen sulfur. Dissolved iron was measured at pH < 2, using an atomic absorption spectrometer, to determine maximal residual pyrite content in the kerogen after the chromium reduction (assuming that all Fe occurs as pyrite in

Table 2TOC, total sulfur, pyrite sulfur contents and $\delta^{34}\text{S}$ values of kerogens and pyrite from the Cambrian and Ordovician source rocks.

Location/well	Depth (m)	Formation	Lithology	TOC (%)	Kerogen after the CrCl_2 treatment					
					$\text{S}_{\text{TR}}^{\text{a}}$ (%)	$\delta^{34}\text{S}_{\text{TR}}$ (‰)	Py_{res} (%)	$\text{Py}_{\text{res}} \text{ S}$ (%)	$\delta^{34}\text{S}_{\text{Py}}$ (‰)	Org. S ² /TS (%)
TD2	4770.5	Cam. ^a	Dark gray mudstone	1.70	7.4	19.4	0.49	0.26	16.9	96.5
Y-4	Outcrop	Cam.	Black shale	3.31	7.0	13.8	– ^b	–	–	–
KN1	5503	Cam.	Dark gray shale	2.04	0.5	17.8	0.07	0.04	7.6	92.8
TC1	5714.55	Cam.	Muddy dolomite	0.80	–	10.4	–	–	9.3	–
T204	5852	O ₁	Dark gray micrite	0.46	4.1	6.68	–	–	–	–
TD1	4361	O ₁	Black mudstone	0.86	–	8.68	–	–	–	–
YG-08	Outcrop	O ₂₊₃	Graptolite shale	4.40	0.5	6.83	0.038	0.02	5.6	96.1
TZ12	5070	O ₃	Gray marlstone	0.82	3.6	6.78	0.64	0.34	–0.94	90.6
TZ72	5061.5	O ₃	Gray marlstone	0.42	3.4	3.81	–	–	–	–
He3	4042	O ₃	Dark gray micrite	0.93	1.2	5.8	0.04	0.02	–10.8	98.2
LN46	6152	O ₃	Gray marlstone	0.62	5.6	–15.3 ^c	0.69	0.36	–20.5	93.6

^a Cam.: Cambrian; S_{TR} : total residual sulfur, including residual pyrite sulfur and organic sulfur in kerogen after the CrCl_2 treatment; Org. S is organic sulfur; and Py_{res} is residual pyrite after the CrCl_2 treatment.

^b Represents no measurement or no data available.

^c Suspect data are not plotted.

the kerogen). Organic sulfur was subsequently calculated by subtraction of the pyrite sulfur from the total residual kerogen sulfur.

Samples of oil (1–4 g) were combusted in a Parr bomb, transforming organically bound sulfur to sulfate, and 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 $\delta^{34}\text{S}$ relative to the Vienna Canyon Diablo Troilite (VCDT) standard. The reproducibility for $\delta^{34}\text{S}$ measurement is $\pm 0.3\%$.

3.2.2. Biological markers

Source rock extracts were separated into saturates, aromatics, resins (NSO) and asphaltenes by column chromatography using *n*-pentane, dichloromethane (DCM) and methanol as chromatographic solvents. The saturated and aromatic fractions were analyzed using a Hewlett Packard 6890GC/5973MSD mass spectrometer. The gas chromatograph (GC) was fitted with a HP-5MS capillary column (30 m \times 0.25 mm \times 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 to 310 °C at a rate of 3 °C/min, and then held at 310 °C for 18 min. Helium was used as the 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.

Identification of *Chlorobiaceae* biomarkers was achieved through analysis of mass spectra, retention time and comparison with literature data (Summons and Powell, 1987; Sun et al., 2003; Brown and Kenig, 2004).

4. Results

TOC and $\delta^{34}\text{S}$ values of pyrite and kerogen after the CrCl_2 treatment along with residual pyrite content in kerogen for the samples are listed in Table 2.

4.1. Efficiency of pyrite removal from kerogen

The kerogen separated from the TD2 source rock using HCl, and then HCl + HF solution contains >20% pyrite by weight (Fig. 4a). After pyrite was removed using conventional hot 6 N HCl, more than 15 wt% pyrite still remained in the residual kerogen as shown by XRD analysis (Fig. 4b). In contrast, the residual kerogen after the two CrCl_2 treatments has pyrite below the detection limits of XRD

(Fig. 4c). This suggests that acidic chromous chloride is a more effective way to remove pyrite than 6 N HCl. This is consistent with previous findings (Acholla and Orr, 1993; Passier et al., 1999).

Total residual kerogen sulfur in the TD2 “high sulfur kerogen” after the treatment calculated from the weight of BaSO_4 (Table 2) is lower than for the direct measurement using Leco 932, suggesting that part of the BaSO_4 remained in the filtrate or was lost during the preparation.

Among the 11 kerogen samples after the chromous chloride treatment, six samples were analysed for pyrite sulfur and thus organic sulfur contents. The results show that the kerogens are composed of 0.038–0.69 wt% pyrite and 0.02–0.36 wt% pyrite sulfur

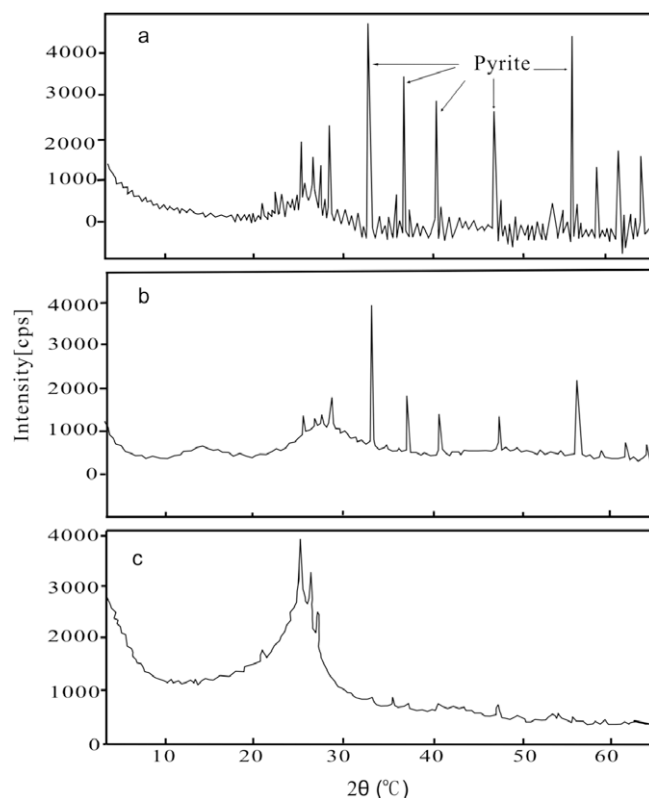


Fig. 4. XRD data showing pyrite of, (a) untreated kerogen, (b) 6 N HCl treated kerogen, and (c) 6 N HCl + CrCl_2 treated kerogen, from well TD2 mudstone at depth of 4770.5 m.

Table 3
Comparison of element composition, atomic ratios of kerogens after acidic chromous chloride treatment.

Well	S (wt%)	N (wt%)	C (wt%)	H (wt%)	O (wt%)	H/C	S/C	O/C	N/C
YG-08	0.51	2.15	76.43	4.46	7.19	0.70	0.003	0.07	0.048
TD2	9.53	1.07	62.80	1.42	7.23	0.27	0.057	0.09	0.029

(Table 2). Total residual kerogen sulfur is composed of 90–98% organic sulfur (Table 2).

4.2. Kerogen and oil sulfur contents and $\delta^{34}\text{S}$ values

The Cambrian kerogen from well TD2 has an atomic S/C ratio of 0.057 (Table 3) and thus is identified as type I-S kerogen (Orr, 1986). This kerogen has a total residual kerogen sulfur content similar to the Y-4 Cambrian kerogen (Table 2), suggesting a similar classification for the Y-4 kerogen.

In contrast, the Upper Ordovician kerogen from well YG-08 has a much lower S/C ratio of 0.003 and sulfur content, and thus is a typical low sulfur type I kerogen. Other kerogen samples from the Middle and Upper Ordovician have sulfur contents mainly from 1.2–3.6%, significantly lower than the Cambrian kerogens.

The Cambrian kerogens from wells TC1, KN1, TD2 and outcrop Y-4 profile have $\delta^{34}\text{S}$ values ranging from +10.4 to +19.4‰ ($n = 4$, Table 2). The values are about -20% lower than those reported for the contemporary seawater sulfates (Claypool et al., 1980; Fig. 5). The difference is similar to that reported by Orr (1974) for unaltered oils from the Big Horn Basin. The $\delta^{34}\text{S}$ values for source rocks from the Lower Ordovician and from the base of the Middle Ordovician in wells T204 and TD1, are +6.7 and +8.7‰, respectively.

The O_3 marlstone and muddy micrite from different areas in the basin have $\delta^{34}\text{S}$ values from -15.3 to $+6.8\%$ ($n = 5$) with the lowest value measured in well LN46 (Table 2). Overall, kerogen $\delta^{34}\text{S}$ values gradually decrease from the Cambrian to the early Ordovician and to the late Ordovician, which is broadly consistent with the interpreted secular change of seawater sulfate $\delta^{34}\text{S}$ value during this period. However, the $\delta^{34}\text{S}$ difference between the kerogen samples (excluding the suspect LN46 sample) and the contemporary seawater sulfate (Claypool et al., 1980) is about 18‰ (Fig. 5).

The changing trend of the kerogen $\delta^{34}\text{S}$ values with age in the Tarim Basin is similar to that of the oils from around the world with source rock age (Fig. 6).

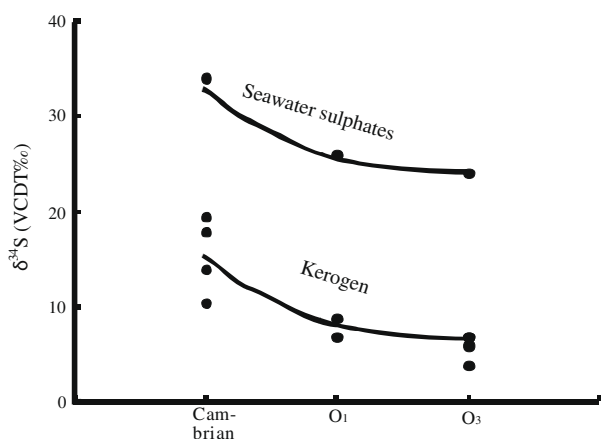


Fig. 5. Variation in sulfur isotopes of kerogens from the Cambrian to Ordovician with age. Seawater sulfate sulfur isotopes (Claypool et al., 1980) are shown for comparison.

Nine oils were measured to have sulfur contents from 0.02–0.63%, $\delta^{34}\text{S}$ values from 11.9–19.9‰ (Table 4). An oil produced from the Cambrian in well TD2 and an oil produced from the Silurian in well TZ62, have been consistently thought from the Cambrian source rock by Chinese researchers (e.g. Ma et al., 2004; Xiao et al., 2005). These two oils have $\delta^{34}\text{S}$ value of 19.6 and 17.2‰, respectively. The other seven oils have an average $\delta^{34}\text{S}$ value of 16.1‰ (Fig. 6).

4.3. Molecular biomarkers of extracted organic matter

Organic matter extracted from the Cambrian to Lower Ordovician source rocks and from the Middle to Upper Ordovician (O_{2-3}) source rocks show considerable similarity in maturity related parameters, for example, C_{29} $\alpha\alpha\alpha$ sterane $20\text{S}/(20\text{S} + 20\text{R})$ ratios from 0.44 to 0.54 (Table 5), most of which are close to equilibrium values. The values suggest that the source rocks are mature to over mature, commensurate with the VRE values. The samples have $\text{T}_s/(\text{T}_s + \text{T}_m)$ ratios from 0.22 to 0.59 and $\text{C}_{29}\text{T}_s/(\text{C}_{29}\text{T}_s + \text{C}_{29}\text{H})$ from 0.13–0.42. The two ratios show a positive relative relationship with R^2 of 0.57 (not shown, Table 5). However,

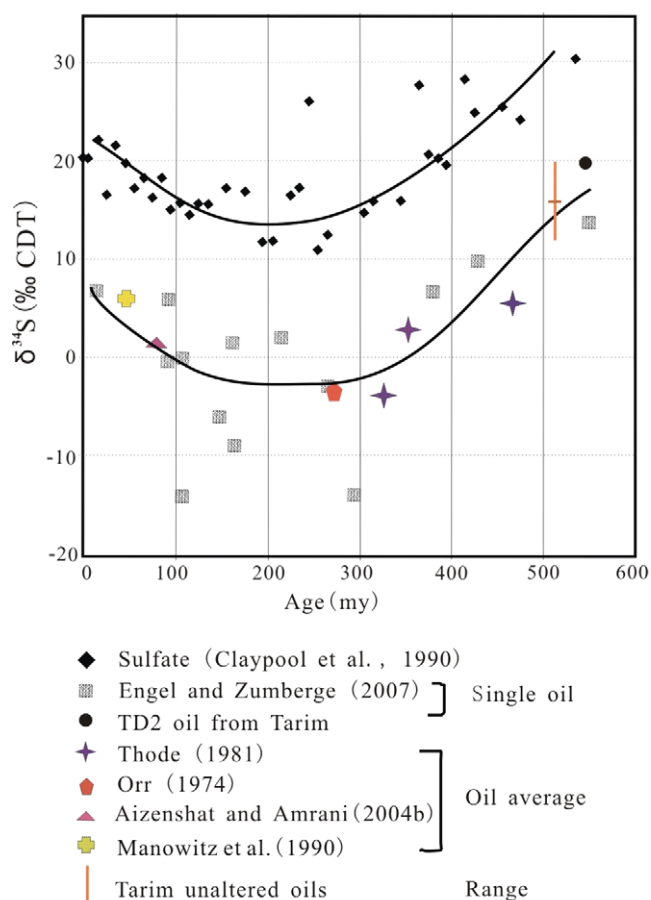


Fig. 6. Variation in sulfur isotopes of oils from around the world relative to source rock age with seawater sulfate sulfur isotopes shown for comparison [modified from Engel and Zumberge (2007), with permission from the authors].

Table 4
Density, sulfur content and $\delta^{34}\text{S}$ values of oils from the Paleozoic strata.

Area	Well	Formation	Depth ^a (m)	Density ^b	Sul (%)	$\delta^{34}\text{S}$
Central Tarim	TZ62	S	4053	0.9265	0.22	17.2
	TZ16	O ₃	4252	0.8794	0.43	14.7
	TZ30	O ₃	4997	0.8326	0.10	18.4
	TZ12	O ₃	4652	0.8198	0.14	19.9
	TZ24	O ₃	4458.5	0.8224	0.023	11.9
	TZ168	O ₃	4460	0.8653	0.02	13.6
	TZ452	O ₁₊₂	6466	0.8486	0.16	15.3
	TZ1	Cam.	3762	– ^c	– ^c	18.9
	Eastern Tarim	TD2	Cam	4801	1.0217	0.51

^a Depth is set as the middle point between perforations in meters.

^b Density in g/cm³.

^c – no data available.

the ratios seem not controlled by maturity alone because they are significantly lower than equilibrium values (1.0 for Ts/(Ts + Tm); Peters and Moldowan, 1993).

In biological precursor related parameters, all the analysed samples have highest percentages of C₂₉ $\alpha\alpha\alpha$ 20R among C₂₇–C₂₉ 20R steranes (Table 5). However, the ϵ -O₁ samples show some differences from the Middle and Upper source rocks (Figs. 7 and 8). Similar to previous reports (Zhang et al., 2000a; Ma et al., 2006), all the analysed ϵ -O₁ samples contain abundant 4,23,24-trimethyl triaromatic dinosteroids. The samples except well KN1 or He4 show that the C₂₃ tricyclic terpane is more abundant than C₂₁ tricyclic terpane, C₂₄ tetracyclic terpane lower than C₂₆ tricyclic terpane, lower C₂₉/C₃₀ 17 α , 21 β hopane ratio (<0.5) and higher C₂₃ tricyclic terpane/C₃₀ 17 α , 21 β hopane ratio. The ϵ -O₁ samples show C₂₈/C₂₇ $\alpha\alpha\alpha$ 20R sterane ratios >1.0. These features are different from the Upper Ordovician source rocks in the Central Tarim and the Tabei uplifts (Fig. 8).

Abundant C₂₄ tetracyclic terpane and higher C₂₉/C₃₀ hopane ratio in the Upper Ordovician marlstones are thought to arise from carbonate depositional environments (Clark and Philp, 1989; Peters and Moldowan, 1993), different from shale/mudstone depositional environments in the Cambrian and Lower Ordovician. Relatively low C₂₃ tricyclic terpane/C₃₀ hopane and high C₂₁/C₂₃ tricyclic terpane ratio in the Upper Ordovician may be related to biological precursors or lower maturity.

Significantly, the ϵ -O₁ source rocks have lower Pr/Ph ratios (from 0.64–1.06), Pr/n-C₁₇ ratios greater than Ph/n-C₁₈, higher gammacerane/C₃₀ 17 α , 21 β hopane ratios (from 0.24–0.27), and C₃₅/C₃₄ hopanes ratios mainly greater than 0.5 (Table 5; Fig. 8). In contrast, most of the O₃ samples have higher Pr/Ph ratios (>1.1) and no significant gammacerane (Figs. 7 and 8 and Table 5; Zhang et al., 2000b; Ma et al., 2006).

The Graptolite shale in the Upper and Middle Ordovician Saergen Formation in the Keping area has very low 4,23,24-trimethyl triaromatic dinosteroids and C₂₈ 20R sterane less than C₂₇ 20R sterane. The features are similar to the Upper Ordovician source rocks from the Tabei and Central Tarim areas. However, this sample has a Pr/Ph ratio of 0.94 and a gammacerane/C₃₀ 17 α , 21 β hopane ratio of 0.11, ranging between the ϵ -O₁ source rocks and the O₃ source rocks, respectively.

Mass chromatograms for *m/z* 134 revealed the distribution of a pseudo-homologous series of aryl isoprenoids in all the analyzed ϵ -O₁ source rocks in the Tarim Basin (Fig. 9). The major components possess the 2,3,6-trimethyl substituted pattern with a predominance of C₁₄–C₂₂ homologs. The components are interpreted to be the diagenetic products of aromatic carotenoids of the green sulfur bacteria (*Chlorobiaceae*) in ancient restricted seas (Summons and Powell, 1987). They were detected in the aromatic and asphaltene fractions of oils in the Tarim basin (Sun et al., 2003; Jia et al., 2007).

Table 5
Biomarker parameters of the Cambrian and Ordovician source rocks.

Sample no.	Strata	Pr/Ph	Pr/nC ₁₇	Ph/nC ₁₈	Gm/C ₃₀ H	Dino-St	Als	C ₂₇ 20R%	C ₂₈ 20R%	C ₂₉ 20R%	Ts/(Ts + Tm)	C ₂₄ Te/C ₂₆ TT	C ₂₃ TT/C ₃₀ H	C ₂₁ TT/C ₂₃ TT	C ₂₉ Ts/(C ₂₉ Ts+C ₂₉ H)	C ₂₉ S/(S+R)	C ₂₉ /C ₃₀ H	C ₃₅ /C ₃₄
TD2	Cam.	1.06	0.25	0.40	0.27	0.86	++	28.4	31.7	39.9	0.44	0.48	0.46	0.82	0.23	0.54	0.48	0.86
Y-4	Cam.	0.67	0.13	0.22	0.26	0.80	+	28.6	33.2	38.2	0.49	0.49	0.52	0.48	0.26	0.51	0.52	0.66
KN1	Cam.	0.89	0.40	0.53	0.24	0.72	+	22.9	34.5	42.6	0.36	1.38	0.72	2.23	0.18	0.46	0.47	0.51
He4	Cam.	0.91	0.42	0.78	0.20	0.82	++	9.9	35.1	55.0	0.38	0.46	0.32	0.69	0.20	0.46	0.36	0.25
TD1	O ₁	0.64	0.29	0.43	0.25	0.77	++	27.0	34.7	38.3	0.45	0.58	0.39	0.55	0.23	0.53	0.49	0.54
YG-08	O ₂₊₃	0.94	–	–	0.11	0.05	×	32.0	28.0	41.0	0.52	0.83	0.54	1.3	0.19	0.50	0.46	0.36
TZ12	O ₃	1.30	0.21	0.16	0.05	0.08	×	32.1	24.3	43.6	0.59	1.63	0.38	0.67	0.42	0.52	0.66	0.32
LN46 ^a	O ₃	1.26	0.41	0.40	–	–	–	–	–	–	0.58	2.23	0.22	–	–	0.48	–	–
He3	O ₃	0.77	0.46	0.43	0.07	0.12	×	31.4	21.7	46.9	0.47	5.11	0.14	1.4	0.22	0.56	0.57	0.37
Z11-5335	O ₃	1.10	0.31	0.30	0.05	0.15	+	21.7	12.2	66.1	0.40	8.90	0.03	1.10	0.27	0.50	0.48	0.38
Z11-5338	O ₃	1.28	0.60	0.45	0.06	0.21	×	24.3	20.9	54.8	0.22	6.23	0.05	1.08	0.13	0.44	0.59	0.40

Pr: Pristane; Ph: Phytane; Gm: Gammacerane, H: Hopane; TT: tricyclic terpane; Te: tetracyclic terpane; Als: Aryl isoprenoids; Ts: 18 α , 21 β –22, 29, 30-trisnorhopane. Tm: 17 α , 21 β –22, 29, 30-trisnorhopane; –: no data available; ++: very abundant, +: abundant, ×: absent or very low.

DinoSt: 4,23,24-trimethyl triaromatic dinosteroids/(4,23,24-trimethyl triaromatic dinosteroids+ 3-methyl-24-ethyl-triaromatic steroid).

Z11-5335 and Z11-5338: marlstone from well Z11 at depths of 5335 m and 5338 m, respectively.

^a From Zhang et al. (2000a).

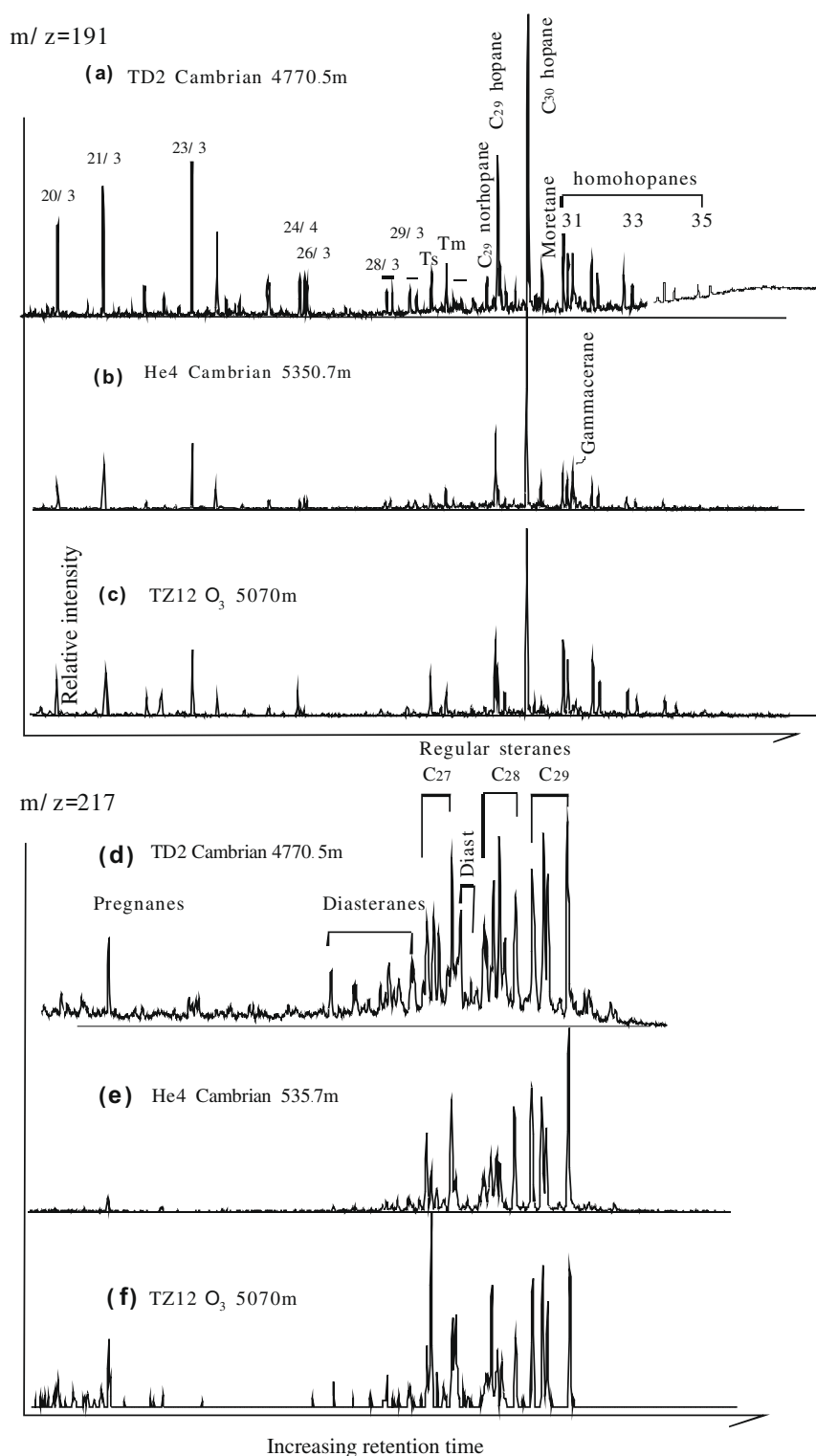


Fig. 7. Partial GC-MS chromatograms ($m/z = 191, 217$) for extractable organic matter from the Cambrian source rock from (a and d) well TD2 (TOC = 1.7%, VRE = 2.3%); (b and e) well He4 (TOC = 0.9%, VRE = 1.4%); and (c and f) from the Upper Ordovician of TZ12 (TOC = 0.82%, VRE = 0.85%).

However, no aryl isoprenoids were detected in the Middle to Upper Ordovician in outcrop sample YG-08 and from wells TZ12, He3 and Z11 (at the depth of 5338 m) (Fig. 9d). Only one sample from well Z11 at the depth of 5335 m contains small amounts of aryl isoprenoids (Table 5). The result is consistent with previous findings, which show significantly less abundant aryl isoprenoids in the Upper Ordovician than in the Cambrian in the basin (Jia, 2004).

5. Discussion

There exists a significant difference in the distribution of triaromatic dinosteroids between the studied Upper Ordovician (previously identified as O₂₋₃) and Cambrian source rocks (Fig. 8c). This is consistent with the result obtained by Zhang et al. (2000a). Thus, the distribution of the biomarkers has been utilized

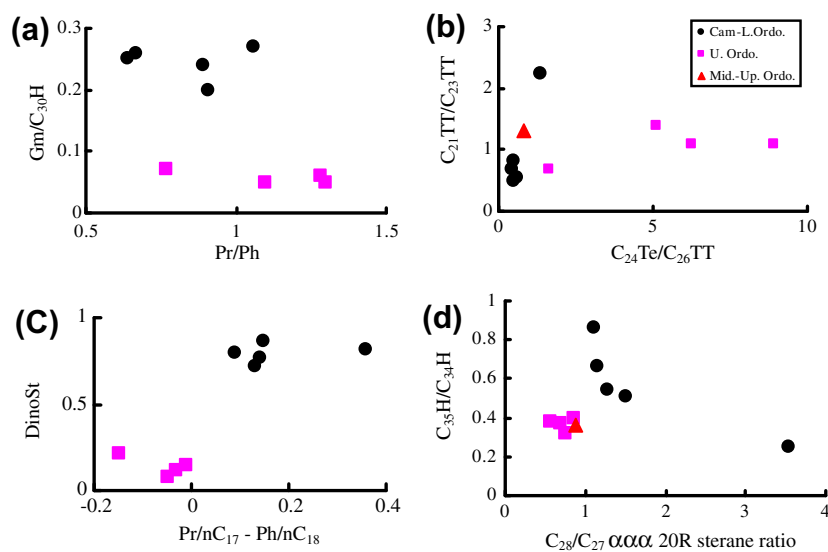


Fig. 8. Crossplots of biomarker parameters showing difference between the Cambrian–Lower Ordovician and Middle–Upper Ordovician source rocks. (a) gammacerane/ C_{30} hopane vs. Pr/Ph; (b) C_{21} tricyclic terpanes/ C_{23} tricyclic terpanes ratio vs. C_{24} tetracyclic terpane/ C_{26} tricyclic terpanes; (c) Dinosterane vs. (Pr/ n - C_{17} - Ph/ n - C_{18}); (d) C_{35} homohopanes/ C_{34} homohopanes vs. C_{28}/C_{27} 20R sterane ratio.

for oil-source rock correlation in the basin although the exact organisms for the biomarkers is not clear.

Previous studies (Zhang et al., 2000a; Sun et al., 2003) show that the O_3 Lianglitage Formation source rocks in the Tabei and Central Tarim areas were deposited in a slope environment controlled by upwelling ocean currents. The environments had relatively high oxygen concentrations near the bottom of the water body, significantly different from the stratified water body during the Cambrian to early Ordovician (Sun et al., 2003). The proposal is supported not only by the difference in Pr/Ph and C_{35}/C_{34} homohopane ratios and the occurrence of gammacerane, but also by aryl isoprenoids and kerogen $\delta^{34}\text{S}$ values in the source rocks analyzed in the study.

5.1. Role of depositional environment

It is generally accepted that H_2S generated during the earliest phase of bacterial sulfate reduction in an anoxic environment, has the lowest $\delta^{34}\text{S}$ values (Tuttle and Goldhaber, 1993). Due to kinetic isotope fractionation, isotopically light H_2S reacts initially with reactive iron to precipitate as sedimentary iron sulfide minerals (eventually to form pyrite). As the reaction proceeds, reactive iron becomes depleted, and so sulfide with increasing $\delta^{34}\text{S}$, from the later phase of bacterial sulfate reduction, is expected to be incorporated into the organic matter. Alternatively, organic sulfur may have been derived from elemental sulfur and polysulfides (Dinur et al., 1980; Werne et al., 2003). Importantly, a percentage of the sulfur in the kerogen is derived directly from the biomass from which it formed, e.g., from amino acids and proteins derived from algae and bacteria (Werne et al., 2003). The primary bio-sulfur will be enriched in ^{34}S , similar if not identical to seawater sulfate. This is because there is minimal fractionation during assimilatory sulfate reduction. Thus sedimentary pyrite has $\delta^{34}\text{S}$ values generally lower than organic matter. In the case of Tarim Basin, pyrite in the Middle to Upper Ordovician has $\delta^{34}\text{S}$ values from -20.5 to $+5.6\text{‰}$ ($n=4$). Most of the $\delta^{34}\text{S}$ values are significantly lower than those of the coexisting organic matter (Table 1), supporting the conclusion that the sulfur species was deposited under a relatively open environment enriched in sulfate supply.

If sulfate supply is limited, or the reaction site is isochemical, sulfur isotope fractionation should be limited and $\delta^{34}\text{S}_{\text{py}}$ values

of bulk samples should approach $\delta^{34}\text{S}$ of seawater (Strauss, 1997). For example, Sælen et al. (1993) found that pyrite in the bottom sediments of the Framvaren fjord was enriched in ^{34}S , reaching $\delta^{34}\text{S}_{\text{py}}$ values around -12‰ ($\delta^{34}\text{S}_{\text{sulfate}} < \delta^{34}\text{S}_{\text{pyrite}}$), compared with values around -35‰ near and above the chemocline. Similarly, $\delta^{34}\text{S}_{\text{py}}$ values of up to $+15\text{‰}$ were reported in the Miocene Monterey Formation (Zaback and Pratt, 1992).

Source rocks with high $\delta^{34}\text{S}_{\text{py}}$ values have correspondingly high $\delta^{34}\text{S}_{\text{kerogen}}$ values. Orr (1986) found $\delta^{34}\text{S}_{\text{kerogen}}$ in the Miocene Monterey Formation $\sim +20\text{‰}$, close to Miocene seawater. Similarly, in Nabi-Musa in the Dead Sea area (Jordan Valley Rift), the Upper Cretaceous Ghareb Formation has pyrite $\delta^{34}\text{S}$ values from $+1.2$ to -6‰ , immature kerogens from $+6$ to $+7\text{‰}$, and extracted bitumens from -8 to $+9\text{‰}$ (Aizenshtat and Amrani, 2004a). All of these values are significantly heavier than those of pyrite, kerogens and bitumens in the same formation in the Zefa Efe area. This narrow range and ^{34}S enrichment for all sulfur species in Nabi-Musa and in the Monterey Formation has been suggested to indicate a depositional environment with restricted sulfate supply (Zaback and Pratt, 1992; Aizenshtat and Amrani, 2004a).

In the case of the Tarim Basin, pyrite from the Cambrian has $\delta^{34}\text{S}$ values from 7.6 – 16.9‰ (Table 2), being about 13 – 22‰ depleted relative to seawater sulfates, suggesting that only part of sulfate was transformed to H_2S and thus pyrite, and thus the supply of sulfate for bacterial reduction is not very limited. However, this difference (-13 to -22‰) is less than that of pyrite from the Upper Ordovician (from -45 to -20‰). Relatively high $\delta^{34}\text{S}_{\text{kerogen}}$ and similar $\delta^{34}\text{S}_{\text{pyrite}}$ values (Table 2) are found in the Cambrian and Lower Ordovician (ε - O_1) and Middle to Upper Ordovician (O_2 – O_3) Saergan Formation; both of these units have high gammacerane/ C_{30} – $17\alpha\beta$ -hopane ratios. Elevated values of this ratio have been used previously to infer marine stratification during source rock deposition (Sinninghe Damsté et al., 1995). In contrast, relatively low $\delta^{34}\text{S}_{\text{py}}$ and $\delta^{34}\text{S}_{\text{kerogen}}$ values are found in the Upper Ordovician (O_3) Lianglitage Formation deposited in a platform slope environment with no stratification. The most likely reasons for the difference in $\delta^{34}\text{S}_{\text{py}}$ and $\delta^{34}\text{S}_{\text{kerogen}}$ values of the ε - O_1 and O_3 source rocks include, (1) significantly higher $\delta^{34}\text{S}$ values of parent sulfate and biomass inherited organic sulfur, (2) stratified, reduced water with a relatively limited sulfate supply due to inhibited overturn, (3) stronger reduction of sulfates, driven by a large

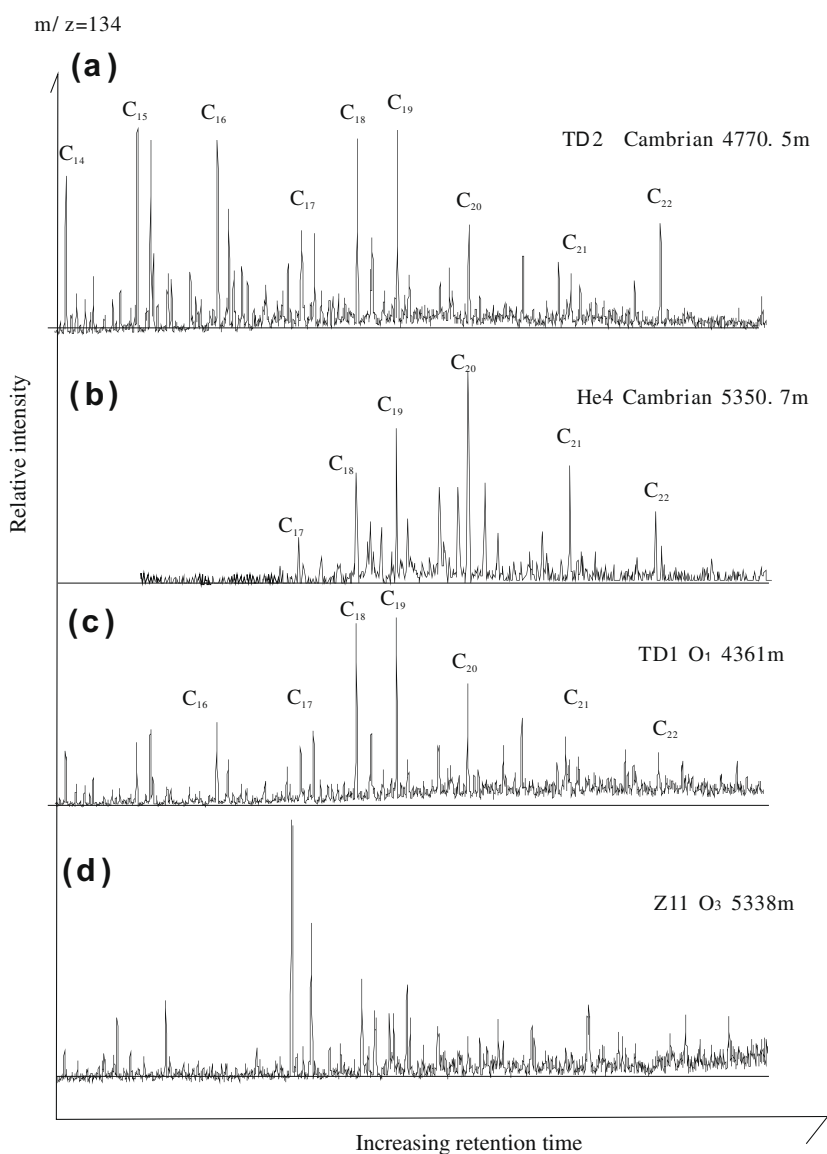


Fig. 9. Summed GC-MS chromatograms ($m/z = 134$) for extractable organic matter from (a) the Cambrian source rock of TD2, (b) the Cambrian source rock of He4, (c) the Lower Ordovician of TD1, and (d) the Upper Ordovician of Z11 at the depth of 5338 m.

reservoir of dissolved organic carbon (cf. high TOC for the source rocks).

The ϵ -O₁ kerogen samples from the Tarim Basin contain derivatives of the biomarker isorenieratene, a diaromatic carotenoid pigment produced exclusively by the brown strain of the green sulfur bacteria *Chlorobiaceae*. These are phototrophic organisms requiring euxinic (anoxic and sulfidic) conditions to survive. The presence of isorenieratene derivatives indicates that the Cambrian to early Ordovician seas in the Tarim area experienced bottom water euxinic conditions during black shale deposition, similar to the middle Devonian to early Carboniferous sea in North America (Brown and Kenig, 2004).

5.2. Secular change of marine kerogen $\delta^{34}\text{S}$ value with age

Secular changes of marine sulfate and pyrite $\delta^{34}\text{S}$ value have been reported (Claypool et al., 1980; Strauss, 1997). However, it is not yet definitively known if there are similar changes of organically bound sulfur (in kerogen or the resulting petroleum) as a function of age of marine source rocks.

Recently, Engel and Zumberge (2007) showed secular change in the $\delta^{34}\text{S}$ values of oil as a function of source rock age and seawater sulfate (Fig. 6). Their conclusion was based on the measurement of $\delta^{34}\text{S}$ values of 15 oils ranging in source rock age from Neoproterozoic to Neogene from different basins around the world. The $\delta^{34}\text{S}$ difference between oil and source rock age seawater sulfate is about +15 to +20‰, similar to that of Thode et al. (1958), Thode and Monster (1965), Orr (1974), Thode (1981) and Tarim oils (Table 4). In essence, an oil inferred to be derived from Cambrian source rocks in the Tarim Basin (e.g. Ma et al., 2004) has a $\delta^{34}\text{S}$ value of +19.6‰, oil sourced from Ordovician age source rocks has a $\delta^{34}\text{S}$ of $+5.8 \pm 1.2\text{‰}$, and oils from Mississippian and Pennsylvanian age rocks have $\delta^{34}\text{S}$ of $+2.8 \pm 0.8\text{‰}$ and $-4.0 \pm 0.7\text{‰}$, respectively (all from Thode, 1981). Unaltered Permian sourced oil has a $\delta^{34}\text{S}$ of $\sim -3.5\text{‰}$ (Orr, 1974). In younger source rocks sulfur isotopic values broadly show an increasing but punctuated trend. Upper Cretaceous sourced oil has $\delta^{34}\text{S}$ values of $+1.6 \pm 1.2\text{‰}$ (Aizenshtat and Amrani, 2004b). Eocene sourced oils have $\delta^{34}\text{S}$ values ranging from +4.0 to +9.5‰ with an average of $+6.5 \pm 1.8\text{‰}$ ($n = 27$; Manowitz et al., 1990).

In summary, oils show a decrease in $\delta^{34}\text{S}$ value from Cambrian source rocks, to the Ordovician, Mississippian, with the lowest values in Pennsylvanian and Permian, then an increase to the Cretaceous and Eocene. This evolutionary trend is consistent with that of contemporary seawater sulfates (Claypool et al., 1980). The pattern also resembles that of the ten kerogen samples from the Tarim Basin (Fig. 5).

Amrani et al. (2005) suggested that oil $\delta^{34}\text{S}$ values from oil fields are likely to be a cumulative product of oils derived from kerogens with different $\delta^{34}\text{S}$ values. Change in organic facies may result in different $\delta^{34}\text{S}$ values of kerogens of the same age (Aizenshtat and Amrani, 2004a). However, groups of oils from similar aged source rocks (Manowitz et al., 1990) were collected from reservoirs of various ages in different oilfields over a distance of up to 320 km and an area of up to 2500 km². These show relatively narrow ranges in $\delta^{34}\text{S}$ values with a standard deviation of less than $\pm 1.8\%$, suggestive of relatively uniform sulfur isotopic composition for the source rocks (Orr, 1974; Thode, 1981; Manowitz et al., 1990), or a very minor contribution from source rocks with deviated $\delta^{34}\text{S}$ values. Thus, it is reasonable to consider that mature kerogens, at least for the kerogens parent to the above oils, show secular change in $\delta^{34}\text{S}$ values with age relative to the seawater. This suggestion is supported by this case study from the Tarim Basin (Fig. 5).

The secular change in the $\delta^{34}\text{S}$ values of the mature to over mature kerogen suggests that accumulative organically bound sulfur was controlled by seawater sulfate isotope evolution and there exists a relatively homogeneous fractionation during bacterial reduction of sulfate.

5.3. Thermal maturity and diagenetic system

Hydrous pyrolysis experiments under a closed system showed that the $\delta^{34}\text{S}$ values of residual kerogen, H₂S and oil have a difference up to only 2.0‰ (Amrani et al., 2005). The results are consistent with those from dry pyrolysis (Idiz et al., 1990) and field data (Thode, 1981; Orr, 1986). The small differences are due to sulfur isotope homogenization under closed system conditions. However, in an open system, the instantaneously generated H₂S would escape and a maximum isotope fractionation would occur, and the residual kerogen would be isotopically heavier (Amrani et al., 2005).

It is not easy to determine whether the system for organic matter maturation in a basin is open or closed. However, it is possible that initial decomposition of organic matter in relatively less compacted sediment to produce pre-oil generation kerogen occurs in a relatively open system, thus producing a small quantity of isotopically lighter H₂S, which might conceivably be removed from the system. Thus, mature kerogen is expected to have a somewhat higher $\delta^{34}\text{S}_{\text{kerogen}}$ value than the organic matter in the immature kerogen. With continual burial, increasing sediment compaction and mineral diagenesis and commensurate porosity loss, the system will become more closed (Charpentier et al., 2003; Worden et al., 2005). For a rapidly buried basin and thus with rapid hydrocarbon generation, peak oil generation from fine grained mudstone, shale and micrite is likely under semi-closed to closed systems, before and after episodic petroleum expulsion. This feature along with high H₂S solubility and rapid sulfur isotope homogenization (Thode, 1981; Amrani et al., 2005) are most likely the reasons for the small variation in the $\delta^{34}\text{S}$ of mature kerogen samples and their subsequent oil samples (Thode, 1981; Orr, 1986), and the secular changes of the kerogens (Fig. 5) and the oils with source rock age (Fig. 6).

The suggestion that petroleum generation is likely under semi-closed to closed systems in a rapidly buried basin was supported by kinetic parameters determined by closed system pyrolysis, which match natural thermal burial histories for the Naokelekan source

rock (Type-II-S kerogen) in the Zagros Basin of Iraq, for the Green River Formation (Type-I kerogen) in the Uinta Basin of Utah (Lewan and Ruble, 2002) and for the $\epsilon\text{-O}_1$ in the Tarim basin (Wang et al., 2006).

Thus, more rapid burial in the Cambrian to Lower Ordovician ($\epsilon\text{-O}_1$) source rocks than the Upper Ordovician (O_3) source rocks in the basin (Fig. 3), indicates a more closed system for petroleum generation from the $\epsilon\text{-O}_1$. Consequently, the kerogens from the $\epsilon\text{-O}_1$ source rocks over thousands of kilometers from similar depositional environments show relatively small changes in their $\delta^{34}\text{S}$ values.

6. Conclusions

1. Pyrite was removed efficiently from kerogen using the method of CrCl₂ reduction, and the kerogen after the treatment has organically bound sulfur up to 98% of total residual sulfur.
2. $\delta^{34}\text{S}$ values of mature kerogen from the basin show a gradual decrease from the Cambrian, to Middle Ordovician, and the Upper Ordovician in the Tarim Basin. This parallels evolving marine sulfate $\delta^{34}\text{S}$ values over this period.
3. The Cambrian to Lower Ordovician black shale and mudstone was deposited under an euxinic bottom water environment with water stratification, leading to the presence of aryl isoprenoids, gammacerane and C₃₅ homohopanes and relatively low Pr/Ph ratios in the organic matter. Such features are significantly different from the Upper Ordovician marlstone.
4. Compared with the Upper Ordovician, the Cambrian to Lower Ordovician source rocks show an abundance of C₂₈ 20R sterane, C₂₃ tricyclic terpanes, 4,23,24-trimethyl triaromatic dinosteroids and depletion of C₂₄ tetracyclic terpane and C₂₉ hopane. Such differences may have resulted from biological precursors and/or shale/mudstone depositional environment in the Cambrian to Lower Ordovician as opposed to carbonate depositional environment in the Upper Ordovician.
5. Rapid burial immediately after the deposition of the Cambrian and Lower Ordovician is likely to have led to a relatively closed system for petroleum generation and thus relatively narrow $\delta^{34}\text{S}$ values of the mature kerogen samples in the basin.

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