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Review

Palaeozoic oil–source correlation in the Tarim Basin, NW China: A review

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ABSTRACT

Oil–source correlation in the cratonic region of the Tarim Basin, NW China has long been controversial. Current knowledge of the potential source rock distribution, end-member selection, oil–source correlation and impacts of secondary alteration processes have been reviewed. Two source rock systems from the Cambrian–Lower Ordovician (Є–O_1) and Middle–Upper Ordovician (O_{2-3}) potentially contributed to oil accumulations in the cratonic region. Geochemical correlations suggest that oils are dominantly derived from the O_{2-3} source rocks, while geological evidence and sulfur isotopic compositions supports the Є–O_1 source rocks as a main contributor. Such inconsistency is rooted in the selection of end-members and their characterization. Changes in some biomarker parameters, such as sterane distribution, gammacerane index and ratio of tricyclic terpanes to pentacyclic terpanes, are mainly controlled by thermal maturation and biodegradation rather than source input and depositional environment variation. No clear boundary between the two source systems can be established using biomarkers except for a few diagnostic components. Some Є–O_1 source signatures, such as even/odd predominance of *n*-alkanes, unusual tricyclic terpane distribution, unusually enriched ^{13}C carbon isotopic compositions of oils and kerogens, and the occurrence of combustion related polycyclic aromatic hydrocarbons, largely result from an abnormal heating influence either from igneous intrusion or hydrothermal fluid activity. Local thermochemical sulfate reduction can also remove most source-related signatures. These so-called markers in currently selected end-members result from extensive secondary alteration processes and do not reflect source input differences. While more research is needed for full reconstruction of oil–source correlation in the cratonic region of the Tarim Basin, the main source rocks most likely reside in the Є–O_1 succession rather than O_{2-3}.

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1. Introduction

The Tarim Basin, with an area of about 560×10^3 km^2, includes the Palaeozoic craton and Meso-Cenozoic foreland basins (Fig. 1). The craton basin is composed of primarily marine sediments of Sinian to Permian ages. During the Sinian–Ordovician, marine carbonate (> 7 km thick) was deposited in the Manjiaer depocenter and about 4–5 km in the plateau region. Two main source units identified in the basin are Cambrian–Lower Ordovician (Є–O_1) and Middle–Upper Ordovician (O_{2-3}) strata. The main reservoirs are Ordovician carbonates in the Yijianfang and Yingshan formations, while minor reservoirs are developed from the Cambrian to Triassic.

Petroleum discovered in the cratonic region varies dramatically from dry gas through to condensate, light, normal, waxy and heavy oils to solid bitumen. Multiple tectonic movements and multiple generation, migration and accumulation processes are generally presumed to have caused physico-chemical changes (Zhang and Huang, 2005; Zhang et al., 2005; Pan and Liu, 2009; Jia et al., 2010; Li et al., 2010a,b; Yu et al., 2011; Zhu et al., 2012). Secondary alteration processes including thermal cracking (Zhao et al., 2005; Wang et al., 2006), biodegradation (Jia et al., 2010; Zhang et al., 2014), gas invasion (Zhang, 2000; Zhang et al., 2011) and thermochemical sulfate reduction (TSR) (Cai et al., 2001, 2009a,b) make oil compositions extremely complex.

Biomarkers, including some polycyclic aromatic hydrocarbons (PAHs), are routinely used to make oil–source correlations (Hanson et al., 2000; Zhang et al., 2000, 2002, 2004a,b;

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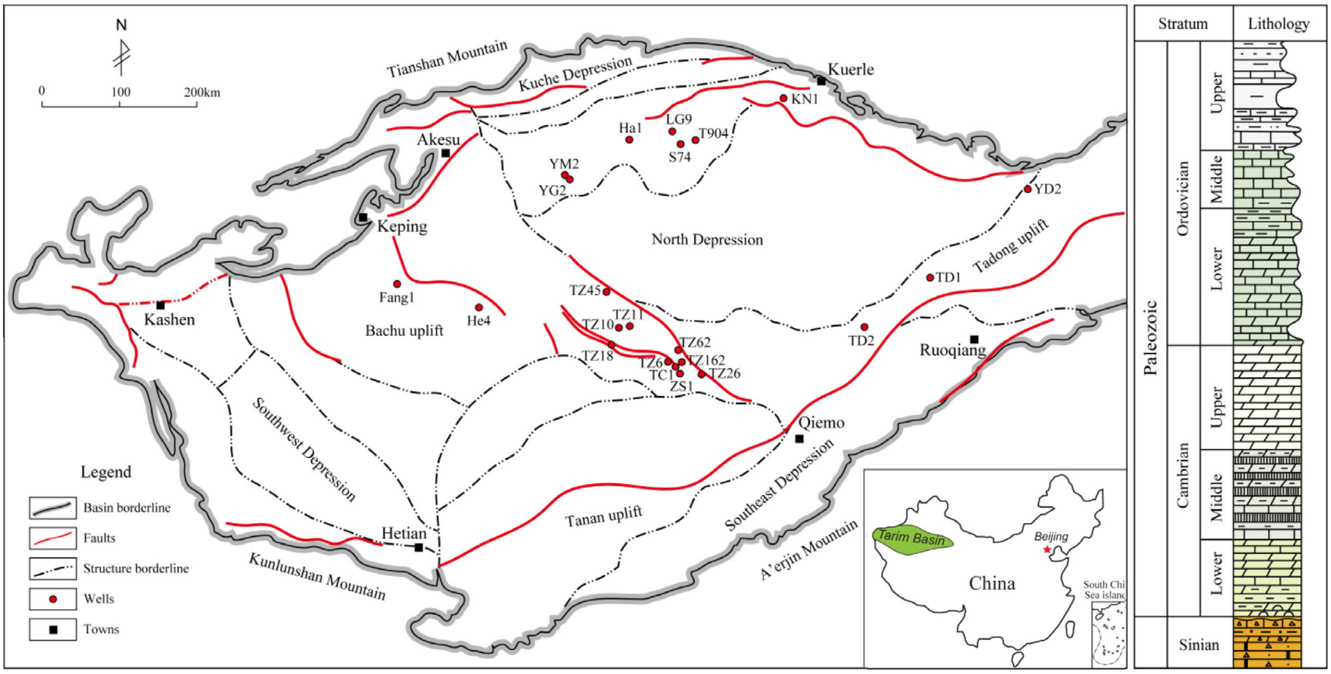

Fig. 1. Tectonic sketch map of the Tarim Basin and stratigraphic column of the Lower Palaeozoic strata.

Wang and Xiao, 2004; Zhang and Huang, 2005; Li et al., 2005, 2010a, 2012a,b; Grice et al., 2009; Yu et al., 2011, 2012; Fang et al., 2015). Biomarker correlation results show that the vast majority of oils in the cratonic region are derived from the O_{2-3} source rocks. A few exceptions include samples that have close affinity to the Є–O_1 source rocks. However, this conclusion seems dubious to many geologists who anticipate that the Є–O_1 would be the main source rocks since the effective source rocks in O_{2-3} strata have limited thickness and low TOC contents (Gu et al., 1994; Jia, 1997; He et al., 2002).

Carbon isotopic composition ($\delta^{13}C$) is another frequently used geochemical tool for oil–oil and oil–source rocks correlation as relatively large variations in the $\delta^{13}C$ values are observed in the cratonic region (Li et al., 2010a,b, 2015; Yu et al., 2011, 2012; Tian et al., 2012a; Jia et al., 2013; Cai et al., 2015). Since the most ^{13}C-enriched oil from well TD2 accumulated in Cambrian strata and no Ordovician source rocks are available in the surrounding area, it was selected as an end-member of a Cambrian source in almost all studies. The isotopically most depleted oil in a data set has automatically been selected as the end-member to represent the O_{2-3} sourced oil. A linear mixing ratio calculation from the two end-members has commonly been performed (Mi et al., 2007; Li et al., 2010a,b, 2015; Tian et al., 2012a). Except for a few samples that show a typical Є–O_1 isotopic character, the majority of oil samples are attributed to mixed origins. Estimates of the proportion of the Є–O_1 contribution have solely relied on carbon isotopic compositions of whole oil or individual *n*-alkanes. This contrasts with biomarker correlation results which imply that oils are generated from an O_{2-3} source in the cratonic region except for a few samples showing clear Є–O_1 source signatures. A greater contribution from Є–O_1 source rocks has been proposed based on isotopic correlation (Li et al., 2010a,b, 2015). However, when biomarker distributions are combined with carbon isotopic compositions, oil–source correlation parameters are inconsistent and the relative contribution from each source rock system is less clear. Yu et al. (2012) suggested that the effective source rocks for the majority of oils in the Tarim Basin have not yet been drilled.

Various other techniques such as sulfur isotopic ($\delta^{34}S$) values of kerogens and oils (Cai et al., 2009a,b, 2015), rare earth elements and transition metals (Jiao et al., 2010), sequential extraction of reservoir rocks (Pan and Liu, 2009), release of occluded hydrocarbons from asphaltenes by sequential extraction (Tian et al., 2012b) and flash pyrolysis combined with GC–MS (Jia et al., 2010) have also been applied for oil–source correlations in the Tarim Basin. The rare earth element and transition metal analysis indicated that crude oil from the cratonic region was characterized by mixed sources (Jiao et al., 2010). Cai et al. (2009a, 2009b, 2015) demonstrated that the $\delta^{34}S$ values of kerogen decrease from the Cambrian, Lower Ordovician to Upper Ordovician source rocks in the Tarim Basin and suggested that the majority of oils not altered by biodegradation and/or TSR largely originated from the Є–O_1 source rocks. However, 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. Sequential extraction performed by Pan and Liu (2009) suggested that the initial oil charge of the reservoirs was from the Є–O_1 source rocks, while a later oil charge was mainly derived from the O_{2-3} source rocks. Similarly, the hydrocarbons released from asphaltenes also suggested two phases of charges from two source rock systems, but current compositions are overwhelmingly dominated by late charges from the O_{2-3} source rocks (Jia et al., 2010; Tian et al., 2012b).

The identity of key source rocks is crucial for petroleum exploration in the Tarim Basin. We believe that the difficulty in assessing the source rocks and oil–source correlation for the widespread marine oils is most likely rooted in improper end-member selection. Potential source rock distributions, current selected end-member and oil–source correlation results are summarized. This review focuses on secondary alteration effects, especially abnormal heating stress on molecular and isotopic compositions, and how these effects obliterate source related signatures.

2. Source rocks

2.1. Cambrian source rocks

The Cambrian source rocks are widely distributed in the cratonic region of the Tarim Basin. Shales, mudstones and marlstones deposited in starved basin facies occur mainly in the eastern part of the basin, while marl and muddy dolomite from evaporites of lagoonal facies are developed largely in the western Tarim (Gu et al., 1994; Zhang et al., 2004a). The net thickness of the Cambrian source rock ranges from 120–415 m with an area of over 300 × 10^3 km^2 (Fig. 2a) (Zhang et al., 2000; Li et al., 2010a). The TOC values are generally in the range from 1.2–2.3%, but can reach a maximum of 5.5%. Strata with TOC > 1.0% occupy 60–70% of the sequence (Cai et al., 2009a; Li et al., 2010a). These source rock samples are currently over mature (%Ro > 2.0; Zhang et al., 2004a; Li et al., 2010a).

2.2. Lower Ordovician source rocks

The Lower Ordovician bathyal sediments, especially the Heituao Formation, are composed of under-compensated basin facies carbonaceous, siliceous mudstone and graptolite or radiolarian shales, which are mostly encountered in the eastern Manjiaer Depression and the Tadong area. Thickness of the Heituao Formation source rock at wells TD1 and TD2 in the Tadong uplift is about 50–60 m, but much greater thickness is expected in the Manjiaer Depression (Fig. 2b) (Cai et al., 2009a; Li et al., 2010a). Limited sample analyses show TOC mainly > 1.0% with a maximum value of 7.6% (Zhang et al., 2004a). They also are highly over mature with equivalent vitrinite reflectance values (%Ro) of 1.7–2.2 (Zhang et al., 2005).

2.3. Middle–Upper Ordovician source rocks

The O_{2-3} source rocks were mainly developed in slope facies at the margins of structural high and open bay or gulf facies (Zhang et al., 2004a). Shales deposited under open bay or gulf facies in the Middle Ordovician Yijianfang Formation are widely distributed in the eastern Manjiaer Depression with thickness up to 150 m. Time-equivalent Saergan Formation at Keping Uplift has a maximum thickness about 30 m (Fig. 2c) (Li et al., 2010a). Argillaceous limestones and marlstones deposited in shelf edge and slope environments mainly in the Upper Ordovician Lianglitage Formation are encountered at Tazhong and Tabei uplifts with maximum thickness about 100 m. Time-equivalent Yingan Formation at Keping Uplift are less thick (Fig. 2d) (Li et al., 2010a). The O_{2-3} source rocks are generally organic poor. TOC values for 298 samples from Tazhong and Tabei uplifts are mostly in the range of 0.3–0.8% with an average value of 0.4%. The cumulative thickness with TOC > 0.5% ranges from 20–80 m (Zhang et al., 2000; Zhang and Huang, 2005). Slightly higher TOC values from 0.6–2.9% with an average of 1.6% have been encountered in the Saergan Formation at the Keping Uplift (Zhang et al., 2000). Recently, Li et al. (2015) reported relatively good O_{2-3} source rocks may occur in the Shuntuoguole Tectonic Belt (between the Tazhong and Tabei Uplift). Effective source rock with TOC in the range of 0.7–1.4% is up to 280 m thick. The O_{2-3} strata are mature to highly mature with equivalent vitrinite reflectance of 0.8–1.3% (Zhang et al., 2000; Zhang and Huang, 2005; Li et al., 2010a, 2015).

Based on the thickness and TOC content of the potential source rocks, the overall scale of the O_{2-3} source rocks is much smaller than that of the Є–O_1, which makes them unlikely to be responsible for the majority of the petroleum resources discovered in the cratonic region (Cai et al., 2009a, 2015).

3. End-member selection and oil–source correlation

3.1. Cambrian end-member

Only a few oils in the cratonic region are commonly referred as originating from Є–O_1 sources. The most typical one is from well TD2 within the Cambrian strata. This is not a commercial production well. Only a few tens of litres of oil were recovered during testing from the Cambrian fractured carbonate at depth 4630–4670 m. It is an ultra-heavy oil (API of 7°) with a viscosity of 2698 cP at 20 °C. The bulk composition is characterized by a low content of saturated hydrocarbons and high contents of resins and asphaltenes. The saturated hydrocarbon, aromatic hydrocarbon and resins plus asphaltenes are 24%, 30.1% and 45.9%, respectively. The whole oil carbon isotope ($\delta^{13}C_{oil}$) is −28.2‰, which is about

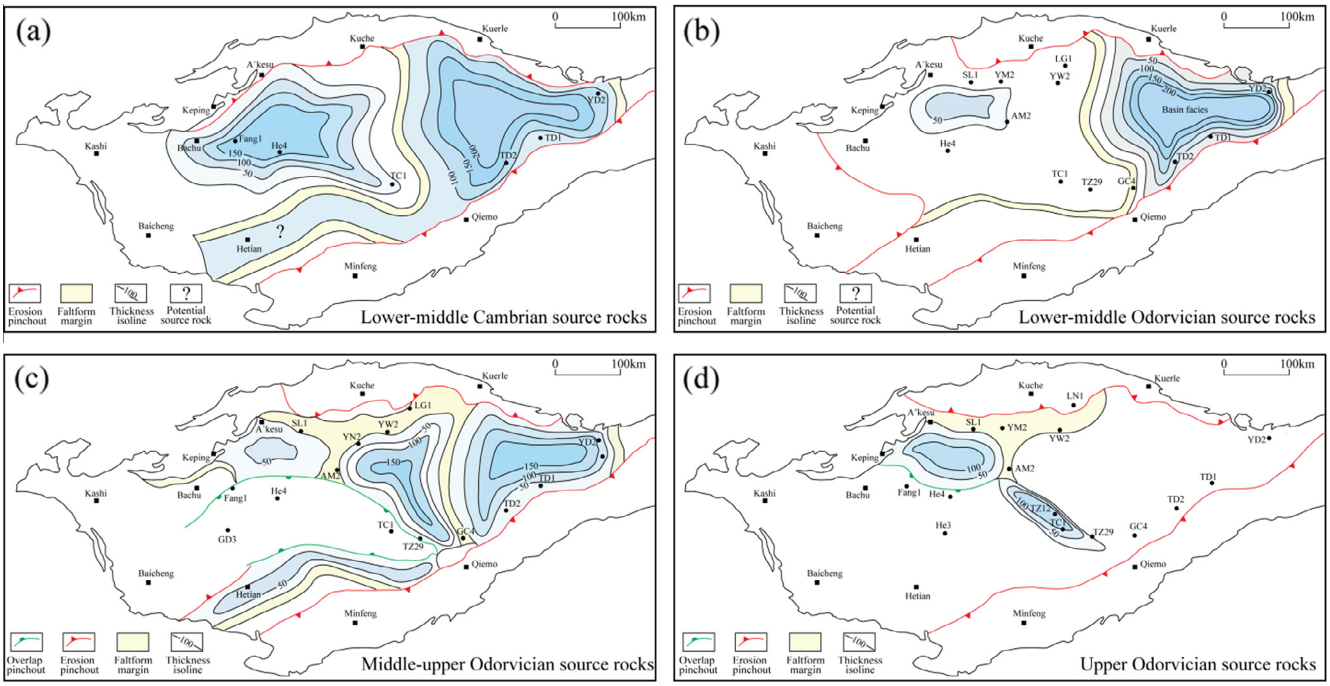

Fig. 2. Schematic maps showing sedimentary facies distributions of potential Cambrian and Ordovician source rocks in the Tarim Basin (data after Zhang et al., 2000, 2004a; Li et al., 2010).

4‰ more enriched than that of normal marine oils in the Tarim Basin (Zhang et al., 2004b). These properties demonstrate a typical residual oil after high thermal alteration, which can be supported by the presence of abundant pyrobitumen with bitumen reflectance (B %Ro) ranging from 2.7–5.0 and coeval aqueous brine inclusions with homogenization temperature of 160–220 °C (Zhang et al., 2004b; Wang et al., 2006). This oil is most likely derived from the Є–O_1 source rocks, but by no means can it represent the end-member from the Є–O_1 source rocks as severe thermal alteration processes may have totally destroyed its original signature.

Another oil from well TZ62 Silurian sandstone at depth 4052.88–4073.88 m is widely accepted as the end-member from Є–O_1 sources. This oil resides in lenticular sandstone and has been excluded from an influence of severe biodegradation. Different from typical Silurian oil sand bitumen, it is moderately heavy with an API gravity of 20.5°. The saturated hydrocarbon, aromatic hydrocarbon and resins plus asphaltenes contents are 49.2%, 36.2% and 14.6%, respectively (Xiao et al., 2005). This oil was regarded as the end-member oil from Є–O_1 sources because it contains similar biomarker signatures as the oil from well TD2, such as relatively high C_{20} and C_{21} tricyclic terpanes, gammacerane and C_{28} regular steranes (Xiao et al., 2005). However, typical diagnostic biomarkers for the Є–O_1 source rocks from well TD2, such as C_{30} dinosteranes and aromatic dinosteroids, have not been detected in the TZ62(S) oil. The TD2 oil is extremely enriched in PAHs (Zhang et al., 2004b; Li et al., 2012a), while only trace amounts of tetracyclic aromatic hydrocarbons and almost no triaromatic steroids can be detected in the TZ62(S) oil (Xiao et al., 2005). Tian et al. (2012) used this oil as the Є–O_1 end-member because of its unusually enriched bulk isotopic value, which is very close to that of the TD2 oil. However, the whole oil carbon isotopic value of TZ62(S) is −31.6‰ (Xiao et al., 2005), which is only slightly more enriched than other oils in the cratonic region. The same oil has been reported to have a carbon isotopic value of −28.61‰ (Tian et al., 2012) and the reason for this difference from the Xiao et al. (2005) data is not clear.

The TZ62(S) oil has suffered moderate to severe biodegradation as indicated by the occurrence of an unresolved complex mixture (UCM) hump and enriched C_{29} 25-norhopane. A slightly enhanced gammacerane index is most likely caused by biodegradation as gammacerane is much more resistant to biodegradation than other pentacyclic terpanes (Peters and Moldowan, 1993). This oil is highly mature as indicated by an unusually high methylphenanthrene index (Xiao et al., 2005). High C_{20} and C_{21} tricyclic terpane contents can result from thermal maturation. Severe fractionation is also diagnosed for this oil as the light ends are absent (Xiao et al., 2005). Again, it is probably derived from the Є–O_1 source rocks, but it is not a suitable end-member because of its high maturity and extensive secondary alteration.

Two condensates were recovered at 6426–6497 and 6439–6458 m from the Middle Cambrian in well ZS1. This is the first commercial liquid hydrocarbon production from Cambrian strata (Wang et al., 2014). A few liters of gas condensate were encountered during drill stem testing from well ZS1C (a deviation well from ZS1) at depth 6861–6944 m in the Lower Cambrian where the main flow is dry gas. Well ZS1 should provide a very good end-member of oil generated from the Cambrian source (Wang et al., 2014). However, based on biomarkers and isotopic compositions of individual *n*-alkanes, Li et al. (2015) concluded that the two ZS1 oils (actually they are condensates) were derived primarily from the O_{2-3} source rocks and oil from well ZS1C (residual condensate) has a good genetic relationship with the Cambrian source rocks. Evidence for such a correlation appears in the $\delta^{13}C$ values of individual *n*-alkane components. The ZS1 condensates are ^{13}C-depleted indicating that they have an O_{2-3} source. Carbon isotopic compositions of ZS1C condensate are ^{13}C-enriched, close to those in well TD2 oil, consistent with an affinity to the Cambrian source rocks. However, Li et al. (2015) also noted that the ZS1C condensate has suffered intensive TSR alteration. Extraordinarily enriched $\delta^{13}C$ values are most likely caused by secondary alteration processes, rather than being source input related. Cai et al. (2015) proposed that both ZS1 and ZS1C oils are derived from the Cambrian source rocks based on sulfur isotopic compositions. The ZS1 oil is unlikely to have migrated downward from the Upper Ordovician, while ZS1C is altered by TSR.

The YM2 oil from the Lower Ordovician carbonate reservoir was regarded as an O_{2-3} source end-member as its biomarkers and individual *n*-alkanes $\delta^{13}C$ values are different from the TD2 and TZ62(S) oils. The majority of oils from the cratonic region show close affinity to the YM2 oils, therefore, O_{2-3} source rocks made the dominant contribution to current oil accumulations (Zhang and Huang, 2005; Li et al., 2010a,b, 2015; Yu et al., 2011, 2012; Tian et al., 2012).

We propose that the currently selected end-members for oils derived from Cambrian/Ordovician sources are not usefully representative of any specific source interval because secondary alterations have removed all the original signatures. Injudicious selection of an end-member may cause an impediment for oil–source correlation, and is probably the root cause for many years of controversy.

3.2. *n*-Alkane distribution pattern

The carbon number distribution of *n*-alkanes can reflect the source of organic matter, sedimentary environment and maturity of organic matter. Even/odd predominance of *n*-alkanes is usually observed from carbonate and evaporite source rocks deposited under hypersaline euxinic conditions and highly reducing environments (Tissot and Welte, 1984). Although no obvious even/odd predominance of *n*-alkanes has been observed in either Cambrian or Ordovician source rock extracts (Hanson et al., 2000; Zhang et al., 2000), Luo et al. (2015) proposed an easy criterion to differentiate oil families in the cratonic region. The O_{2-3} source rock extracts and their derived oils show odd/even predominance in the *n*-C_{15} to *n*-C_{19} range, while an even/odd predominance occurs in the Є–O_1 source rock extracts and oils. However, their 10 Upper Ordovician source rock extracts show no predominance at all as indicated by an average odd even predominance (OEP) value of 1.0. Some source rock extracts from the Є–O_1 in wells KN1, TC1, TD2 and He4 have OEP values < 0.8 for *n*-C_{14} to *n*-C_{18} alkanes, which is correlated to oils from wells TZ45 and TZ162, but no OEP values are provided in their context (Luo et al., 2015).

Pan and Liu (2009) noticed even/odd carbon predominance in the range *n*-C_{12}–*n*-C_{18} in well TZ11 in Silurian oil sand bitumen and in well TZ45 in Ordovician carbonate extracts. Jia et al. (2010) observed a similar predominance from wells Ha1 (6080 m) and Jinan 1 (5486 m) in Silurian oil sand bitumens (Fig. 3). They concluded that even/odd predominance in the range *n*-C_{12}–*n*-C_{18} is a characteristic of the Є–O_1 source rocks, which can be applied as an effective method for oil–source correlation in the cratonic region of the Tarim Basin. The correlation results seem consistent with the prevailing viewpoint that contributions of Є–O_1 source rocks to oil accumulation exist in the cratonic region, but they are masked by late charges overwhelmingly from the O_{2-3} source rocks.

No robust evidence can be established for oil–source correlation based on carbon preference index because no oils with such predominance have been discovered from the cratonic region. Even if such oils are found, it seems unlikely that even/odd predominance can be used to characterize the Cambrian source rocks. First, the even/odd predominance is not restricted to a specific depositional environment. It has been found in recent and ancient

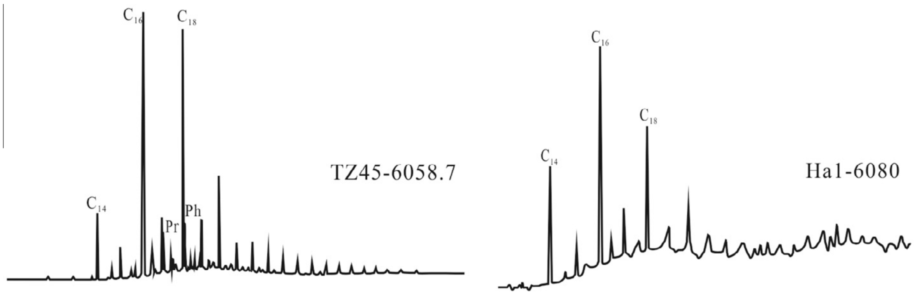

Fig. 3. Gas chromatograms of saturated hydrocarbon fraction of oil sand extracts showing even/odd carbon predominance of *n*-alkanes. (a) Carbonate extract from O_3 in well TZ45 at 6058.7 m (after Pan and Liu, 2009); (b) Sandstone extract from Silurian in well Ha1 at 6080 m (after Jia et al., 2010). Pr: pristane; Ph: phytane.

sediments, which include marine, brackish and freshwater (river and lacustrine) environments and oxic and anoxic depositional conditions (Grimalt and Albaiges, 1987). There is no reason why an even/odd predominance would only occur in the Cambrian strata. Second, if it is formed in a very strongly reducing (euxinic) environment by reduction of *n*-alkanoic acids, a wide range of *n*-alkane carbons up to C_{30} might be expected to have an even predominance, rather than simply a few components present in these oil sand extracts. Third, if specific inputs from organisms already containing this predominance are involved, such predominance only persists in the early oil generation stage (Tissot and Welte, 1984).

Pan and Liu (2009) reported a very complicated situation in their sequential extraction observations. The predominance in inclusion fractions (the earliest charge) is weaker than that in the adsorbed fractions. They assumed that inclusions contain both early and late charged oils, but did not explain how a late charge can be trapped in inclusions without affecting the adsorbed fraction coated on sand grains. In order to avoid the difficulty of deciphering the coexistence of *n*-alkanes and 25-norhopanes in oil sand extracts where even/odd predominance has been observed, Jia et al. (2010) assumed that the even carbon dominated *n*-alkanes are generated from the Cambrian source rocks after the Late Permian when biodegradation ceased. However, the authors did not consider the source rock maturity evolution. When biodegradation ceased after the late Hercynian orogeny, the Cambrian source rocks are almost exhausted (Zhang et al., 2014). Proof of how a source rock at very high maturity stage can generate even/odd predominance *n*-alkanes and why such a predominance only occurs in very few oil sand extracts is required for this hypothesis to be accepted. In summary, the occurrence of even/odd predominance of *n*-alkanes in a few oils, oil sand and source rock extracts most likely reflects a peculiar formation mechanism, which is not relevant to depositional environments and/or source input and cannot be applied for oil–source correlation (see Section 4 for more details).

3.3. Biomarkers

Biomarkers indicative of the source rocks for oils in the Tarim Basin have been comprehensively investigated. Oils from the Є–O_1 source rocks are characterized by a relatively high abundance of gammacerane, C_{35} homohopanes, 24-*iso*propylcholestanes, 24-*nor*cholestanes, C_{28} regular steranes and C_{30} dinosteranes (4α,23, 24-trimethylcholestanes), but depleted in diasteranes. Oils from O_{2-3} sources show reverse characteristics and yield a "V" shaped regular sterane distribution pattern (Hanson et al., 2000; Zhang et al., 2000, 2002, 2004; Wang and Xiao, 2004; Zhang and Huang, 2005; Ma et al., 2006; Cai et al., 2009b; Li et al., 2010a, 2015; Yu et al., 2011; Li et al., 2012a). Two oil families have been identified accordingly. The majority of oils produced in Tazhong and Tabei uplifts show amazing similarity to the extracts from the O_{2-3} source rocks. Only a few oils from wells TD2, TZ62(S) and T904 show typical characteristics of the Є–O_1 source origin. These biomarker distributions suggest that the contribution from the Є–O_1 source rock is negligible. However, Cai et al. (2015) found "V" shaped C_{27}–C_{29} sterane distributions from the Cambrian source rocks, questioning the sterane distribution pattern as a criterion to differentiate the Cambrian from Upper Ordovician sources.

Recently, Bao et al. (2012) defined a new oil family based on tricyclic terpane distributions. Typical Cambrian sourced oils represented by TZ11(S) are characterized by relatively high gammacerane and low C_{29} hopane, while Ordovician oils represented by TZ10(C) show relatively low gammacerane and high C_{29} hopane. Their tricyclic terpanes are dominated by C_{23} component with C_{24} tetracyclic terpane slightly higher than C_{26} tricyclic terpanes. A new oil type represented by wells TZ52 and TZ162 from Ordovician reservoirs was proposed based mainly on the relative abundance of tricyclic terpane components, which decreases with increasing carbon with $C_{19} > C_{20} > C_{21} > C_{23} > C_{24} > C_{25} > C_{26}$. The C_{24} tetracyclic terpane is abnormally high (Fig. 4) (Bao et al., 2012). An unknown source rock type may exist in the Cambrian to Ordovician succession, but no oil–source correlation has been performed. However, our recent work suggested that the distribution patterns of tri- and tetracyclic terpanes are not necessarily valid as an oil–source correlation indicator. The so called Cambrian source end-member or unknown source rocks in the Tarim Basin are most likely derived from the thermal alteration of normally distributed tri- and tetracyclic terpanes (Huang et al., 2015a).

3.4. Aromatic hydrocarbons

Although most aromatic hydrocarbons are products of diagenesis and catagenesis, triaromatic steroids (TAS) and triaromatic dinosteroids are interpreted as source signatures and can be used for oil–source correlation. Relatively higher abundances of C_{26} 20S, C_{26} 20R + C_{27} TAS and aromatized dinosteroids characterize oils derived from Cambrian source rocks, whereas a relatively high abundance of C_{28} TAS and near absence of aromatized dinosteroids indicates oils that originated from the O_{2-3} source rocks (Fig. 5) (Zhang et al., 2000, 2002; Li et al., 2012a). Oils from wells TD2, T904, LK1 and TZ26 show close affinity to the Є–O_1 source rocks from wells TD2, KN1 and Yuli1. Some oils in the Sangtamu fault zone of the Lunnan oil field are thought to be a mixture of these two oil types, while the majority of current oil accumulations originated from the O_{2-3} carbonates (Zhang et al., 2002; Mi et al., 2007; Li et al., 2012a). This correlation is quite consistent with the conclusion derived from other biomarkers in the saturated hydrocarbon fraction.

Some other PAHs have also been applied for oil–source correlation by Li et al. (2012b) and Fang et al. (2015). Є–O_1 derived oils represented by TD2 are unusually rich in benzo[*a*]anthracene with

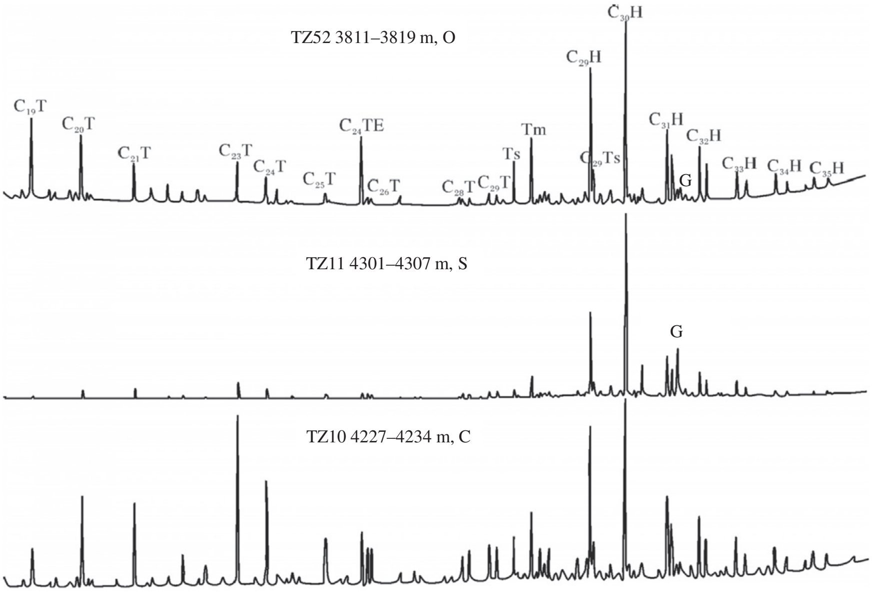

Fig. 4. The distributions of terpanes in three types of crude oils from the Tarim Basin (after Bao et al., 2012). T: tricyclic terpanes; TE: C_{24} tetracyclic terpanes; Ts: 18α(H)-trisnorneohopane; Tm: 17α(H)-trisnorhopane; H: hopanes; G: gammacerane.

fluoranthene more abundant than pyrene, while the O_{2-3} oils are deficient in benzo[*a*]anthracene with fluoranthene less abundant than pyrene. Based on the relative abundance of coupled compounds of fluoranthene–pyrene and benzo[*a*]anthracene–chrysene and their methylated isomers, the Є–O_1 derived oils can be distinguished from the O_{2-3} derived oils in the cratonic region of the Tarim Basin. Oils from wells TD2, TZ26, TZ162 and TZ451 fall into the category of an Є–O_1 origin, while the majority of other oils were generated from O_{2-3} carbonate source rocks (Li et al., 2012b; Fang et al., 2015).

A series of aryl isoprenoids has been identified in cratonic oils in the Tarim Basin. As these compounds are often regarded as the diagenetic products of di-aromatic carotenoids (e.g., isorenieratene) from anaerobic photosynthetic green sulfur bacteria (Chlorobiaceae; Grice et al., 1996), Sun et al. (2003) suggested that the source rocks for these oils were deposited under euxinic conditions related to the Є–O_1 depositional environment rather than the O_{2-3} slope facies on the margins of structural uplifts. However, no oil–source correlation based on aryl isoprenoids has ever been performed. Interestingly, Zhang et al. (2014) noticed that commonly cited Cambrian derived oil from TZ62(S) contains almost no aryl isoprenoids. They suggested that oils enriched in aryl isoprenoids are most likely formed at a relatively low maturity stage, while the depletion of aryl isoprenoids may be influenced by both source input/depositional environment and thermal maturity.

3.5. Isotopic compositions

The carbon isotopic value of an oil is dependent upon the value of the kerogen in the source rock from which it is derived. The kerogen value depends, in turn, on the types of organisms preserved and paleo-climate conditions especially the isotopic compositions of CO_2 in atmospheric gases and water (Tissot and Welte, 1984). Therefore, the carbon isotopic value is widely used as oil–source correlation parameter. There are no systematic carbon isotopic data for the Palaeozoic source rocks in the Tarim Basin. Zhang et al. (2004a) reported a few $\delta^{13}C$ values from well TC1 at the Tazhong Uplift with $\delta^{13}C$ values in the range from −29.2‰ to −30.3‰ for the Upper Ordovician kerogens, from −28.1‰ to −31.3‰ (11 samples) for the Lower Ordovician kerogens, and from −28.5‰ to −30.9‰ (6 samples) for the Cambrian kerogens. Li et al. (2015) recently documented a wide variation of $\delta^{13}C$ values in kerogens especially for Є–O_1 source rocks. Very ^{13}C-depleted kerogens with $\delta^{13}C$ values as low as −35‰ were encountered in the Keping area in the western Tarim Basin, although Li et al. (2015) emphasized that source rocks in the Є–O_1 are more enriched in ^{13}C than these from the O_{2-3} (Fig. 6a) (Li et al., 2015 and references therein). Cai et al. (2015) reported that source rocks from the Lower Cambrian outcrops have $\delta^{13}C$ values ranging from −33.7‰ to −35.3‰ for kerogens, which are significantly depleted compared to those from the Upper Ordovician.

Most of the Palaeozoic oils in the Tarim Basin have $\delta^{13}C$ values in the range of −31.0‰ to −33.0‰ with a few exceptions (Zhang et al., 2004a; Cai et al., 2009b, 2015; Li et al., 2010b, 2015; Tian et al., 2012; Yu et al., 2012; Jia et al., 2013). Because the TD2 oil has the most enriched $\delta^{13}C$ value and is situated in Cambrian strata, it is commonly regarded as the end-member for the Cambrian derived oils (Li et al., 2010b, 2015; Tian et al., 2012; Yu et al., 2012; Jia et al., 2013). Only a few oils from wells TZ62(S), T904(O) and ZS1C(Є) have similar bulk carbon isotopic values to the TD2 oil and were regarded as having a pure Є–O1 origin (Tian et al., 2012; Yu et al., 2012; Jia et al., 2013; Li et al., 2015). The most ^{13}C-depleted oil is automatically selected as the O_{2-3} sourced end-member. Previously, an oil from well YM2 with a $\delta^{13}C$ around −35‰ was used as an end-member (Li et al., 2010b; Tian et al., 2012; Yu et al., 2012; Jia et al., 2013). Recently, Li et al. (2015) reported one more ^{13}C-depleted oil from well YG2 with a $\delta^{13}C$ value of −37‰, which was selected as the new end-member for O_{2-3} sourced oil. Consequently, most oils have been interpreted to be mixtures from the O_{2-3} and the Є–O_1 source rocks.

The ratios from two end-member mixtures are quantitatively assessed by either linear mixing of bulk isotopic values (Mi et al., 2007; Tian et al., 2012) or individual *n*-alkane isotopic values (Li et al., 2010b, 2015). Mi et al. (2007) suggested that about 40% of the oils in the east of the Lunnan sub-uplift were derived from Є–O_1 source rocks. Tian et al. (2012) listed detailed percentages of the Є–O_1 source contribution ranging from 10–100% for samples from Tazhong Uplift purely based on bulk isotopic variations between two end-members. Li et al. (2010a, 2010b, 2015) used isotopic values of individual *n*-alkanes to quantify the mixing ratios of

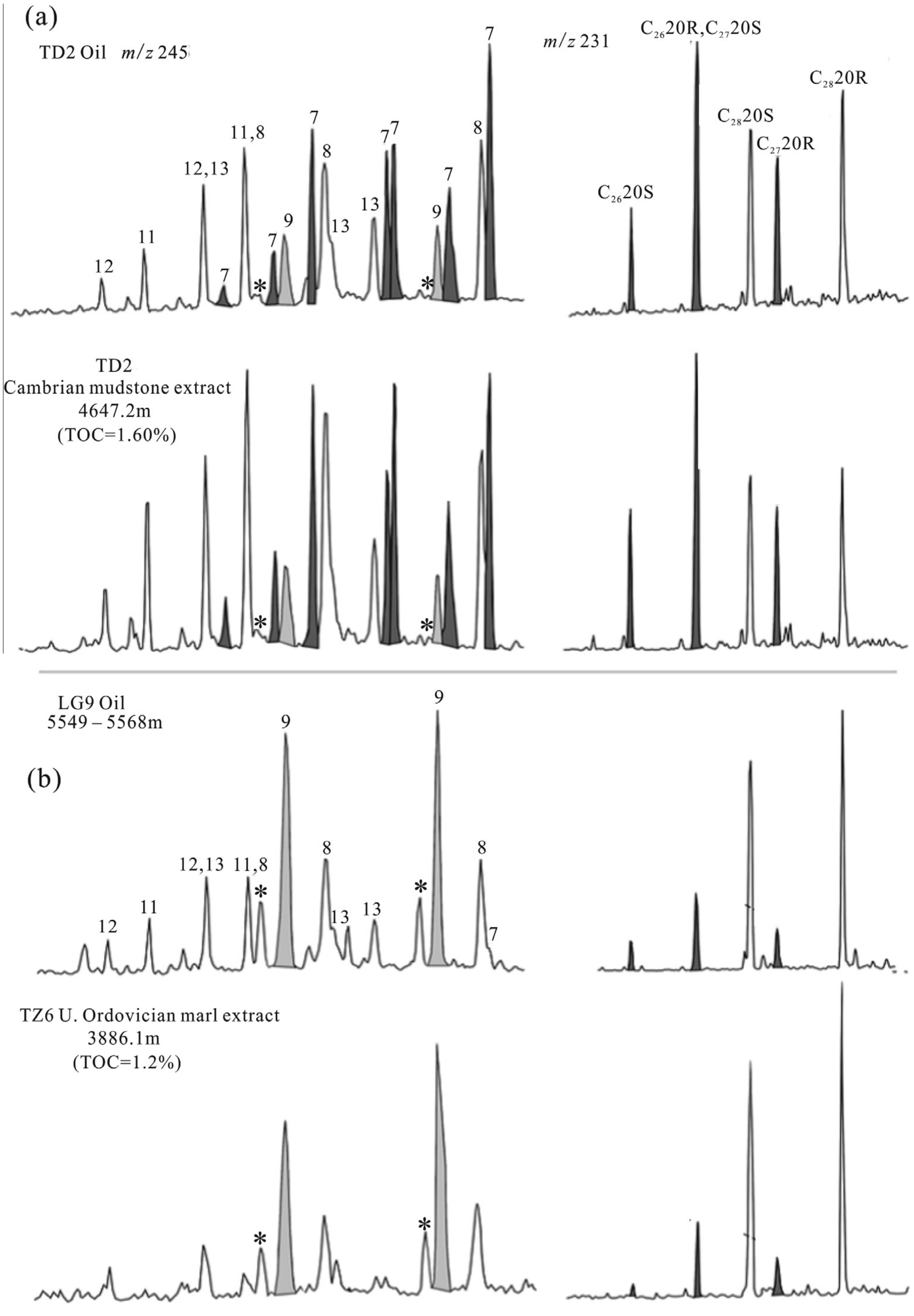

Fig. 5. The distribution of methyl triaromatic steroids (*m*/*z* 245) and triaromatic steroids (*m*/*z* 231) in Tarim oils and rock extracts. (a) Heavy oil from well TD2 and extract of Cambrian mudstone from depth of 4674.2 m in the same well; (b) heavy oil from LG9 and extract of Upper Ordovician muddy limestone from TZ6 at depth of 3886.1 m. Peak 7: 4,23,24-trimethyltriaromatic steroids (C_{29} triaromatic steroids); peak 8: 4-methyl-24-ethyltriaromatic steroids (C_{29}); peak 9: 3-methyl-24-ethyltriaromatic steroids; peak 11: 4-methyltriaromatic steroids (C_{27}); peak 12: 3-methyltriaromatic steroids (C_{27}); peak 13: 3-methyl-24-methyltriaromatic steroids (C_{28}) (after Zhang et al., 2002).

two end-members (Fig. 6b). The proportions of the Є–O_1 derived oils in the cratonic region ranges from 13–91% when the YM2 oil was used as the end-member to represent an O_{2-3} origin (Li et al., 2010b), however, a higher proportion ranging from 19–100% was interpreted if the end-member from well YG2 is applied (Li et al., 2015). A similar conclusion was drawn by Jia et al. (2013). All these correlations indicate significant contributions from the Є–O_1 source rocks, which differ from the conclusion based on biomarkers. Clearly, end-member selection has a significant impact on interpretations. If the end-member selection is unreliable, all these correlations and quantification estimates are misleading in such a complicated basin.

The sulfur isotopic composition ($\delta^{34}S$) of kerogen reflects the processes of organic matter sulfurization at the time of sedimentation and the $\delta^{34}S$ of oil is believed to be affected mainly by sulfur incorporation reactions into the sedimentary organic matter during early diagenesis (Orr, 1986; Aizenshtat and Amrani, 2004). Therefore, $\delta^{34}S$ values have a high potential for oil–source

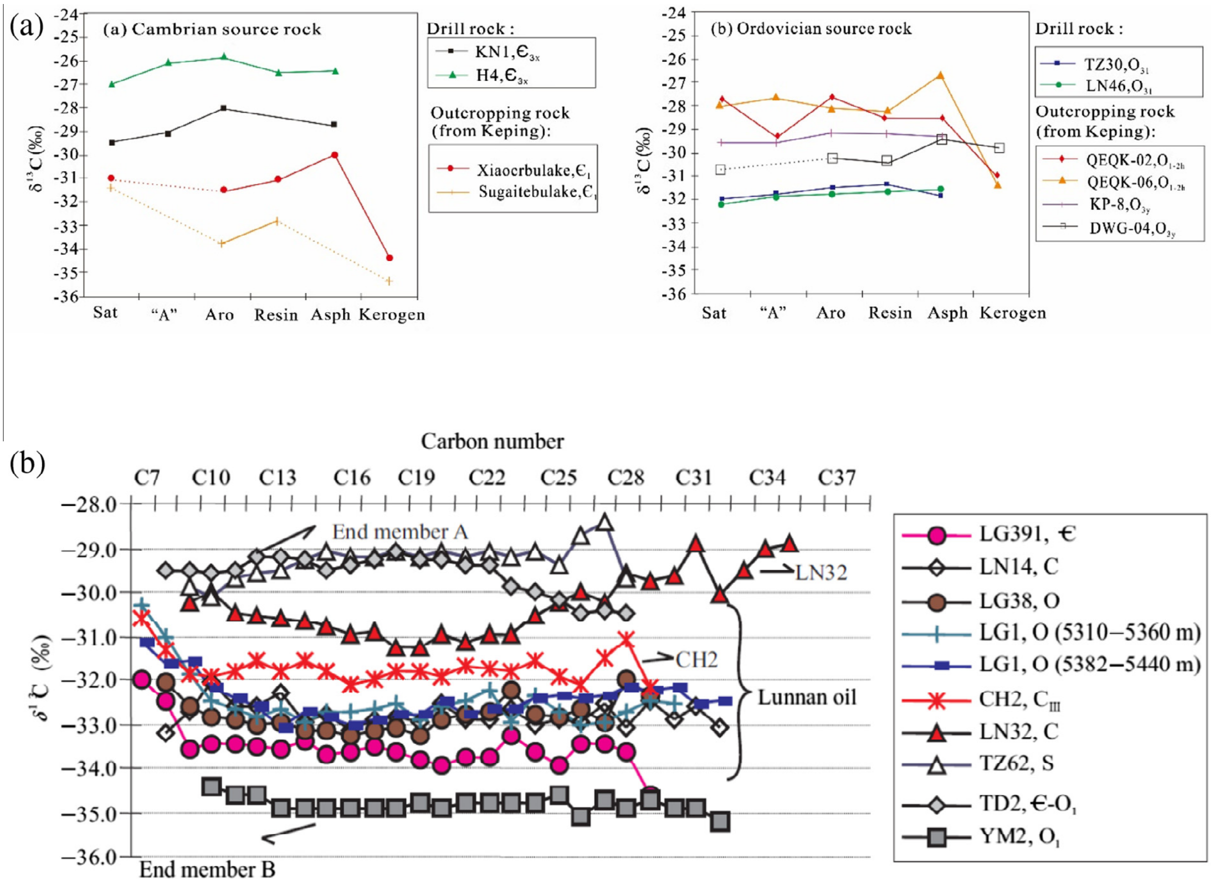

Fig. 6. (a) Carbon isotopic values of rock extracts and kerogens from potential Palaeozoic source rocks; (b) distribution features of the compound-specific carbon isotopic curves in representative oils from the Tarim Basin (data from Li et al., 2010b, 2015).

correlation. If sulfur in the oils is mainly derived from source rocks in a rapidly buried basin with rapid hydrocarbon generation, δ^{34}S value can be applied for oil–source correlation (Cai et al., 2009a). However, if secondary alteration processes occur, the original δ^{34}S value of the oil will be altered by the effect of microbial biodegradation (Mehay et al., 2009), bacterial sulfate reduction (Thode, 1981; Cai et al., 2005, 2009b) and TSR (Manzano et al., 1997; Machel, 2001).

In the case of the Tarim Basin, δ^{34}S values of mature kerogen show a gradual decrease from the Cambrian to Middle–Upper Ordovician. Non-biodegraded oils without associated H_2S have δ^{34}S values closely correlated with those in the Є–O_1 source rocks, indicating a genetic affinity. Non-biodegraded oils with associated H_2S may have been derived from either the O_{2-3} or the Є–O_1 source rocks as TSR-derived inorganic sulfur may be incorporated into the oil. The δ^{34}S values of heavily biodegraded oils are significantly heavier than those of any of the potential source rocks, but close to Cambrian and Ordovician age seawater sulfates, suggesting that isotopically enriched sulfides have been incorporated into the biodegraded oils (Cai et al., 2009a,b).

The ZS1 oils have bulk and individual alkyldibenzothiophene δ^{34}S values between 15‰ and 23‰ VCDT, which are similar to those for some Cambrian source rocks with kerogen δ^{34}S values of 10.4–21.6‰ (Cai et al., 2015). The oil produced from the Lower Ordovician in well YM2 has similar features to the ZS1 Cambrian oils. These new lines of evidence indicate that most of the oils in the Tazhong Uplift were probably derived from the Cambrian source rocks, and not from the Upper Ordovician. Abnormally ^{13}C- and ^{34}S-enriched values in ZS1C oil is caused by TSR rather than source input (Cai et al., 2015).

4. Secondary alteration effects on oil–source correlation

Source rock organofacies and maturity are the primary controls on oil composition in reservoirs, while multiple alteration processes including thermal cracking, biodegradation, mixing, evaporative fractionation and TSR among many others have secondary effects on oil after it is accumulated in the trap. Recognizing the intensity and extent of each process in the field and their impact on molecular and isotopic compositions is critical in oil–source correlation parameter selection.

4.1. Normal and abnormal thermal maturation impact

In a conventionally matured sedimentary basin, the formation of crude oils is generally attributed to progressive catagenesis of kerogen. Heavy oil, normal oil, light oil, condensate, wet gas and dry gas are formed sequentially during increasing temperature and burial depth with pyrobitumen as the mass balance residue (Tissot and Welte, 1984). Contact metamorphism represents a different thermal regime in which temperatures are well above the normal petroleum generation window. The rapid heating by igneous activity causes extensive and important modifications to molecular distributions compared with the relatively slow heating of burial maturation (Raymond and Murchison, 1992). Contact metamorphism and/or hydrothermal fluid activity may make oil compositions completely different from those in normal thermal maturation regime.

The Tarim Basin has experienced multiple phases of igneous intrusion. Permian igneous rocks are widely distributed and occur throughout the basin (Jia and Wei, 2002; Jin et al., 2006;

Dong et al., 2013; Pu et al., 2013). Permian basalt and dacite sills and dikes within the mid-western part of the Ordovician reservoir comprise up to 200 m in the Tabei Uplift (Pu et al., 2013). For example, a 94 m thick black diabase intrusion occurs in the Silurian oil sands at a depth of 4615–4709 m in well TZ18 (Fig. 7) (Zhu et al., 2008). Supportive evidence of igneous intrusions and/or hydrothermal activity include: (1) the wide occurrence of hydrothermal minerals including barite, fluorite, anhydrite, chalcedony and pyrite; (2) karstification; (3) unusually high homogenization temperatures of fluid inclusions; (4) unusual enrichment of some rare earth elements and sulfur; and (5) strontium and oxygen isotopic compositions (Jin et al., 2006, 2013; Cai et al., 2008; Dong et al., 2013). Zhu et al. (2008) noticed that oils preserved in the Silurian sandstone reservoir are altered into black pyrobitumen by abnormally high heat stress induced by igneous intrusions. The %Ro value of the pyrobitumen reaches as high as 3.54. Ran et al. (2008) noticed abnormal vitrinite reflectance values in all 7 studied wells in the Tadong area. Abnormally high vitrinite reflectance occurs near the hydrothermal fluid conduits.

4.1.1. Even/odd predominance

The even/odd preference of *n*-alkanes in oil is generally controlled by the relative amount of precursor compounds that were preserved in the kerogen. However, the *n*-alkanes in well TZ18 bitumen, which are affected by igneous intrusion, show strikingly different *n*-alkane distribution patterns from other oils (Zhu et al., 2008). They are dominated by low molecular weight components in the range n-C_{14} to n-C_{20} and peaked at n-C_{16} or n-C_{18}. The Σn-C_{21-}/Σn-C_{22+} ratios of four studied samples are 39.1, 4.7, 7.1 and 4.6, respectively, while ratios of normal oils from adjacent wells are around 1.0 (Zhu et al., 2008). Carbon cleavage of long chain *n*-alkanes to form short chain *n*-alkanes by unusually high thermal stress is understandable. However, the enigmatic feature is that these *n*-alkanes show strong even/odd predominance with OEP values of 0.22–0.49 (Fig. 8). Zhu et al. (2008) interpreted such even carbon number predominance as a result from abnormal heating stress alteration rather than inherited from source rocks, but the mechanism leading to such predominance during thermal cracking of high molecular weight hydrocarbons has not been provided.

Similar even/odd preference has been reported for samples from hydrothermal systems where oil is generated by reductive processes occurring during the accelerated diagenetic/catagenetic alteration of immature organic matter (Elias et al., 1997). Hydrothermal dehydration/reduction of *n*-alkanols and/or *n*-alkanoic acids in lipids or bound in the organic detritus could provide ample even chain length *n*-alkanes to account for an OEP < 1.0 in the alkane distributions (Rushdi and Simoneit, 2002). The precursors for the occurrence of even carbon number predominance in well TZ18 bitumen are not clear since thermal cracking of long chain *n*-alkanes generally has no carbon number discrimination. Nevertheless, the even numbered *n*-alkane predominance in the low molecular weight range observed in oil sand extracts in wells TZ45(O), TZ11(S) and Ha1(S) (Pan and Liu, 2009; Jia et al., 2010) is very similar to that present in well TZ18 oil sand extracts (Zhu et al., 2008). In addition, wells TZ45, TZ162 and Ha1 are close to volcanic and hydrothermal fluid conduits (Jin et al., 2006; Lu et al., 2007; Pu et al., 2013). The predominance of even numbered *n*-alkanes in these oil sand extracts is likely to be a characteristic of igneous intrusion/hydrothermal activity rather than a defined signature for the Є–O_1 source rocks.

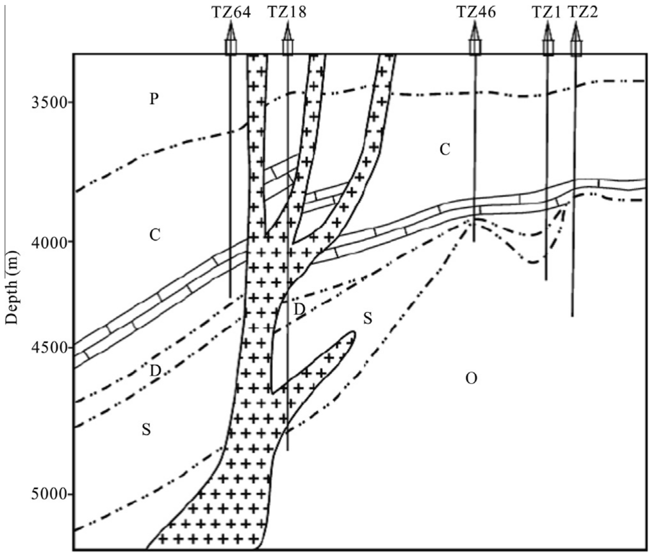

Fig. 7. Igneous intrusion in well TZ18 (after Zhu et al., 2008).

In order to verify whether the even/odd predominance is a genetic character of the Є–O_1 source rocks or not, Yu et al. (2011, 2012) have systematically analyzed of the Є–O_1 source rocks from well TD2. As expected an even/odd predominance of *n*-alkanes does occur in some rock extracts. They noticed that an even/odd predominance of *n*-alkanes only occurs in some organic-poor samples. The organic-rich samples (TOC 2.99% in the Lower Ordovician and 3.42% in the Cambrian) do not exhibit a clear even/odd predominance (Yu et al., 2011). Coupled with abnormal thermal events diagnosed by Ran et al. (2008) in well TD2, the occurrence of even/odd predominance of light *n*-alkanes likely results from abnormal thermal alteration.

4.1.2. Biomarkers

Biomarkers (steranes and hopanes) are mainly formed in the early oil window. With increasing thermal maturation, these biomarkers are cracked to form low molecular weight components (Peters and Moldowan, 1993; Requejo, 1994). Therefore, biomarker signatures of high maturity oil phases are normally not easily recognized (masked) due to relatively low concentration of the biomarker compounds. Erroneous oil–source correlation may occur based on biomarker fingerprints (Wang and Xiao, 2004) as increasing thermal maturity will cause systematic changes in biomarker compositions in oils. A detailed review of biomarker variation with maturity is out of the scope of present study. Rather, we illustrate here the maturity influence on a few biomarker parameters commonly used for oil source correlation in the Tarim Basin. Generally, the biomarker compositions of the Palaeozoic oils in the cratonic region of the Tarim Basin are very similar (Zhang et al., 2000, 2002, 2005; Li et al., 2010a, 2015), suggesting that their source rock organofacies are relatively uniform. However, biomarker ratios indicate a wide range of source rock thermal maturity from early to middle oil window through to the gas window (Zhang et al., 2005). Li et al. (2015) noticed that 5000 m is a critical point of thermal stability for the steranes and terpanes in the Tazhong oils. Biomarkers are largely depleted in oils with burial depths > 5000 m. The ratio of C_{23} tricyclic/C_{30} hopane is a commonly used parameter for oil family classification and oil–source correlation (Yu et al., 2011, 2012; Bao et al., 2012). Maturity influence on this parameter is inevitable for a wide range of thermal maturities as the C_{23} tricyclic is more stable than the C_{30} hopane. The gammacerane index (gammacerane/C_{30} or C_{31} hopane) is a critical parameter for oil–source correlation as Cambrian source rocks and oils are enriched in gammacerane (Zhang et al., 2000). Subtle variation in this parameter can be caused by regional variations of organic facies as more shales developed in the eastern part of the basin, while more marls developed in the western part during the Cambrian. The effect of geological maturation on the gammacerane

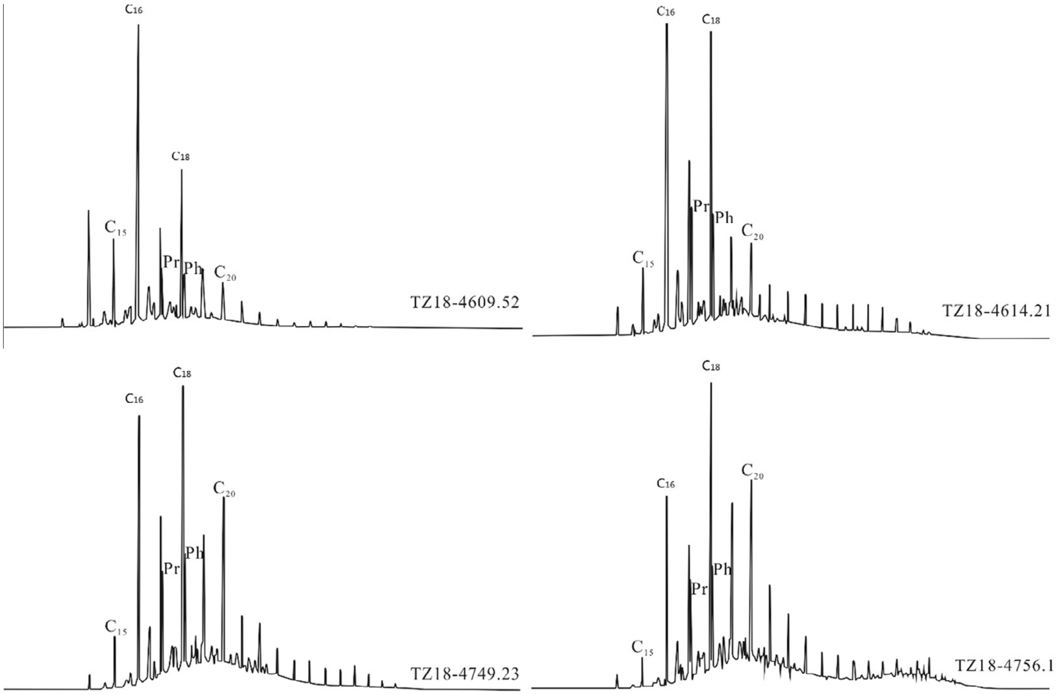

Fig. 8. Gas chromatograms of saturated hydrocarbons in oil sand extracts from well TZ18 showing even/odd predominance (after Zhu et al., 2008).

index has not been demonstrated in the literature. However, thermal simulation experiments of a heavy oil from the Tabei Uplift in the Ordovician reservoir of well S74 conducted by Liu (2008) illustrated that gammacerane index shows a wide variation with heating temperature especially in the residual extracts (Fig. 9a). For an initial gammacerane index of around 0.2, the expelled oils had gammacerane index values slightly < 0.2 at various heating temperatures. The residual extracts had gammacerane index values of 0.2 at 300 °C, rising to 0.75 at 350 °C. The gammacerane index values decrease to below 0.2 with further temperature increase.

Another source related parameter is the distribution pattern of tricyclic terpanes. The Є–O_1 source rocks and related oils have higher C_{20} and C_{21} tricyclic terpanes, while these O_{2-3} source rocks and related oils have higher C_{23} and C_{24} tricyclic terpanes (Zhang and Huang, 2005; Li et al., 2010a, 2015). However, thermal maturity has a defined impact on the tricyclic terpane distribution especially when abnormal heating stress occurs. Asphaltene pyrolysis of Silurian oil sand from the Tazhong Uplift performed by Jia et al. (2010) illustrated that almost no C_{19} tricyclic terpane was detected in raw oil sand extracts, while C_{19} and C_{20} tricyclic terpanes are enriched dramatically in the pyrolysates. Oil sand extracts from the igneous intrusion influenced well TZ18 have very different C_{21}/C_{23} tricyclic terpane ratios from those oils and source rock extracts which have not been affected by igneous intrusion. The C_{21}/C_{23} ratios are < 0.6 in normal samples, while the ratios in TZ18 oil sand extracts are > 1.0 (Zhu et al., 2008) (Fig. 9b). Abnormally high thermal stress may cause C–C bonds cleavage resulting in a relatively high abundance of low molecular weight (LMW) tricyclic terpanes. The so-called typical Cambrian signature of the tricyclic terpane distribution pattern in TD2 oil most likely resulted from unusual heating rather than source input (Huang et al., 2015a). A similar deduction can be applied to wells TZ52 and TZ162 (Bao et al., 2012), where igneous intrusion rather than an unknown source rock might be involved.

Previous studies illustrated that biomarker concentrations in source rocks increase from the Cambrian to Upper Ordovician

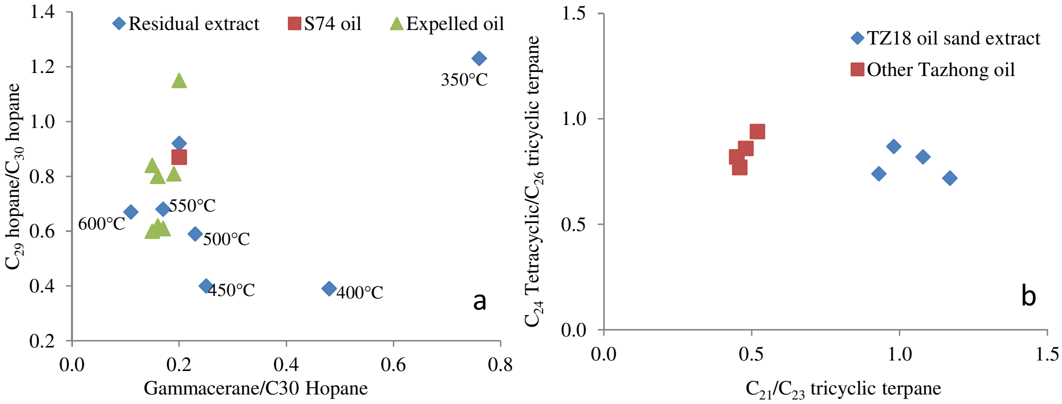

Fig. 9. Maturity influence on biomarker ratios. (a) Simulation results from well S74 heavy oil illustrating relationship between gammacerane indexes and C_{29} hopane/C_{30} hopane ratios (data from Liu, 2008); (b) igneous intrusion influence on tricyclic terpane distributions (data from Zhu et al., 2008).

source rocks (Zhang et al., 2000; Li et al., 2015). However, some age diagnostic biomarkers including 24-*iso*propylcholestanes, dinosteranes (4α,23,24-trimethylcholestanes), triaromatic dinosteroids and 24-*nor*cholestanes are concentrated in the Cambrian source rocks and related oils (Zhang et al., 2000, 2002, 2005; Li et al., 2010a, 2012a), which seems to conflict with a maturity control interpretation. Ma et al. (2006) found that these diagnostic biomarkers for the Є–O_1 occur in the Upper Ordovician source rocks with very high concentrations at the Keping outcrop, indicating that they are not age-specific. Subtle compositional irregularities of oils are attributed to geographical variability in the maturity and composition of source kerogen. However, the occurrence of these diagnostic biomarkers in an unusually high maturity oil like that from well TD2 remains mysterious. Cai et al. (2015) suggested that there are two facies of Cambrian source rocks that have different biomarker distribution and $\delta^{13}C$ values. Additional characterization of TD2 and TZ62(S) source rocks is required.

4.1.3. Aromatic hydrocarbons

Benzanthracene, benzofluoranthene and benzopyrene are typically used as markers of combustion (Yunker et al., 2002). These compounds have been used for oil–source correlation in the Tarim Basin as combustion from coal deposits is impossible due to the absence of land plants during the Cambrian–Ordovician. As these compounds mainly occur in TD2 oil and a few Є–O_1 source rock extracts, they were regarded as diagnostic of the Є–O_1 source system (Li et al., 2012b). However, these components can be formed as a result of igneous intrusion and/or hydrothermal activity. Although no obvious igneous intrusion has been encountered at well TD2, abnormally high fluid inclusion homogenization temperatures (Zhang et al., 2004b) and an unusual vitrinite reflectance profile (Ran et al., 2008) indicate hydrothermal fluid influence. Unusually high contents of fluoranthene, pyrene, benzo[*a*]anthracene and benzofluoranthene detected in well TZ18 oil sand extracts clearly illustrate the impact of igneous intrusion (Zhu et al., 2008). During igneous intrusion, oil was partially cracked to LMW fragments, mostly free radicals, which form PAHs by pyro-synthesis as temperature drops.

The relatively higher concentration of benzo[*a*]anthracene and other combustion-derived PAHs in the Є–O_1 source rocks and related oils can most likely be attributed to igneous intrusion/hydrothermal fluid effects rather than differences in depositional environment and/or organic matter input. The widespread spatial and temporal occurrence of igneous activity within the Palaeozoic succession in the Tarim Basin makes the derivation of the latter PAHs from pyrolytic sources probable. Exposure to high temperatures results in the pyrolysis of the oil reservoir, adding high-temperature aromatic artefacts to the oil. Geochemical measurements show the wide occurrence of mixing processes between pyrolytically derived PAHs and diagenetically derived hydrocarbons. The concentrations and distributions of combustion-derived PAH in the cratonic oils reflect their proximity to igneous intrusions/hydrothermal fluid conduits and mixing ratios (Huang et al., 2015b). It is difficult to unambiguously determine a background combustion-derived PAH level for samples in which PAHs are not affected by igneous intrusion/hydrothermal fluid due to oil migration and other secondary processes affecting PAH distributions and concentrations. Consequently, use of these pyrolytically derived PAHs in oil–source correlations lead to misinterpretations. The presence of pyrolytically derived aromatics in the Tarim oils can most likely be attributed to igneous intrusion/hydrothermal fluid effect on the oils in the reservoirs, rather than differences in depositional environment and/or organic matter input (Huang et al., 2015b).

4.1.4. Carbon isotope compositions

The most ^{13}C-enriched oil (–28‰) in the Tarim Basin is commonly selected as the end-member for Є–O_1 source rocks while the isotopically most depleted oil (–37‰) has been selected as the end-member of the O_{2-3} source rocks. A temporal trend of isotopic depletion from Cambrian to Upper Ordovician is widely accepted (Li et al., 2010a,b, 2015; Jia et al., 2013); however, this trend is opposite that of the global carbon isotopic composition trend. Carbon isotopic values of the Cambrian derived oils are in the range of −36.13‰ to −33.40‰ with an average value of −34.81‰ and standard deviation of 0.97‰, while oils derived from the Ordovician source rocks have $\delta^{13}C$ values ranging from −30.35‰ to −28.31‰ with an average value of −29.16‰ and standard deviation of 0.75‰ (Andrusevich et al., 1998). The overall trend of enrichment in ^{13}C with decreasing age appears to be independent of source rock facies type (Stahl, 1977). The major, abrupt shift in ^{13}C enrichment coincides with the Cambrian/Ordovician boundary. The geologic record of positive carbon isotope excursion from Cambrian to Ordovician represents a perturbation in the global cycling of carbon, which reflects trends in the abundance and nature of the paleo-biomass, fluctuations in organic and carbonate carbon preservation and the concentrations of atmospheric gases, i.e., CO_2 and O_2 (Andrusevich et al., 1998; Glumac and Walker, 1998). Although local climate and biomass variation may cause some complications, the Palaeozoic organic matter preserved in the Tarim Basin should be consistent with the same trend based on the following considerations.

Although some kerogens from the Є–O_1 are isotopically enriched, ^{13}C-depleted kerogens with values around −35‰ have been documented from the Keping Uplift (Cai et al., 2015; Li et al., 2015). However, ^{13}C-depleted kerogens from O_{2-3} source rocks have never been identified to support a correlation with ^{13}C-depleted oils. Li et al. (2010, 2015) proposed that the Є–O_1 source rocks should be isotopically more enriched than the O_{2-3} rocks because they are associated with a bottom water euxinic environment, but no supportive evidence has ever been provided (Yu et al., 2011; Cai et al., 2015).

A radiation of eukaryotes among single celled organisms, mostly acritarchs, occurred at the base of the Cambrian (Tissot and Welte, 1984). The organic matter is enriched in isotopically depleted lipids because microorganisms consumed the proteins and carbohydrates of organic-walled phytoplankton. Many Ordovician source rocks are unique in their abundance of *Gloeocapsomorpha prisca*, which had extremely resistant organic walls. The relatively enriched isotopic value of Ordovician oils may stem from the contribution of this species to Ordovician kerogens (Andrusevich et al., 1998). The paleo-biomass in the Tarim Basin experienced the same evolution history as the global biomass. The changes in carbon isotopic compositions must be caused by factors which influence all organic matter, that is, by secular changes in the biosphere. There is no reason for the Tarim Basin to show the opposite isotopic trend to the global trend over the same time period.

A strong positive excursion (up to 4‰) of carbon isotope values for carbonate from the Lower–Ordovician to the O_{2-3} in the Tarim Basin (Wang and Song, 2002) was cited as evidence of a negative excursion of oil carbon isotope values by Tian et al. (2012). However, such decoupled ($\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ shifting in the opposite direction) variation only occurred in organic-poor carbonates ($TOC < 0.1\%$) while coupled ($\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ shifting in the same direction) occur in organic-rich black shale and carbonates (Jiang et al., 2012). The phytoplankton blooms that occurred during the O_{2-3} would be expected to produce isotopic enrichments of both organic and carbonate carbon (Andrusevich et al., 1998).

Carbon isotopes of bulk organic matter can be influenced by many factors including carbon isotope fractionation during primary and secondary production, detrital organic carbon input, post-depositional alteration through diagenesis/metamorphism, and hydrocarbon contamination (Jiang et al., 2012). It has been frequently stated that diagenesis and thermal maturation do not substantially alter carbon isotope values of organic matter in sedimentary rocks (Li et al., 2010a,b, 2015; Tian et al., 2012). However, after detailed isotope-maturity correlation, Jia et al. (2013) noticed kinetic isotopic fractionation exerts a significant impact on the $\delta^{13}C$ value of *n*-alkanes. For bulk isotopic compositions, highly matured oils are slightly enriched in ^{13}C (−31‰ to −32‰) while heavy or normal oils are slightly depleted in ^{13}C (−32‰ to −34‰).

The most dramatic carbon isotopic compositional variations will occur if abnormal heating events such as igneous intrusion and hydrothermal fluid activity are involved. Thermal loss of isotopically depleted components is evident in the Swiss Alps Liassic black shale samples where average $\delta^{13}C$ values of kerogen shows progressive ^{13}C enrichment from −27.1‰ within diagenetic zone to −10.5‰ near a metamorphic contact that underwent the highest thermal stress (Schwab et al., 2005). Preferential loss of isotopically depleted forms of carbon from oil has been observed from well TZ18 (Zhu et al., 2008). The $\delta^{13}C$ values of oils from adjacent wells where there was no apparent igneous intrusion are between −32.5‰ and −33.4‰, however, the $\delta^{13}C$ values of the carbonaceous bitumen from well TZ18 are between −27.2‰ and −29.3‰ (Zhu et al., 2008). Thermal simulation experiments of the heavy oil from well S74 illustrated that the $\delta^{13}C$ values of the residual extracts increase gradually with temperature. The bulk carbon isotopic value is more than 6‰ enriched than the original oil after heating at 600 °C for 24 h (Fig. 10) (Liu, 2008).

Well TD2 contains a small amount of residual oil that has experienced abnormal heating (Zhang et al., 2004b). The ZS1C condensate is a residual after TSR and thermal cracking (Cai et al., 2015; Zhu et al., 2015). In a large oil pool, removal or alteration of a portion of the primary organic carbon may not substantially change the $\delta^{13}C$ values of the oil, but for an isolated oil accumulation as in wells TD2 and ZS1C, once *n*-alkanes are largely removed after thermal cracking and/or TSR, the isotopically heavier residue no longer retains the source input signature. Some source rock extracts, especially those from organic poor source rocks from wells TC1 and KN1 showing enriched carbon isotopic values (Li et al., 2010a), can be caused by a similar maturity influence. Current knowledge of isotopic compositions in source rocks and oils in the Tarim Basin are most likely limited to a few abnormal samples and systematic reconstruction is required.

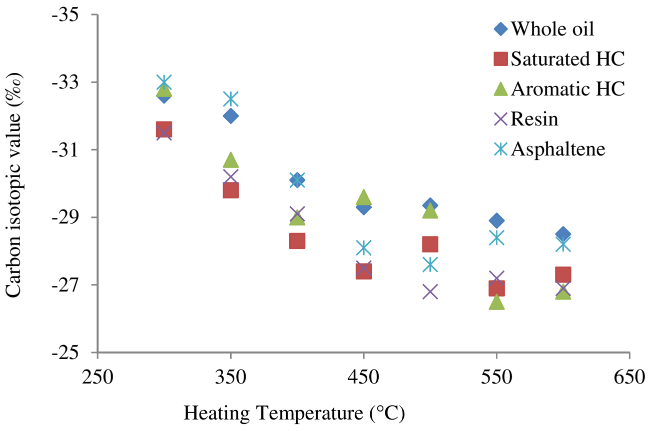

Fig. 10. Isotopic compositional variations with increasing heating temperatures in bulk fraction of residual extracts from simulation experiments (data from Liu, 2008).

4.2. Biodegradation

Fresh oil charging and mixing after biodegradation is common in the cratonic region owing to the multiple source rock systems and tectonic activity (Zhang et al., 2000; Zhang and Huang, 2005; Jia et al., 2010). Most oils display biodegradation signatures, characterized by variable size of the UCM and variable amounts of 25-norhopanes and 17-*nor*tricyclic terpanes. The ubiquitous occurrence of *n*-alkanes suggests that the petroleum accumulated in these fields is mainly a mixture of previously biodegraded oils with later migrated fresh oils. Biodegradation and mixing of molecular compositions have been systematically investigated by Zhang et al. (2014).

Relatively high amounts of gammacerane in marine oils from the Tarim Basin are usually considered an important parameter for oil/source correlations, because the Cambrian source rocks are characterized by relatively high abundances of gammacerane (Li et al., 2010a; Yu et al., 2011). However, gammacerane is more resistant to biodegradation than other hopanoids (Peters and Moldowan, 1993). Fifty-three oil samples from Paleozoic marine reservoirs of the Tarim Basin have gammacerane/C_{30} hopane ratios that are positively correlated with C_{23} tricyclic terpane/C_{30} hopane ($C_{23}TT/C_{30}H$) and C_{28} 25-norhopane/C_{29} hopane ratios (Zhang et al., 2014). These correlations cannot be explained by depositional environment control. Although maturity is inevitably also reflected in these ratios, biodegradation is certainly another factor.

Tricyclic terpanes are generally more abundant in highly mature oils because they are thermally more stable than other terpanes (Peters and Moldowan, 1993) and thus the ratio of tricyclic terpanes/hopanes increases with increasing maturity. As a class, the tricyclic terpanes are highly resistant to biodegradation and may remain unaltered in heavily biodegraded oils, even after the hopanes have been removed (Seifert and Moldowan, 1979). Some moderately high $C_{23}TT/C_{30}H$ ratios are generally caused by high thermal maturity, while unusually high $C_{23}TT/C_{30}H$ ratios in Halahatang heavy oils and Tazhong Silurian bitumens are definitely caused by biodegradation (Zhang et al., 2014).

Slightly more abundant C_{35} homohopanes than C_{34} homohopanes is another characteristic of Cambrian sourced oils making it potentially useful as a source rock depositional environment signature (Li et al., 2010b; Yu et al., 2011). However, Zhang et al. (2014) noted that the C_{35} homohopanes become predominant over the C_{34} homohopanes with increasing biodegradation intensity. Although overall sterane carbon number distributions have not been affected significantly by biodegradation, the regular steranes are generally biodegraded at a considerably faster rate than the diasteranes. Variations in diasteranes/steranes ratios might represent a biodegradation influence on sterane distributions (Zhang et al., 2014).

Because the effects of biodegradation and thermal maturation cannot be unambiguously differentiated on the basis of molecular marker approaches alone, previous interpretations generally ignored the biodegradation effects (Li et al., 2010a; Yu et al., 2011). As noted above, molecular parameters commonly used for oil–source correlation such as $C_{23}TT/C_{30}H$, C_{29} hopane/C_{30} hopane, gammacerane to C_{30} hopane, C_{35} homohopanes/C_{34} homohopanes, C_{27}–C_{29} diasteranes to C_{27}–C_{29} regular steranes are at least partially controlled by biodegradation. Caution should be applied when these parameters are used for oil–oil and oil–source correlation when extensive biodegradation is also involved.

4.3. Thermochemical sulfate reduction (TSR)

In the absence of TSR, the aromatic sulfur compounds present in an oil are dependent on its source and maturity level. Plots of the ratio of dibenzothiophene/phenanthrene (DBT/P) against pristane/phytane (Pr/Ph) proposed by Hughes et al. (1995) are commonly used to assess source rock depositional environments. However, unusually high abundances of DBTs are encountered in the cratonic oils from the Tarim Basin due to TSR alteration and sulfur incorporation into hydrocarbons (Cai et al., 2009b; Zhang et al., 2015). The DBT/P ratio reaches 23.3 in the ZS1C condensate (Li et al., 2015). This means that the classification criteria for source rock paleoenvironment of Hughes et al. (1995) may not be applicable to samples with ultra-high maturity and/or that are TSR altered (Zhang et al., 2015). Interestingly, the Ordovician oils with high DBT/P ratios have similar individual DBTs compounds $\delta^{34}S$ value to those low DBT/P oils (Cai et al., 2015; Li et al., 2015). TSR can significantly affect the compositions of oil and gas reservoirs before completely destroying them (Heydari, 1997). If liquid oil is present, TSR will decrease the saturated/aromatic hydrocarbon ratio, density and C_{15+} hydrocarbon content of the petroleum, but increase the gas/oil ratio (GOR) and concentration of organosulfur compounds (Manzano et al., 1997). As for the gaseous hydrocarbons, gases associated with TSR are found to be relatively dry. The residual hydrocarbon gases become ^{13}C-enriched as TSR progresses (Krouse et al., 1988; Cai et al., 2013). Relatively high H_2S contents in gas condensates have been found in the Palaeozoic marine reservoirs of the Tarim Basin, especially in the Tazhong Uplift area, implying varying intensities of TSR alteration in the cratonic region (Cai et al., 2001, 2009b, 2015).

The ZS1C condensate is a typical TSR alteration residue. The total ion chromatogram of the saturated hydrocarbon fraction contains an obvious UCM hump with very low *n*-alkanes concentrations, while that of aromatic hydrocarbon fraction is dominated by the DBT series. Unusually enriched $\delta^{34}S$ values of DBTs suggest a close genetic relationship with TSR alteration (Cai et al., 2015; Li et al., 2015). High $\delta^{13}C$ values in the bulk fraction and individual *n*-alkanes are mostly likely a result from TSR alteration rather than indicating a Cambrian source signature. The coincidence of extraordinarily high $\delta^{13}C$ values with those of the TD2 and TZ62(S) oils is caused by different alteration processes, precluding using the carbon isotope signature as a robust correlation tool.

5. Conclusions

The Є–O_1 source rocks are organic rich with high thickness and are currently over mature, while effective source rocks in the O_{2-3} strata are moderately matured and they are organic poor with a limited distribution. Various techniques have been applied in oil–source correlation including distributions of *n*-alkanes, biomarkers, polycyclic aromatic hydrocarbons, bulk and individual hydrocarbon carbon isotopic compositions, bulk and individual dibenzothiophene sulfur isotopic compositions, sequential extraction and asphaltene pyrolysis. All studies suggest that the oils in the cratonic region of the Tarim Basin are mixtures of two source rock systems, however, the criteria of differentiation and proportion from each end-member are controversial. Many older studies suggest that oils are overwhelmingly derived from the O_{2-3} source rocks with only a few samples bearing the Є–O_1 source characteristics, while more recent studies emphasize a greater contribution from Є–O_1 source rocks. The root cause for this controversy is the injudicious selection of end-members that has impeded robust oil–source correlation. TD2 oil, widely used as an end-member for the Cambrian, has lost its original signature due to an abnormally high thermal stress. Some biomarker variations such as sterane distribution, gammacerane index and ratio of tricyclic/pentacyclic terpanes are closely related to thermal maturation and biodegradation. In addition, the even/odd predominance of *n*-alkanes, unusually enriched $\delta^{13}C$ values, occurrence of combustion related PAHs most likely resulted from igneous intrusion and hydrothermal fluid influences. TSR also exerts significant impacts on local oil compositions. All these factors need to be properly accounted for before the contribution from the Cambrian strata can appropriately be assessed.

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