



Original Paper

Extended hopanes and 8,14-secohopanes up to C₄₀ in unbiodegraded marine oils from the Tarim Basin, NW China

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ABSTRACT

Extended 17 α (H), 21 β (H)-hopanes and three series of 8,14-secohopanes up to C₄₀, including 8 α (H), 14 α (H), 17 α (H), 21 β (H)-, 8 α (H), 14 α (H), 17 β (H), 21 α (H)- and 8 α (H), 14 β (H), 17 β (H), 21 α (H)-, were detected by GC-MS-MS method in the branched/cyclic hydrocarbon fractions of some unbiodegraded marine oils from the Tazhong uplift in the Tarim Basin, NW China. The coexistence of extended hopanes and 8,14-secohopanes up to C₄₀ in unbiodegraded oils suggests that they are primary and independent on biodegradation. The similarity of distribution and composition for extended hopanes and 8,14-secohopanes up to C₄₀ in unbiodegraded oils proposes that they could be derived from a similar biological precursor. However, an abrupt decrease up to 3–5 times in the relative abundance from C₃₅ to C₃₆ in C_{31–40} extended hopanes and extended 8,14-secohopanes suggests that C_{31–35} and C_{36–40} extended hopanes and extended 8,14-secohopanes should have their own biological precursor. The known C₃₅ bacteriohopanetetrol should be biological precursor of C_{31–35} extended hopanes and 8,14-secohopanes, but an unknown C₄₀ functionalized hopanoid could be biological precursor of C_{36–40} extended hopanes and 8,14-secohopanes. More attention should be paid to their potential roles in oil-source correlation for severely biodegraded oils based on their widespread occurrence in various source rocks, unbiodegraded and severely biodegraded oils.

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1. Introduction

Hopanoids are a kind of widespread but relatively complex biomarkers related to prokaryotes in various source rocks and crude oils, including hopanes, moretanes, diahopanes, 8,14-secohopanes, hexacyclic hopanes and benzohopanes etc. (Schmitter et al., 1982; Hussler et al., 1984; Connan and Dessert, 1987; Moldowan et al., 1991; Ourisson and Albrecht, 1992; Ourisson and Rohmers, 1992). Extended hopanes up to or beyond C₄₀ (Rullkötter and Philp, 1981; Wang et al., 1996) and C_{27–35} 8,14-secohopanes (Schmitter et al., 1982; Fazeelat et al. 1994, 1995; Silva et al., 2011; Oliveira et al., 2012; Scarlett et al., 2019) were usually detected in biodegraded oils.

Extended 17 α (H), 21 β (H)-hopanes up to C₄₀ were firstly detected in the saturated hydrocarbon fraction of a distillation cut of Thornton bitumen without *n*-alkanes from the Thornton Quarry in

just south of Chicago (Illinois) of US (Rullkötter and Philp, 1981). Extended 17 α (H), 21 β (H)-hopanes and 17 β (H), 21 α (H)-moretanes beyond C₄₀ were identified in a moderately biodegraded oil nearly devoid of *n*-alkanes from the well Gao-2-4-052 in the Liaohe Basin, NE China (Wang et al., 1996). So far, these extended hopanes and moretanes up to or beyond C₄₀ seem to be mainly identified in biodegraded oils.

C_{27–31} 8,14-secohopanes were firstly detected by GC-MS analysis in a Nigerian crude oil, and the C₃₀ homologues was identified by comparison with a mixture of synthetic isomeric standards (Schmitter et al., 1982). They were also reported in other biodegraded oils (Rullkötter and Wendisch, 1982; Silva et al., 2011; Oliveira et al., 2012; Scarlett et al., 2019). Fazeelat et al. (1994) firstly detected the extended 8,14-secohopanes up to C₃₅ in some severely biodegraded oil seeps from Pakistan. Based on their gas chromatographic retention behavior and relative abundance (stability), Fazeelat et al. (1995) found six series of 8,14-secohopanes for C_{31–35} in a biodegraded crude oil, and tentatively identified them as 8 β (H), 14 α (H), 17 α (H), 21 β (H)-(I), 8 α (H), 14 α (H), 17 α (H), 21 β (H)-(II), 8 β (H), 14 α (H), 17 β (H), 21 α (H)-(III), 8 α (H), 14 α (H), 17 β (H), 21 α (H)-(IV),

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$8\alpha(\text{H})$, $14\beta(\text{H})$, $17\alpha(\text{H})$, $21\beta(\text{H})$ -(V) and $8\alpha(\text{H})$, $14\beta(\text{H})$, $17\beta(\text{H})$, $21\alpha(\text{H})$ -(VI), respectively (see Appendix). Rullkötter and Wendisch (1982) suggested that 8,14-secohopanes were formed from $17\alpha(\text{H})$ -hopanes analogues by microbial opening of C-ring. In addition, C_{27-30} 8,14-secohopanes were also detected in some unbiodegraded oils from Argentina, found that their relative abundances increased with increasing their maturity (Villar and Püttmann, 1990).

Wang et al. (1990) detected C_{27-32} 8,14-secohopanes in the aliphatic fraction of bitumen from a Chinese boghead coal of Middle Jurassic, suggested that the genesis of 8,4-secohopanes, i.e. the opening of ring C of the hopanoids skeleton, could happen during the early stages of hydrocarbon generation based on vitrinite reflectance of the sample ($R_o = 0.65$ – 0.67%). Del Rio et al. (1994) detected a trace amount of C_{27-31} 8,14-secohopanes in the Puer-tollano immature oil shale from Spain. Bao et al. (1996) found that C_{27-30} 8,14-secohopanes were widely distributed in the extracts of Lower Paleozoic over-mature marine source rocks from the Lower Yangtze area, East China (vitrinite-like reflectance value $> 2.0\%$). Therefore, 8,14-secohopanes are present in different geological samples such as various source rocks, unbiodegraded and biodegraded oils, suggesting that C-ring opening of hopane skeleton could happen during early diagenesis, and is probably related to thermal maturation of organic matter.

In this paper, we firstly reported the occurrence of the extended $17\alpha(\text{H})$, $21\beta(\text{H})$ -hopanes and 8,14-secohopanes up to C_{40} in some unbiodegraded marine crude oils from the Tazhong Uplift in the Tarim Basin, NW China, and discussed their possible origin based on their distributions and compositions.

2. Samples and experimental methods

2.1. Geological backgrounds and samples

The Tarim Basin, about $56 \times 10^4 \text{ km}^2$, is the largest petroliferous basin in China, in which two sets of marine source rocks in the Cambrian–Lower Ordovician ($\text{E}-\text{O}_1$) and Middle–Upper Ordovician (O_{2+3}) sequences were developed in the cratonic region (Zhang et al., 2004; Zhou et al., 2010; Jin et al., 2017; Guan et al., 2019). A great amount of crude oils and natural gas have been discovered and produced in the Tazhong Uplift (Zhang et al. 2004, 2014; Jiang et al. 2010, 2020; Song et al., 2016). However, the main sources for these oils have been controversial for a long time (Zhang et al. 2004, 2005; Cai et al. 2009, 2015; Li et al., 2010; Yu et al., 2011; Huang et al., 2016; Zhu et al., 2017). The reason is related to a big difference in maturity of organic matter between two sets of $\text{E}-\text{O}_1$ and O_{2+3} source rocks, resulting in the direct oil-source correlation very difficult or even impossible. Analytical results show that the equivalent vitrinite reflectance values (R_o) in the $\text{E}-\text{O}_1$ source rocks are more than 1.7% and up to high or over mature stage, but the R_o values for O_{2+3} source rocks are about between 0.8% and 1.3% and within liquid hydrocarbon window (Zhang et al. 2004, 2005; Wang et al., 2010; Li et al. 2010, 2015).

Based on distributions and compositions of various biomarkers, marine crude oils in the Tarim Basin can be divided into two types. The first one is relatively common and characterized by very low gammacerane, a general “V” shape for C_{27-29} $\alpha\alpha\alpha$ -20R regular steranes and relative abundant C_{19-26} tricyclic terpanes and C_{21-22} short chain side steranes (Zhang et al., 2004; Li et al. 2010, 2015), but their source remains controversial (Zhang et al. 2004, 2005; Cai

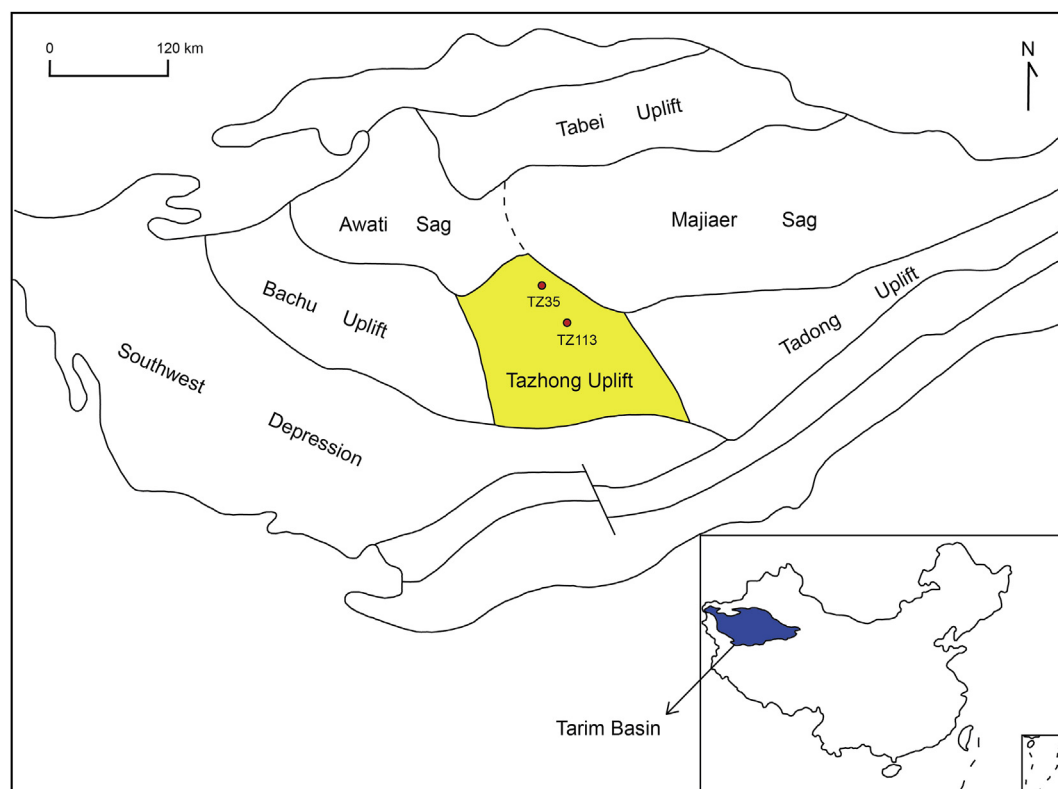


Fig. 1. The tectonic units and the well positions of crude oil samples in the Tarim Basin.

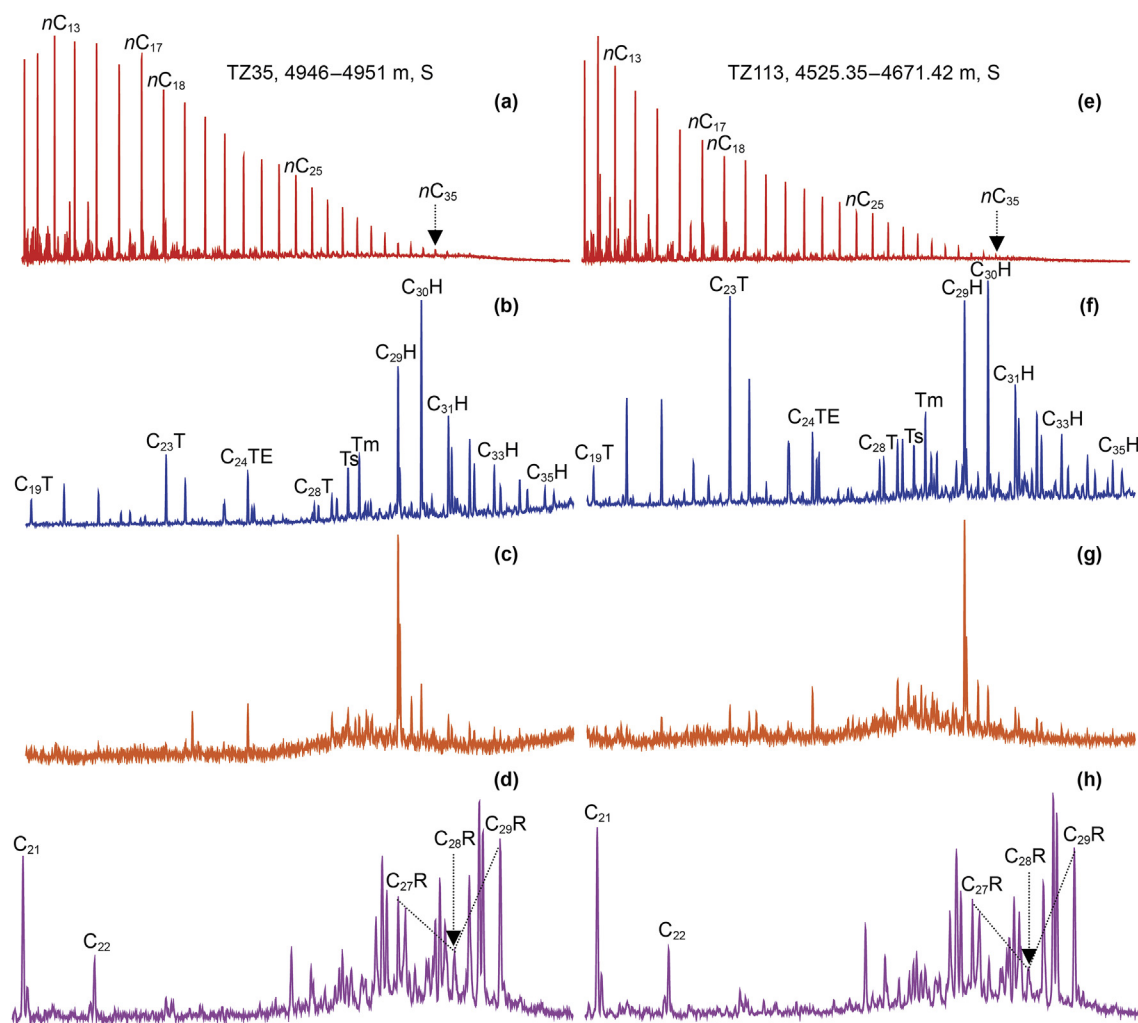


Fig. 2. The m/z 57 (a, e), m/z 191 (b, f), m/z 177 (c, g) and m/z 217 (d, h) mass chromatograms showing the distributions of chain alkanes, tricyclic terpanes, hopanes and steranes in unbiodegraded oils from the Tazhong Uplift of the Tarim Basin. nC_{13} – nC_{35} = normal alkanes; $C_{19}T$, $C_{23}T$ and $C_{28}T$ = C_{19} , C_{23} and C_{28} tricyclic terpanes; $C_{24}TE$ = C_{24} tetracyclic terpene; Ts = $18\alpha(H)$ -22,29,30-trisnorhopane; Tm = $17\alpha(H)$ -22,29,30-trisnorhopane; $C_{29-35}H$ = C_{29-35} $17\alpha(H)$, $21\beta(H)$ -hopanes; C_{21-22} = short side chain steranes; $C_{27}R$, $C_{28}R$ and $C_{29}R$ = C_{27-29} $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ -20R-regular steranes.

et al. 2009, 2015; Li et al., 2010; Yu et al., 2011). Recently, some primary oil and gas reservoirs were discovered in the Lower Paleozoic dolomite reservoir in the Zhongshen area of the Tazhong Uplift in the Tarim Basin, and generated mainly from the Lower Cambrian source rocks although these crude oils had a similar distributions and compositions of steranes and terpanes like in the crude oils mentioned above (Wang et al., 2014; Song et al., 2016; Zhang et al., 2017). The second one is rare in the Tarim Basin and produced only in the well TZ11 (S) and TZ30 (O) in the Tazhong Uplift so far (Bao et al., 2018). In this kind of crude oils mainly derived from the $C-O_1$ source rocks (Zhang et al., 2004), gamma-cerane and the C_{28} steranes in C_{27-29} regular steranes are relatively abundant, the C_{19-26} tricyclic terpanes and C_{21-22} short chain side steranes are very low, but the concentrations of hopanes and steranes are much more than those in the first kind of crude oils (Bao et al., 2018). In this study, the first kind of marine crude oils was collected from the Tazhong Uplift in the Tarim Basin (Fig. 1) and studied in detail.

2.2. Experimental methods

Asphaltene in the crude oils (about 30 mg) was precipitated in

n -hexane, and then de-asphalted oil was separated into the saturated hydrocarbon, aromatic hydrocarbon and NSO fractions using an aluminum/silica column chromatography, with n -hexane, toluene and chloroform/ethanol (1:1) as eluents, respectively. The saturated hydrocarbon fraction was further separated into normal alkane and branched/cyclic hydrocarbon fraction using urea adduction as described by Sun et al. (2005).

The GC-MS analysis of the saturated hydrocarbon fractions was conducted on an Agilent 6890 gas chromatograph coupled to a 5975 mass selective detector. GC conditions: the column was a HP-5MS fused silica capillary column (30 m $\times$ 0.25 mm $\times$ 0.25 μ m film thickness). The temperature program was at 50 $^{\circ}$ C for 2 min, and then from 50 $^{\circ}$ C to 100 $^{\circ}$ C at 20 $^{\circ}$ C/min, from 100 $^{\circ}$ C to 315 $^{\circ}$ C at 3 $^{\circ}$ C/min, finally maintained at 315 $^{\circ}$ C for 16.83 min. The injector and ion source temperatures were 310 $^{\circ}$ C and 230 $^{\circ}$ C, respectively. Helium was used as a carrier gas at a rate of 1.04 mL/min. The scan range was from 50 to 580 amu in full scan and multiple ion modes. The ionization electron energy was 70 eV.

The GC-MS-MS analysis of branched/cyclic hydrocarbon fractions was carried out using a Thermo Fisher Scientific TSQ Quantum-XLS, equipped with Trace GC Ultra. GC conditions: the column was a HP-5MS fused silica capillary column

(30 m × 0.25 mm × 0.25 μm film thickness). The temperature program was at 50 °C for 1 min, and then from 50 °C to 100 °C at 20 °C/min, from 100 °C to 320 °C at 3 °C/min, finally maintained at 320 °C for 15.17 min. The injector and ion source temperatures were 310 °C and 230 °C, respectively. Helium was used as a carrier gas at a rate of 1.04 mL/min. The ionization electron energy was 30 eV. The GC-MS-MS analysis was run in parent ions (m/z 372 + 14*n* or m/z 370 + 14*n*, $n = 0–12$) → daughter ions (m/z 123 or m/z 191) modes for the extended 8,14-secohopanes and hopanes, respectively. Argon was used as collision gas, and collision energy was

20 eV. Their peak areas for extended hopanes and extended 8,14-secohopanes up to C₄₀ were integrated in the corresponding chromatograms in the GC-MS-MS analysis.

3. Results and discussion

3.1. Distributions and compositions of various biomarkers

As shown in Fig. 2, *n*C_{11–36} normal alkanes are whole and abundant, and do not have carbon number predominance to be

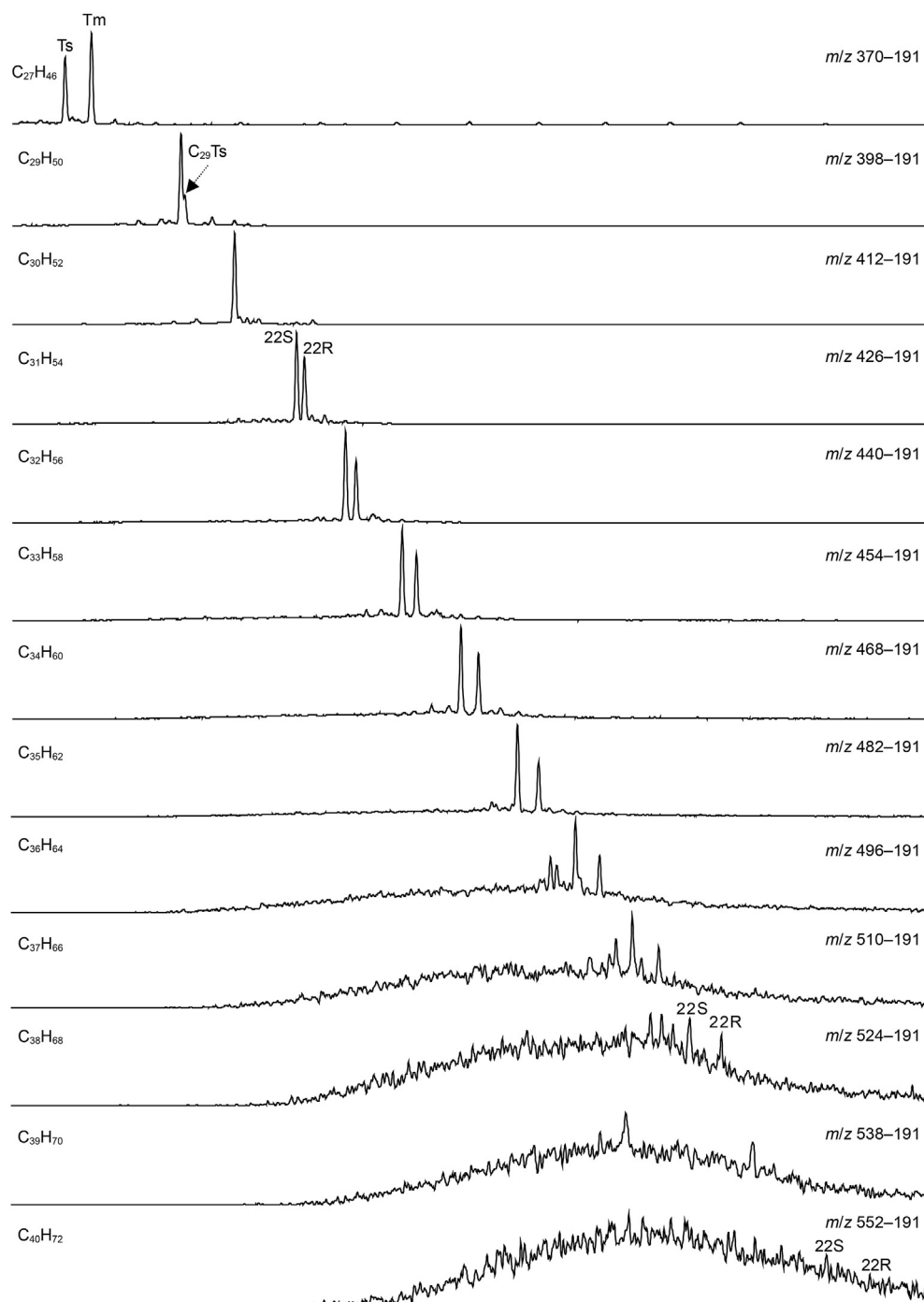


Fig. 3. Metastable ion monitoring data showing the parent ion (m/z 370 + 14*n*, $n = 0–12$) to daughter ion (m/z 191) transitions for the extended 17α(H)-hopanes up to C₄₀ in the crude oil from the well TZ 35.

observed in the m/z 57 mass chromatograms of the saturated hydrocarbon fractions in two marine oil samples from the well TZ35 and TZ113 (Fig. 2a and e). Moreover, the relative abundances of nC_{17} and nC_{18} are much more than those of pristane and phytane in the crude oils, and the Pr/nC_{17} and Ph/nC_{18} ratios are about 0.40. Considering that normal alkanes are a kind of compounds firstly biodegraded during biodegradation in crude oils (Wenger et al., 2002; Peters et al., 2011), abundant normal alkanes and lower Pr/nC_{17} and Ph/nC_{18} ratios suggest that the two crude oils seem not to be biodegraded. In addition, no 25-norhopanes, usually occurred in severely biodegraded oils (Rullkötter and Wendisch, 1982), were detected in the m/z 177 mass chromatogram in their saturate hydrocarbon fractions (Fig. 2c and g), indicating that those crude oils have not been biodegraded and are normal marine crude oils.

In the m/z 217 mass chromatograms (Fig. 2d and h), the C_{21-22} short chain side steranes are relatively abundant, and their relative abundances are similar to those of regular C_{27-29} steranes. Moreover, the C_{29} regular steranes are more abundant than the C_{27} regular steranes, and the C_{28} regular steranes are relatively low, the $C_{27}R/C_{29}R$ and $C_{28}R/C_{29}R$ ratios are about 0.64 and 0.72, 0.41 and 0.27, respectively. In the m/z 191 mass chromatograms (Fig. 2b and f), $17\alpha(H)$, $21\beta(H)$ -hopane series are predominant, and $17\beta(H)$, $21\alpha(H)$ -moretane series are very low and almost not detected. Furthermore, C_{24} tetracyclic terpane ($C_{24}TE$) is more abundant than C_{26} tricyclic terpanes ($C_{26}T$), the $C_{24}TE/C_{26}T$ ratios are about 1.56 and 0.75, respectively. The $17\alpha(H)$, $21\beta(H)$ -norhopane is relatively abundant in the two crude oils, the $C_{29}H/C_{30}H$ ratios are about 0.74 and 0.89, respectively. In addition, gammacerane is very low in these crude oils, the ratios of gammacerane to C_{30} hopane are only about 0.07 and 0.12, respectively. In the two crude oils, the $C_{29} 20S/(20S + 20R)$ and $C_{29} \beta\beta/(\alpha\alpha + \beta\beta)$ ratios are about 0.50 and 0.55, and the Ts/Tm ratios are about 0.81 and 0.64, respectively, showing that they are mature marine oils.

3.2. C_{27-40} extended hopanes

Based on parent (m/z 370 + 14n, $n = 0-12$) → daughter (m/z 191) chromatograms by GC-MS-MS analysis, C_{27-40} extended hopanes, including $18\alpha(H)$ -neohopanes such as Ts and $C_{29}Ts$, were detected in the branched/cyclic hydrocarbon fractions of the crude oils, and there were a pair of C-22 diastereomers with a significant predominance of 22S over 22R isomer for the C_{31-40} extended hopanes (Fig. 3). Combined with the m/z 191 mass chromatograms in Fig. 2b and f, the extended hopanes up to C_{40} should be $17\alpha(H)$, $21\beta(H)$ -hopane series.

Moreover, the linear relationships clearly exist between retention times and the carbon number of the C_{31-40} extended hopanes for 22S and 22R isomers (Fig. 4), showing that they have a linear alkyl side chain, consistent with the results by Rullkötter and Philp (1981) and Wang et al. (1996). It is noted that in the previous studies, the extended hopanes up to or beyond C_{40} were detected in some biodegraded oils (Rullkötter and Philp, 1981; Wang et al., 1996), but in this study, the extended $17\alpha(H)$, $21\beta(H)$ -hopanes up to C_{40} were detected in unbiodegraded crude oils, suggesting that this kind of biomarker in the crude oils could be independent on biodegradation.

As shown in the m/z 191 mass chromatograms in Fig. 2b and f, the C_{27-35} $17\alpha(H)$, $21\beta(H)$ -hopanes are absolutely predominant, and the corresponding moretanes almost can not be detected probably due to low abundance, consistent with the result by GC-MS-MS

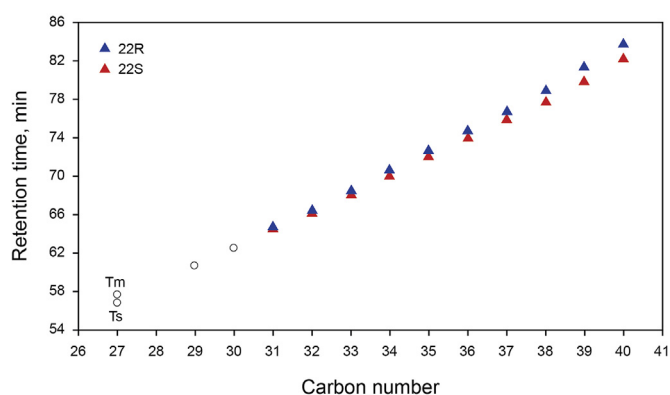


Fig. 4. Plots of the retention times versus their carbon numbers for the extended $17\alpha(H)$, $21\beta(H)$ -hopanes up to C_{40} in the crude oil from the well TZ35.

analysis (Fig. 3). This case is similar to that in the Thornton bitumen (Rullkötter and Philp, 1981), but in a moderately biodegraded oil from the Liaohe Basin, both of the C_{31-44} $17\alpha(H)$, $21\beta(H)$ -hopanes and $17\beta(H)$, $21\alpha(H)$ -moretanes were detected (Wang et al., 1996). Therefore, the presence or absence of moretanes in crude oils could depend on their maturity levels. For example, the maturity of the moderately biodegraded oil from the Liaohe Basin of NE China is relatively low because of abundant C_{27-29} $5\beta(H)$ -steranes and the low $20S/20S + 20R$ and $\beta\beta/\alpha\alpha + \beta\beta$ ratios (<0.30) for C_{29} steranes (Wang et al., 1996), but Thornton bitumen has higher maturity, as indicated by the dominance of $14\beta(H)$, $17\beta(H)$ -steranes (Rullkötter and Philp, 1981). Based on the distribution of C_{27-29} steranes as shown in the m/z 217 mass chromatograms (Fig. 2d and h), $14\beta(H)$, $17\beta(H)$ -steranes are relatively abundant in the crude oils from the well TZ35 and TZ113, suggesting that their low moretanes could be related to relatively high maturity.

3.3. C_{27-40} extended 8,14-secohopanes

Corresponding to the extended hopanes in the crude oil from the well TZ35 as shown in Fig. 3, there were at least three relatively abundant series of extended 8,14-secohopanes up to C_{40} to be detected in the branched/cyclic hydrocarbon fraction based on parent (m/z 372 + 14n, $n = 0-12$) → daughter (m/z 123) chromatograms by GC-MS-MS analysis, and there were a pair of stereoisomeric isomers at C-22 for 22S and 22R in the C_{31-40} range (Fig. 5). Based on their relative retention times, the three series of extended 8,14-secohopanes up to C_{40} correspond to series II ($8\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$, $21\beta(H)$ -), series IV ($8\alpha(H)$, $14\alpha(H)$, $17\beta(H)$, $21\alpha(H)$ -) and series VI ($8\alpha(H)$, $14\beta(H)$, $17\beta(H)$, $21\alpha(H)$ -), other three series (I, III and V) were difficultly determined because of relatively low abundances (Fazeelat et al. 1994, 1995). As shown in Fig. 5, a pair of 22S and 22R isomers for C_{31} 8,14-secohopanes in the series II and VI could be detected at the m/z 428 → 123 chromatogram. But in the series IV, only one peak, not a pair of peaks, could be observed. It may be related to very close retention times for 22S and 22R isomers of C_{31} 8,14-secohopanes in this series not to be resolved, consistent with two isomers of C_{31} moretanes (Fazeelat et al., 1995).

Moreover, the relative abundances of three series of extended 8,14-secohopanes gradually decrease from series II, IV to VI. It is noteworthy that the series IV and VI, probably having moretane-

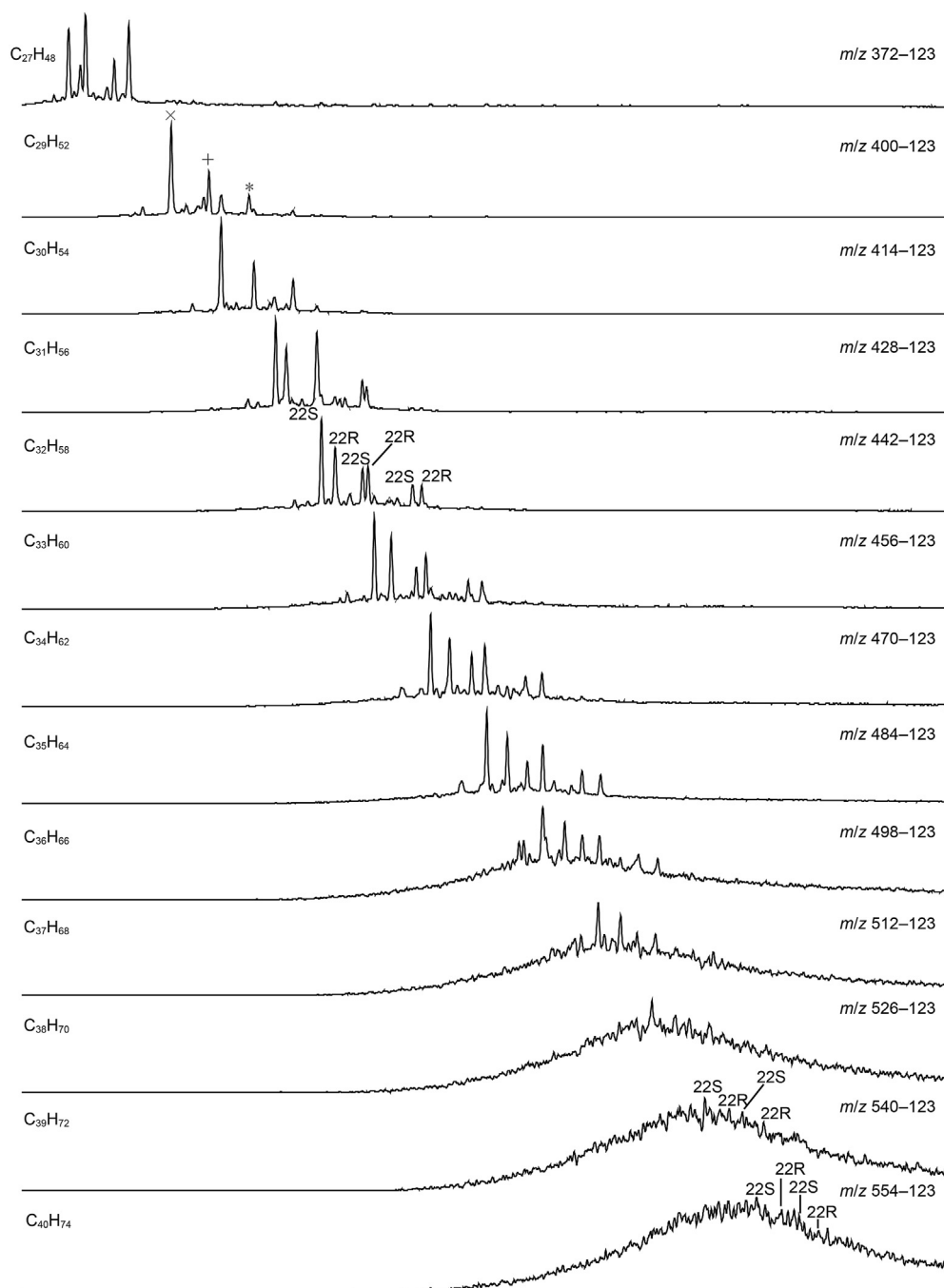


Fig. 5. Metastable ion monitoring data showing the parent ion (m/z 372 + 14n, $n = 0-12$) to daughter ion (m/z 123) transitions for the three series of extended 8,14-secohopanes up to C_{40} in the crude oil from the well TZ35. Symbols "x", "+", and "*" refer to series II, IV and VI, respectively (referred to Fazeelat et al., 1995).

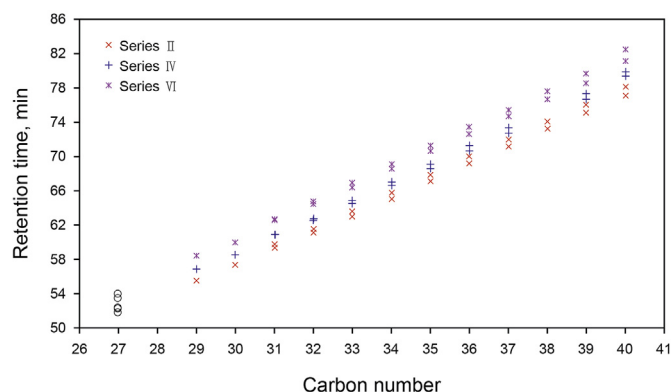


Fig. 6. Plot of the retention times versus their carbon numbers for the three series of extended 8,14-secohopanes up to C₄₀ in the crude oil from the well TZ35.

type structure (Fazeelat et al., 1995), are moderately abundant in the crude oil, but the extended moretanes almost were not detected in the m/z 191 mass chromatograms by GC-MS analysis (Fig. 2b and f) and the parent (M^+) → daughter (m/z 191) chromatograms by GC-MS-MS analysis (Fig. 3). In other words, in the studied oil, the extended hopanes have only 17 α (H), 21 β (H)-hopane configuration, but in the three series of extended 8,14-secohopanes, both hopane-type and moretane-type 8,14-secohopanes are present, and have a significant content. Although the exact reason resulting in this phenomenon remains unknown, it is probably related to the origin

of 8,14-secohopanes and the starting time of C-ring opening for hopane skeleton in the geological samples. Because in the previous studies, 8,14-secohopanes have been detected in different source rocks having varied maturity from immaturity to over maturity (Wang et al., 1990; Del Rio et al., 1994; Bao et al., 1996) and normal crude oils with different maturity (Villar et al., 1990), it suggests that C-ring opening probably happen in early diagenesis or early maturation of hydrocarbon generation during thermal evolution of sedimentary organic matter. In this case, the formation and occurrence of 8,14-secohopanes having moretane-type structure should be predictable.

Based on the results by the GC-MS-MS analysis, the three series of 8,14-secohopanes can be easily determined from C₂₉ to C₄₀ (Fig. 5). However, on the parent ion (m/z 372) → daughter ion (m/z 123) chromatogram for C₂₇ 8,14-secohopane, there were at least five peaks to be detected, consistent with the previous results in biodegraded seep oils (Fazeelat et al., 1994) and the extract of a Chinese boghead coal (Wang et al., 1990). But it is impossible to determine their corresponding relationship between the five isomers of C₂₇ 8,14-secohopanes and the three series of extended 8,14-secohopanes mentioned above, i.e., their possible configurations are unknown at present.

According to the plots between the retention times of gas chromatography and the carbon numbers of compounds in the three series of extended 8,14-secohopanes up to C₄₀, the clear linear relationships can be observed in C_{31–40} ranges (Fig. 6), suggesting that there is a linear side chain in their molecular structures like the extended hopanes mentioned above (Fig. 4). Therefore, the clear

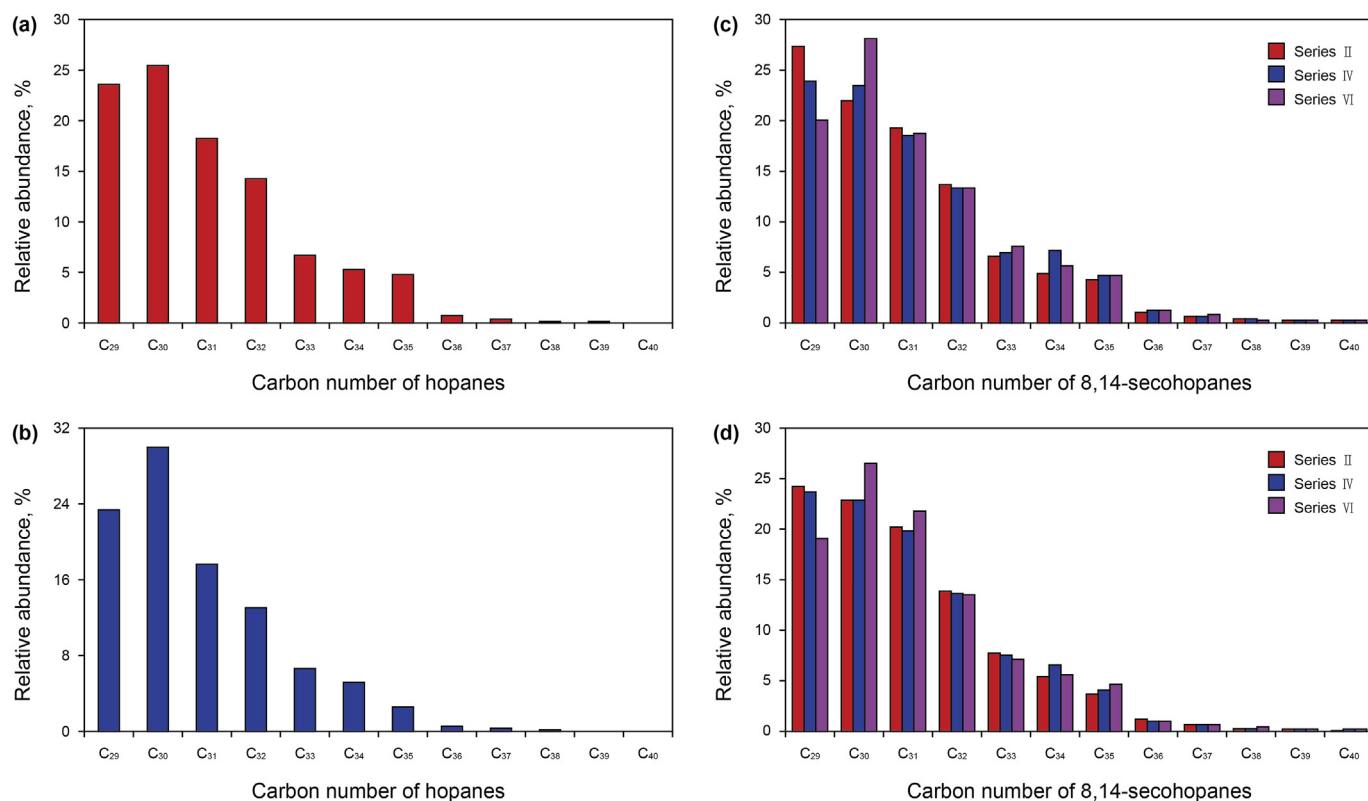


Fig. 7. The histograms of relative abundances for the C_{29–40} hopanes and three series of C_{29–40} 8,14-secohopanes in the unbiodegraded crude oils from the well TZ113 (a, c) and TZ35 (b, d).

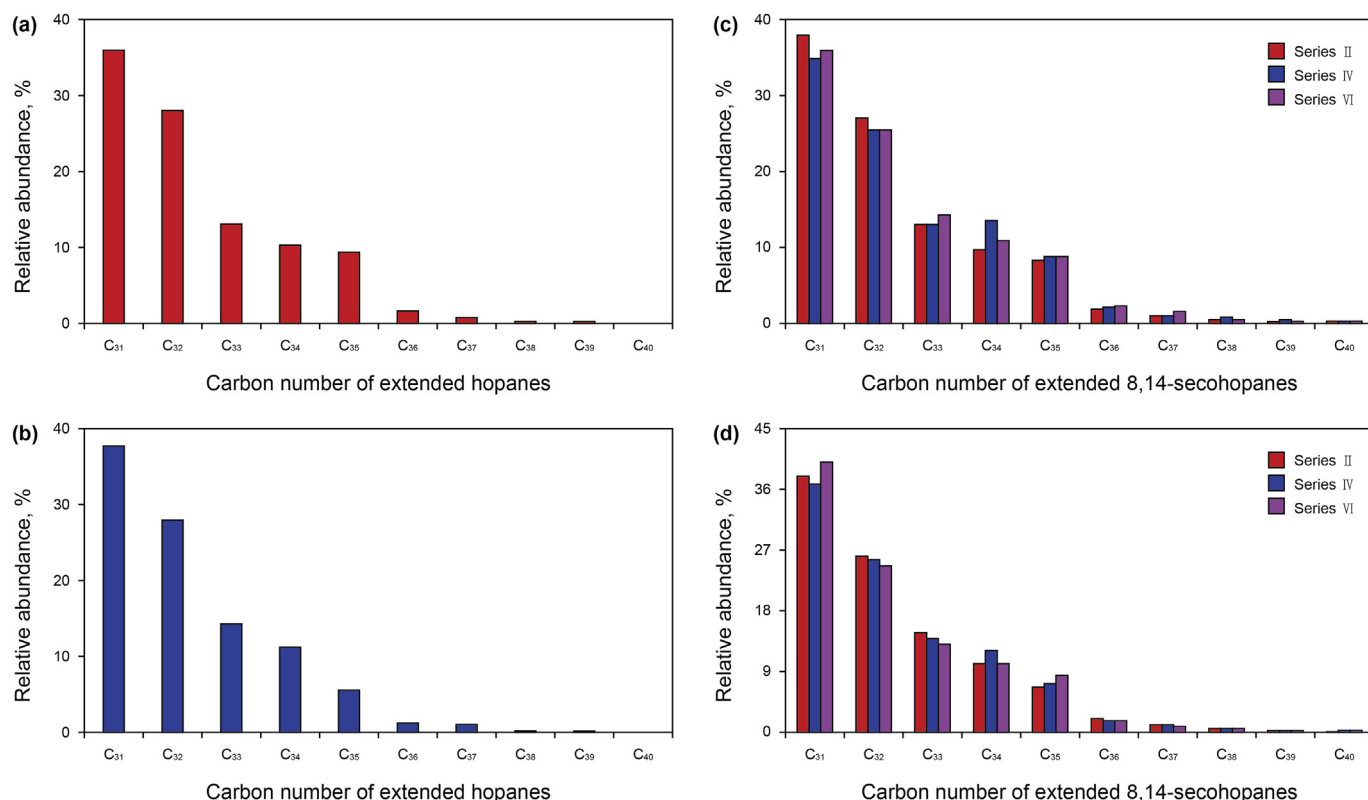


Fig. 8. The histograms of relative abundances for extended hopanes and three series of extended 8,14-secohopanes in the unbiodegraded oils from the well TZ113 (a, c) and TZ35 (b, d).

relationship between extended hopanes and extended 8,14-secohopanes up to C₄₀ in the unbiodegraded crude oil from the well TZ35 suggests that they could have a similar origin.

Based on the previous results, 8,14-secohopanes could be detected not only in a marginal mature boghead coal (Wang et al., 1990) and immature oil shale (Del Rio et al., 1994), but also in some Low-Paleozoic over-mature source rocks (Bao et al., 1996), suggesting that the formation of 8,14-secohopanes may be independent on maturity of organic matter, but could have high thermal stability. Moreover, they are detected not only in biodegraded oils (Schmitter et al., 1982; Fazeelat et al. 1994, 1995; Oliveira et al., 2012; Scarlett et al., 2019), but also in unbiodegraded crude oils (Villars et al., 1990; this study), proposing that this kind of biomarkers in crude oils could not depend on biodegradation.

However, the presence of 8,14-secohopanes in the severely biodegraded oils demonstrates that they may have a very strong ability to resist biodegradation. In fact, in severely biodegraded oils, predominant components such as normal and branched alkanes have been mostly destroyed or completely removed, and most of cyclic biomarkers are also affected such as common steranes and terpanoids (Peters and Moldowan, 1993; Wenger et al., 2002). At this time, 8,14-secohopanes survived from severely biodegradation are easily detected by GC-MS analysis due to relatively high content. On the contrary, the presence of C₂₇₋₃₂ 8,14-secohopanes in a boghead coal ($R_o = 0.65-0.67\%$, Wang et al., 1990) and an immature oil shale ($R_o = 0.40\%$, Del Rio et al., 1994) proposed that the genesis of 8,14-secohopanes, i.e. the ring-C opening of the hopanoids skeleton, could have happened during the early diagenesis or early stages of hydrocarbon maturation. Therefore, it may predict that this kind of biomarkers may be very common in crude oils and the extracts of source rocks.

4. Possible precursor for the C₃₆₋₄₀ extended hopanes and 8,14-secohopanes

The biological precursor for extended hopanes up to or beyond C₄₀ remains unknown so far, needless to say extended 8,14-secohopanes up to C₄₀. Considering that there are long alkyl-chains in highly alkylated porphyrins in petroleum, Rullkötter and Philp (1981) suggested that extended hopanes were the catagenetic products of the bacteriohopanetetrol (C₃₅) specifically bound into the kerogen matrix during diagenesis through a covalent carbon-carbon bond. Wang et al. (1996) proposed a directly biosynthesized precursor with a higher molecular weight for the extended hopanes beyond C₃₅ and beyond C₄₀ through extension of the side chain of bacteriohopanetetrol derivative by consecutive enzymatic addition of C₅ sugars. However, these hypothesis mentioned above remain to be determined due to absence of necessary evidences. The variation of the relative abundances for extended hopanes and 8,14-secohopanes up to C₄₀ may provides some useful information to understand their origin.

This study shows that the extended hopanes and three series of the extended 8,14-secohopanes up to C₄₀ coexist in unbiodegraded crude oils from the Tazhong Uplift in the Tarim Basin. It is interesting that as shown in Fig. 7, the variation of the relative abundance of every carbon number in the C₂₉₋₄₀ hopanes and three series of 8,14-secohopanes are very similar and comparable in the same unbiodegraded crude oil, suggesting that two kinds of biomarkers could be derived from the same biological precursor.

However, the changes of the relative abundances for extended hopanes and three series of extended 8,14-secohopanes in C₃₁₋₄₀ range are also very similar and generally decrease with increasing their carbon numbers, and this decrease is gradual in C₃₁₋₃₅ and C₃₆₋₄₀ ranges, but very abrupt and up to 3–5 times from C₃₅ to C₃₆ in the

studied oils (Fig. 8). This special phenomenon seems to be difficult to be understood and explained by any known viewpoint. If C_{31-40} extended hopanes and 8,14-secohopanes could be derived from the same biological precursor, the variation of relative abundance for every carbon number should be gradual, not abrupt from C_{35} to C_{36} . Therefore, this abrupt decrease in relative abundance from C_{35} to C_{36} in the C_{31-40} range suggests that C_{31-35} and C_{36-40} extended hopanes and 8,14-secohopanes could be derived from different biological precursor.

The previous results demonstrated that C_{35} bacteriohopanetetrol (see Appendix) or other functionalized hopanoids in prokaryotes are the biological precursor of the C_{31-35} extended hopanes in fossil fuels (Ourisson et al., 1984; Ourisson and Albrecht, 1992; Ourisson and Rohmer, 1992), and the variation of their relative abundances from C_{31} to C_{35} is gradually decreased with increasing carbon number in non-marine crude oils and source rocks (Peters et al., 2011). But there is a predominance of C_{35} homohopane in crude oils and source rocks related to saline and strongly reduced environment (Peters and Moldowan, 1991). The abrupt decrease in the relative abundance from C_{35} to C_{36} in C_{31-40} extended hopanes and 8,14-secohopanes suggests that C_{31-35} and C_{36-40} extended hopanes and 8,14-secohopanes could have their own biological precursor. C_{35} bacteriohopanetetrol should be the biological precursor of C_{31-35} extended hopanes and 8,14-secohopanes in the geological samples. But for C_{36-40} extended hopanes and 8,14-secohopanes, their biological precursor may be derived from a C_{40} functionalized hopanoid unknown so far. In addition, the obviously low abundances for C_{36-40} relative to C_{31-35} in C_{31-40} extended hopanes and 8,14-secohopanes may related to the low content of C_{40} biological precursor in microorganisms or this kind of biological precursor difficultly to be preserved during preservation and diagenesis of sedimentary organic matter. However, their presence in the unbiodegraded marine oils suggests that they should be primary, and independent on biodegradation.

As mentioned above, the extended $17\alpha(H)$, $21\beta(H)$ -hopanes are absolutely predominant, but the corresponding moretanes almost can not be detected in the crude oils from the well TZ35 and TZ113 (Figs. 2 and 3). However, series IV and VI having moretane-type structure in three series of 8,14-secohopanes are moderate, and the contents of three series of 8,14-secohopanes are about 55.60%, 28.05%, 16.35% and 55.37%, 27.36%, 17.27% in two crude oils from the well TZ113 and TZ35, respectively. It is very different from extended hopanes in the same crude oils.

According to stereochemistry, hopanes mainly have three configurations, including $17\beta(H)$, $21\beta(H)$ -biological hopane, $17\beta(H)$, $21\alpha(H)$ -moretane and $17\alpha(H)$, $21\beta(H)$ -hopane, and their distributions depend on maturity level of organic matter in the geological samples (Seifert and Moldowan, 1980). Compared with $17\alpha(H)$, $21\beta(H)$ -hopane, moretanes gradually decrease with increasing maturity because of relatively low stability (Seifert and Moldowan, 1980). Therefore, in the mature crude oils and source rocks, $17\alpha(H)$, $21\beta(H)$ -hopanes are generally predominant, and moretanes are very low.

As well known, 8,14-secohopanes are derived from the ring C opening of hopanoids at the bond between C-8 and C-14. The process of the ring C opening for hopanoids may occur during the early stages of hydrocarbon maturation (Wang et al., 1990). At this maturity level, moretanes, hopanes and 8,14-secohopanes having moretane-type and hopane-type configuration should be present in geological samples. However, it is noted that the ring C opening

not only changes the molecular structure of hopanoids from pentacyclic alkanes to tetracyclic alkanes, but also the stability of 8,14-secohopanes having moretane-type configuration may be different from that of moretanes. In other words, the tetracyclic 8,14-secohopanes having moretane-type configuration may be more stable compared with pentacyclic moretanes, or 8,14-secohopanes having moretane-type and hopane-type configuration may have similar stability. Therefore, once formed in the geological samples, the moretane-type 8,14-secohopanes will not probably change with increasing maturity. It may be the reason that the 8,14-secohopanes having moretane-type structure are moderately abundant, but moretanes are very low in the unbiodegraded mature oils from the well TZ35 and TZ113.

Considering that the extended hopanes and 8,14-secohopanes up to C_{40} were detected in unbiodegraded oils at the same time, it suggests that these biomarkers are primary and independent on biodegradation of crude oil, and could have similar geochemical significance like common hopanes. The presence of 8,14-secohopanes in unbiodegraded and severely biodegraded oils suggests that they could have very strong resistance to biodegradation, and play some important roles in the oil-source correlation for severely biodegraded oils in which common steranes and terpanoids have almost completely destroyed.

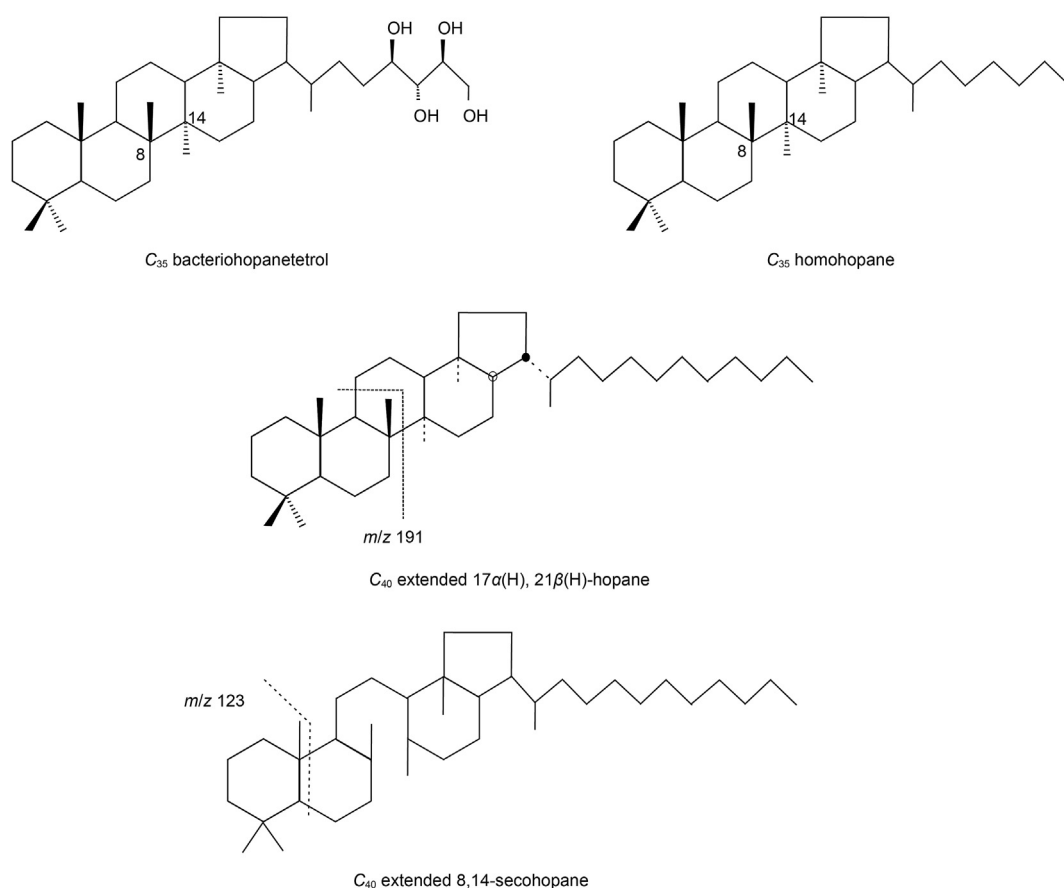
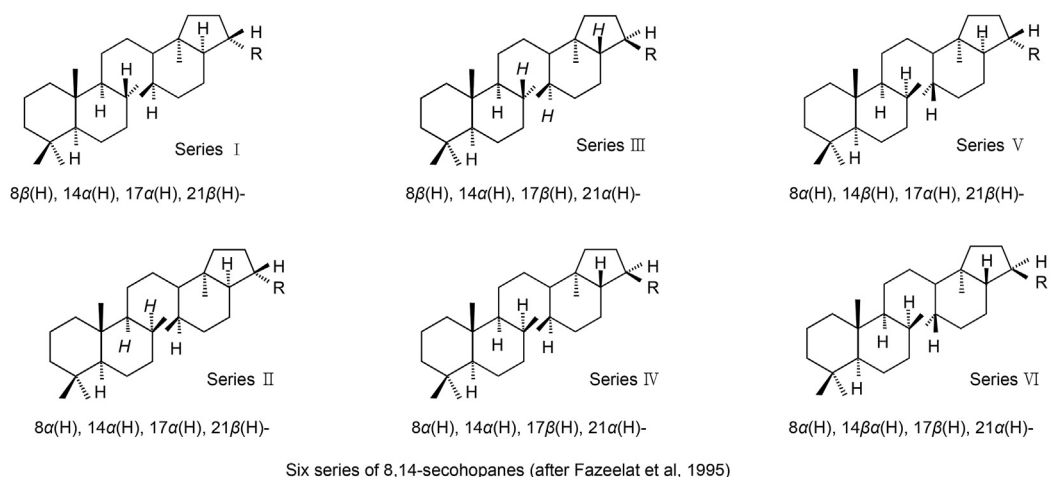
5. Conclusions

Extended $17\alpha(H)$, $21\beta(H)$ -hopanes and three series of extended 8,14-secohopanes up to C_{40} have been detected in unbiodegraded marine mature oils from the Tazhong Uplift of the Tarim Basin, suggesting that they should be primary biomarkers and independent on biodegradation. The similar distributions and compositions for the C_{29-40} extended hopanes and three series of extended 8, 14-secohopanes in the unbiodegraded oils suggest that they could be derived from a similar biological precursor. The variation of relative abundance for C_{31-40} extended hopanes and 8,14-secohopanes generally decreases with increasing carbon number, but a abrupt decrease in the relative abundance up to 3–5 times can be observed from C_{35} to C_{36} , suggesting that the C_{31-35} and C_{36-40} extended hopanes and 8,14-secohopanes could be probably derived from different biological precursors. C_{35} bacteriohopanetetrol should be the biological precursor of the C_{31-35} extended hopanes and 8,14-secohopanes, but the C_{36-40} extended hopanes and 8,14-secohopanes could be derived from an unknown C_{40} functionalized hopanoids. As a kind of primary biomarker widely distributed in various source rocks, unbiodegraded and severely biodegraded oils, they could play some important roles in oil-source correlation for severely biodegraded oils.

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Appendix



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