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Differences in the thermal evolution of hopanes and steranes in free and bound fractions

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ABSTRACT

Hopanes and steranes are the two of the most commonly used biomarker classes in the application of organic geochemistry to petroleum exploration. The same carbon skeletons also occur as a bound fraction, and can be used in a relatively high maturity range compared to their extractable (free) counterparts as a result of protection by the kerogen macromolecular structure. The pools of free and bound biomarkers are expected to be thermally degraded over geological time. There has been little work to address the chemical stabilities of hopanes and steranes in both free and bound forms. This study uses anhydrous pyrolysis to simulate the thermal evolutions of biomarkers from two Type II kerogens. The bound biomarkers within the above thermally altered kerogen residues were also released by catalytic hydropyrolysis and discussed in this study. The anhydrous pyrolysis results show that source-related parameters based on hopanes are more stable than those based on steranes. The hydropyrolysis results show that the bound hopane distributions are quite stable even at 460 °C (Easy%Ro = 2.86), while the bound sterane distributions are changed beginning at 430 °C (Easy%Ro = 2.27). This indicates that the thermal stability of steranes is lower than that of hopanes in both free and bound fraction which can be explained by the different chemical structure and mode of incorporation of their precursors into kerogen.

1. Introduction

Hopanes and steranes are among the two most abundant biomarker classes in that portion of most sedimentary rock samples that is soluble in organic solvents because their biogenic precursors, namely the hopanoids and steroids, occur ubiquitously in living organisms (Peters et al., 2005). They are widely used in thermal maturity assessment, organofacies studies and oil–oil/oil–source rock correlations (Peters et al., 2005 and references therein). Generally, the extract of source rocks (bitumen) or the crude oil which contains free biomarkers will be routinely analyzed in molecular geochemistry studies. The use of such solvent-soluble (free) biomarkers is limited to the immature through oil-generation window, because molecular indices based on relative thermal stability and stereochemical changes are completed in that range. Hopane and sterane biomarkers are seldom utilized where high levels of thermal stress have been attained (van Graas, 1990; Farrimond et al., 1998; Liang and Chen, 2005).

A great number of studies have reported that hopanes and steranes also can be released from kerogen and/or solid bitumen by thermal pyrolysis, chemical degradation and catalytic hydropyrolysis (Seifert, 1978; Tissot and Welte, 1978; Mackenzie et al., 1982a, 1982b; Mycke and Michaelis, 1986; Eglinton and Douglas, 1987; Mycke et al., 1987; de Leeuw et al., 1989; Abbott et al., 1990; Hoffman et al., 1992; Richnow et al., 1992; Adam et al., 1993; Love et al., 1995; Muhammad and Abbott, 2012). Various conditions (temperature and time) have been used for thermal pyrolysis. Generally, the temperature used for thermal pyrolysis is > 250 °C. Chemical degradation is a mild degradation method. Many kinds of chemical reagents were used for chemical degradation, such as Li/$EtND_2$ and Ni(0)cene/$LiAlD_4$ (Hoffman et al., 1992; Richnow et al., 1992), and BCl_3/$LiAlH_4$ (Michaelis et al., 1988; Jenisch et al., 1990). The nature of bonding inferred from the reagents used in chemical degradation processes (Mycke and Michaelis, 1986; Hoffman et al., 1992; Richnow et al., 1992) and the pyrolysis temperatures at which products are obtained (Seifert, 1978; Eglinton and Douglas, 1987) strongly indicated that such hopanes and steranes were covalently bound. The covalently bound hopanes and steranes are different from solvent soluble hopanes and steranes in composition and distribution characteristics (Tissot and Welte, 1978; Love et al., 1995, 2005; Lockhart et al., 2008; Liao et al., 2012; Wu et al., 2013). Because the steranes and hopanes obtained by the different methods (extraction and pyrolysis) are chemically distinct, previous workers have developed the idea of bound biomarkers and free biomarkers (e.g.,

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Abbott et al., 1990). Additionally, previous work also points out that the compounds released by various degradation processes were not covalently bonded to macromolecular structure but rather were occluded within it (Strausz et al., 1999a, 1999b; Liao and Geng, 2002; Russell et al., 2004; Gordadze et al., 2015; Snowdon et al., 2016). Thus, it is not clear that bound moieties released by pyrolysis and HyPy technique can be readily differentiated from occluded species (Snowdon et al., 2016). Therefore, most workers use the term bound biomarker (including both covalently bound and occluded biomarkers) to represent the products released from geological macromolecular structures.

The thermal evolution of bound biomarkers may be retarded to some extent compared to their free counterparts due to protection afforded by the macromolecular structure (Tissot and Welte, 1978; Love et al., 1995, 2005; Abbott et al., 2001; Lockhart et al., 2008; Muhammad and Abbott, 2012). This is especially apparent at low maturity stages (Love et al., 1995; Murray et al., 1998; Meredith et al., 2008; Wu et al., 2013). Maturity-related parameters based on bound biomarkers show constant values with increasing maturity in highly mature source rocks (T_{max} > 460 °C) (Lockhart et al., 2008; Wu et al., 2013; Liao et al., 2015) and artificially matured solid bitumen (simulation temperature > 350 °C) (Liao et al., 2012). It therefore seemed that assessment of maturity based on the bound biomarkers at high- to over maturity stage was not possible. However, recently, Liao et al. (2012) reported that source-related biomarkers, including the distribution of regular steranes, are quite stable in hydropyrolysis (HyPy) products from laboratory heated bitumens of various maturities (Easy%Ro = 1.08–2.86). Wu et al. (2013) also found that the bound source-related biomarkers from the Permian Dalong Formation in the Sichuan Basin, China at the mature Guangyuan outcrop sections and overmature Wangcang outcrop sections are very similar. Those data indicate that biomarkers released from kerogen can be used in oil-source correlation studies in highly mature to over-mature areas. The bound biomarkers released by HyPy also were also used for oil–source correlation in the Majiang paleo-reservoir (Fang et al., 2014).

Although it was widely accepted that source-related biomarkers within kerogen (bound fraction) are more stable than their free counterparts, we still know little about the thermal stability and thermal evolution of different kinds of biomarkers. The Dalong Formation was deposited under very similar conditions, but shows quite different maturity at different locations. Biomarkers obtained by both Soxhlet extraction and HyPy from these rocks have been well investigated (Wu et al., 2013). In the present study, two early mature Type II kerogens from the Dalong Formation were selected for artificial thermal alteration followed by HyPy experiments on the kerogen residues. The aim of this study is to compare the effects of thermal maturation on source-related biomarker parameters based on free biomarkers and bound biomarkers. This is very important for the interpretation of bound biomarkers released from high to over-mature samples.

2. Experimental

2.1. Samples and preparation

The investigated samples are siliceous rock (GY-8) and mudstone (GY-17) selected from the fresh outcrop of the Permian Dalong Formation in Sichuan Basin, China (Lat. 32°19′11″N, Long. 105°27′18″E). None of the selected samples were strongly weathered. The Dalong Formation contains interbedded marine dark siliceous rock and mudstones, and mainly occurs in the Guangyuan-Wangcang trough and Western Hubei-Chengkou trough (Wang et al., 2006; Tenger et al., 2008; Li et al., 2009). The basic geochemical characteristics of the samples have already been presented by Wu et al. (2012, 2013) and are summarized in Table 1. The TOC (total organic carbon) content is 8.76% for GY-8 and is 3.67% for GY-17. Their measured vitrinite reflectance are in the range of 0.58–0.68 %Ro. They also have very similar values of T_{max} (438 °C) and hydrogen Index (343–357 mg/g TOC). The investigated samples are classified as early mature Type II kerogens.

The source rock samples were crushed to ⩽ 80 mesh powders. Then, kerogen isolation was performed by acid treatment. First the ground samples were treated with 3 M HCl (80 °C for 4 h), and washed with distilled water and separated by centrifugation. Then a mixture of 1 M HCl and HF (1:1, v:v) was used (80 °C for 4 h) and recovered by additional water washing and centrifugation. Before the artificial thermal alteration experiment was conducted, the isolated kerogen from GY-8 was Soxhlet extracted using an azeotropic ternary solvent system (benzene/acetone/methanol, 5:5:2, v:v:v) for 2 weeks to remove the residual bitumen, while the GY-17 kerogen was not Soxhlet extracted with the ternary solvent (Fig. 1). The aim of different kerogen preparations was to study the influence of free bitumen on the thermal evolution of bound biomarkers within kerogen.

2.2. Artificial thermal alteration experiments

Tubes were loaded with about 0.6 g of the prepared kerogen (GY-8 and GY-17) and sealed under an inert nitrogen atmosphere. Isothermal pyrolysis was then performed for 72 h at 350, 380, 400, 430 and 460 °C, and each sample was heated from room temperature to the final temperature. The calculated vitrinite reflectance (% Ro) by the Easy%Ro method (Sweeney and Burnham, 1990) for the kerogens heated at 350 °C, 380 °C, 400 °C, 430 °C and 460 °C were 1.08, 1.49, 1.74, 2.27 and 2.86, respectively (Table 2). After thermal pyrolysis, the pyrolysate (pyrolysis product) was recovered by repeated dichloromethane (DCM) sonication. Prior to HyPy, kerogen residues were further Soxhlet extracted for two weeks using the ternary solvent azeotrope to remove soluble organic matter (Fig. 1).

2.3. Hydropyrolysis experiments

Catalytic hydropyrolysis (HyPy) of the samples was conducted using the apparatus and procedure described in detail elsewhere (Snape et al., 1989; Love et al., 1995; Wu et al., 2013). The solvent-extracted kerogen was impregnated with an aqueous solution of ammonium dioxydithiomolybdate [$(NH_4)_2MoO_2S_2$] to give a nominal loading of 5 wt% molybdenum as catalyst. Then, the catalyst loaded kerogen was put into the HyPy reactor tube. The HyPy experiment involves two steps at the same hydrogen pressure (15.0 MPa) and hydrogen flow (4 L/min). The first step was heating from ambient temperature to 300 °C (5 min) at 250 °C/min. The aim of the first step is to remove the weaker covalent bonds

Table 1
Basic information on the investigated source rocks.

Sample ID	Lithology	$\delta^{13}C$ (‰)	%Ro	TOC (%)	S1	S2	T_{max} (°C)	HI
GY-8	Silicalite	−27.6	0.58	8.75	1.22	30.1	438	343
GY-17	Mudstone	−27.8	0.68	3.67	0.61	13.3	438	357

Data from Wu et al. (2013).

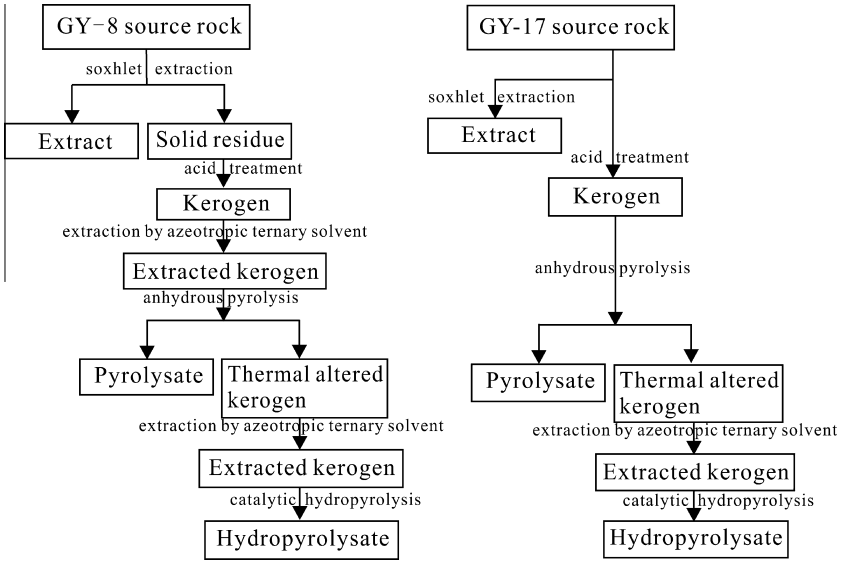

Fig. 1. Sample preparation and experiment process scheme.

Table 2
The TOC-normalized yields of the total EOM and the saturated, aromatic and polar fractions for pyrolysates of kerogen at different temperatures and their corresponding hydropyrolysates.

Sample no.	Temp (°C)	Easy%Ro	Anhydrous pyrolysis (mg/g TOC)			HyPy (mg/g TOC)		
			Total EOM	Saturated	Aromatic	Total EOM	Saturated	Aromatic
GY-8 series								
Original	–	0.58	56.0	4.1	17.3	497.7	112.8	171
GY-350	350	1.08	15.5	0.6	6.7	45.1	1.2	18.9
GY-380	380	1.49	13.5	0.5	5.7	37.5	0.3	16
GY-400	400	1.74	2.7	1.1	0.8	16	0.6	8
GY-430	430	2.27	1.5	0.1	0.7	2.4	0.4	0.4
GY-460	460	2.86	0.9	0.2	0.3	2.6	0.7	0.4
GY-17 series								
Original	–	0.68	45.4	8.3	20.6	205	19.3	163.3
GY-350	350	1.08	21.8	8.7	3.6	68.9	21.0	33.0
GY-380	380	1.49	8.7	2.2	2.2	56.6	14.9	17.9
GY-400	400	1.74	7.3	5.1	–	56.4	14.8	38.6
GY-430	430	2.17	–	–	–	99.9	6.1	46.4
GY-460	460	2.86	–	–	–	50.8	5.2	20.6

"–" = undetectable.

leaving the stronger bonds for HyPy (Love et al., 1995, 1997, 1998). After this step, the silica gel in the collecting tube was replaced. The second heating run was from ambient temperature to 250 °C (5 min) at 300 °C/min and then to 520 °C (5 min) at 8 °C/min. The hydropyrolysates (hydropyrolysis products) were collected in a liquid nitrogen cold trap and recovered by DCM/methanol (93:7, v:v) for subsequent analysis (Meredith et al., 2004).

2.4. Product analysis

The hydropyrolysates of the thermally altered kerogen residues were conducted as follows. First, the asphaltenes were precipitated from the products by adding 50:1 (v:v) cold *n*-hexane, and then removed by centrifugation. The maltene fractions were then fractionated by silica/alumina (3:1, v:v) column chromatography into saturated, aromatic and polar fractions by elution with *n*-hexane, DCM/*n*-hexane (3:1, v:v) and DCM/methanol (2:1, v:v), respectively.

The saturated biomarkers were analyzed using a Thermo Scientific Trace GC Ultra gas chromatograph coupled to a Thermo Scientific Trace DSQ II mass spectrometer. A DB-1 fused silica capillary column (60 m × 0.32 mm i.d. × 0.25 μm film thickness) was used. The GC oven was held isothermal at 70 °C for 2 min, programmed to 290 °C at 4 °C/min, with a final hold time of 30 min. Helium was used as carrier gas with a constant flow rate of 1.5 mL/min. The ion source temperature was 250 °C, and the temperature of injector was 290 °C. The ion source was operated in the electron impact (EI) mode with electron energy of 70 eV. GC–MS analyses were operated in SIM mode. The selected ions monitored included *m*/*z* 191 (hopanes) and *m*/*z* 217 (steranes).

3. Results and discussion

Table 2 shows the total EOM (extractable organic matter), saturated, and aromatic yields normalized to TOC from anhydrous pyrolysis products (pyrolysates) of kerogen at different temperatures and their corresponding HyPy products (hydropyrolysates). The Rock Eval data of thermal altered GY-8 kerogen residues were also shown in Table 3. The yield of kerogen pyrolysates (C_{15+}) decreases from 15.5 mg/g TOC (350 °C) to 0.9 mg/g TOC (460 °C) for GY-8 kerogen and decreases from 21.8 mg/g TOC (350 °C) to 7.3 mg/g TOC (400 °C) for GY-17 kerogen with increasing tempera-

Table 3
Rock Eval data for the artificial thermal altered kerogens of GY-8.

Sample ID	Temp (°C)	S1 (mg/g kerogen)	S2 (mg/g kerogen)	T_{max} (°C)	HI
GY-350	350	2.24	7.29	482	11
GY-380	380	1.15	5.61	562	8
GY-400	400	1.15	3.56	581	5
GY-430	430	1.98	2.05	602	3
GY-460	460	1.05	1.27	605	2

ture due to more and more severe thermal decomposition. The yield of hydropyrolysates (C_{15+}) also decreases from 45.1 mg/g TOC (350 °C) to 2.6 mg/g TOC (460 °C) for GY-8 kerogen, while they are nearly constant (ca. 60 mg/g TOC) for GY-17 with increasing temperature. For the same sample, the yields of saturated and aromatic hydrocarbon for both pyrolysates and hydropyrolysates also decrease with increasing temperature. However, the yield of hydropyrolysates for GY-17 kerogen residues is higher than that for GY-8 kerogen residues at the same temperature. This is probably because the free bitumen that is not removed from the GY-17 kerogen was incorporated into the kerogen residue during pyrolysis (cf. secondary reactions as per Vu et al., 2008) and released by the following HyPy experiment (see also following discussion on the distribution of C_{27}–C_{29} steranes for hydropyrolysates).

3.1. Results of laboratory heating experiment on GY-8 and GY-17 kerogens

Fig. 2 shows the hopane and sterane profiles for the pyrolysates of GY-8 and GY-17 kerogens at various temperatures (GY-8 series and GY-17 series). For GY-8 series, most of the biomarkers including hopanes and steranes were not detected or their relative concentration is very low in its pyrolysates at all temperature. This is probably because the pyrolysis-released biomarkers were destroyed by thermal stress. Previous studies also found that hopanes and steranes are absent in both hydrous and anhydrous pyrolysis of kerogen at temperature above 330 °C (Comet et al., 1986; Lewan et al., 1986; Lewan, 1997). Comet et al. (1986) pointed out that the existence of elemental sulfur within kerogen can considerably destroy free polycyclic biomarkers. The work by Abbott et al. (1985) also pointed out that elemental sulfur can catalyze the degradation of steranes and aromatic steroids. Of course, the inefficient recovery of sonication with DCM might be another possible reason for the absence of biomarkers in pyrolysates of GY-8 kerogen at various temperatures. However, hopanes and steranes were detected in pyrolysates of GY-17 kerogen at temperatures from 350 °C to 400 °C. Only trace of hopanes and steranes were detected at 430 °C. Hopanes and steranes were not observed in pyrolysate at 460 °C due to the severe thermal decomposition. Since the free biomarkers in bitumen were not removed from GY-17 kerogen before anhydrous pyrolysis, the biomarkers detected in pyrolysates of GY-17 kerogen should be the mixed thermally altered products of free bitumen from source rock and liquid products released from kerogen. The work by Murray et al. (1998) demonstrated that free bitumen is a more important pool of hopanes and steranes than kerogen at the beginning of the oil-generation window (%Ro = 0.5–0.6). Additionally, hopanes and steranes were not detected or their relative concentration is very low in the pyrolysates released from GY-8 kerogen in which the free bitumen had been removed. Thus, the hopanes and steranes detected in pyrolysates of GY-17 kerogen are probably mainly from free bitumen.

The distribution of C_{27}–C_{29} regular steranes is very stable in the oil-generation window and can be used for oil-oil and oil-source rock correlation and to assess source and depositional environment (Seifert et al., 1984; Peters et al., 1989, 2005). With the temperature increasing from 350 °C to 400 °C, the relative abundance of C_{27} 5α,14α,17α, 20R-cholestane for GY-17 kerogen increases from 0.49 to 0.64 (Table 4), while C_{28} 5α,14α,17α, 20R-24-methylcholestane decreases from 0.30 to 0.19. Previous studies on the pyrolysis of source rocks or kerogens have also reported that the relative abundance of C_{27} regular steranes gradually increases with simulation temperature (Comet et al., 1986; Lewan et al., 1986; Lu et al., 1989; Lewan, 1997).

C_{21} and C_{22} steranes (pregnane and homopregnane and their geological isomers) may originate from the hormones, pregnanol and pregnanone (de Leeuw and Baas, 1986) or from thermal cracking of C_{27}–C_{29} regular steroids (Huang et al., 1994; Abbott et al., 1995). The ratio of C_{21}/C_{22} steranes (S21/S22) can also be used for oil-source correlation (Huang et al., 1994; Fang et al., 2011; Wu et al., 2012): S21/S22 is in the range 1.22–1.45 for pyrolysates of the GY-17 series.

The ratios based on free hopanes and tricyclic terpanes, such as gammacerane/C_{30} 17α(H),21β(H)-hopane (Gam/H30), C_{29} 17α(H), 21β(H)-hopane to C_{30} 17α(H),21β(H)-hopane (H29/H30), C_{23} tricyclic terpane/C_{30} 17α(H),21β(H)-hopane (TT23/H30), C_{23} tricyclic terpane to C_{23} and C_{24} tricyclic terpanes (TT23/(TT23 + TT24)) are also commonly used to assess the source (Peters et al., 2005). Except for TT23/H30, other ratios are all quite stable with increasing temperature from 350 °C to 400 °C for pyrolysates of the GY-17 series (Table 5). For example, the value of H29/H30 is in the range of 0.65–0.75, and the value of Gam/H30 is in the range of 0.09–0.12. The value of TT23/H30 is 0.78 for thermally altered kerogen of GY-17 at 350 °C, while it is nearly 0.20 at 380 °C and 400 °C (Table 5). Thus, the source related biomarkers parameters based on hopanes seems to be more stable than those based on steranes in the pyrolysates of GY-17 kerogen at various temperatures.

3.2. Results of HyPy experiment on artificially matured kerogens

The HyPy technique was used to release the bound steranes and hopanes from laboratory heated products from the two investigated Dalong Formation kerogens (GY-8 and GY-17) at various temperatures. Their bound hopane (m/z 191) and sterane profiles (m/z 217) are shown in Fig. 3. For the same kerogen series, the distributions of bound hopanes released from the thermally altered kerogens at all temperatures are quite similar, whereas the relative abundance of bound C_{29} 5α,14α,17α, 20R-ethylcholestane are gradually decreased with increasing temperature (Fig. 3). However, the distributions of bound C_{27}–C_{29} regular steranes are quite similar for pyrolysis temperatures < 430 °C (Easy%Ro = 2.27). This is consistent with our previous results for a natural maturity sequence in the Dalong Formation in which the distributions of C_{27}–C_{29} regular steranes in hydropyrolysates from overmature samples (%Ro = 1.8; Wu et al., 2015) are still similar to those in the mature samples (Wu et al., 2013). These results confirm the suggestion that the bound biomarkers are protected to some extent from thermal degradation by the macromolecular structure of kerogen (Love et al., 1998; Lockhart et al., 2008; Liao et al., 2012; Wu et al., 2013).

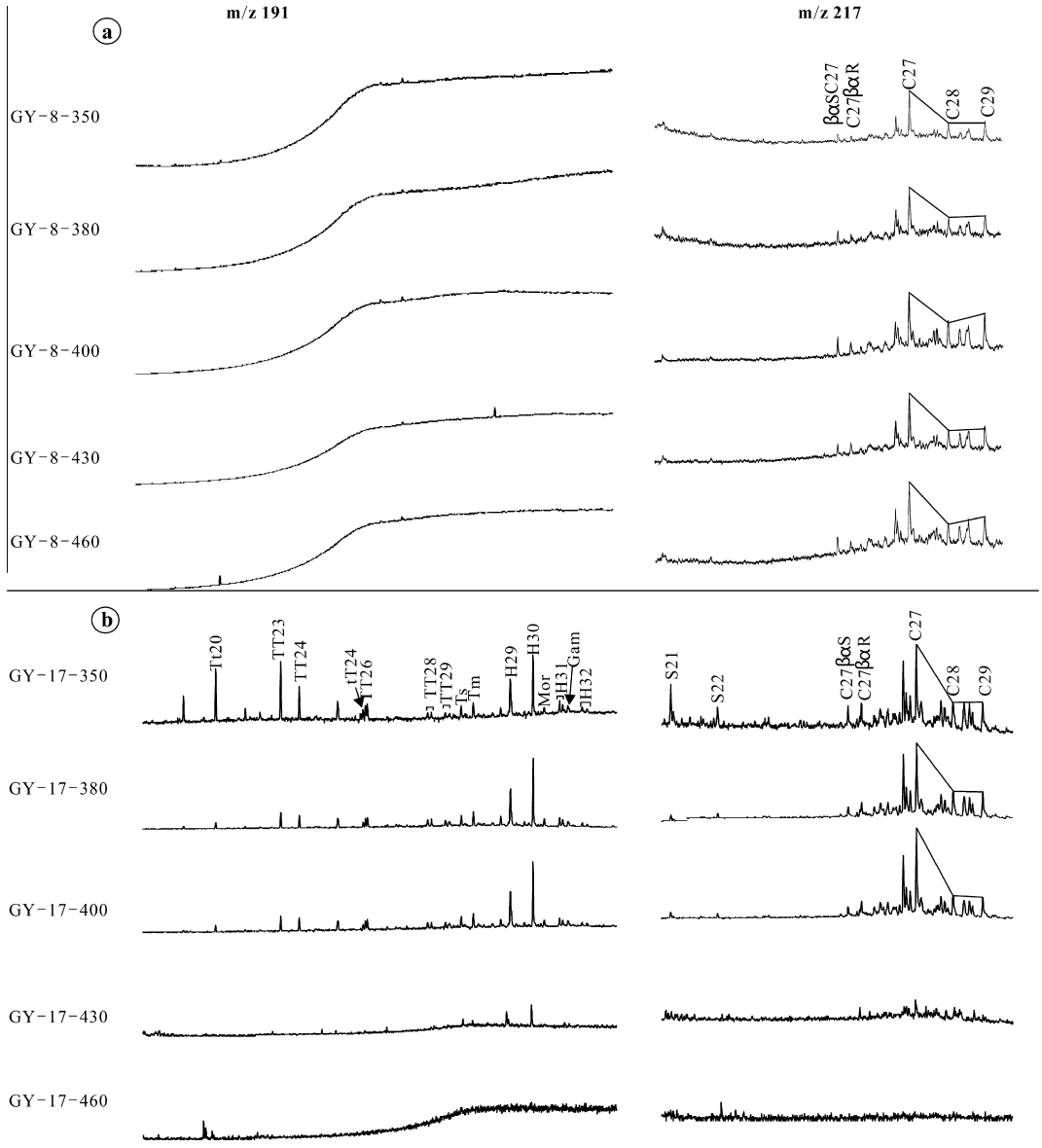

Fig. 2. Selected ion chromatograms (SIM) for *m/z* 191 and *m/z* 217 of the saturated fractions in pyrolysates of thermally altered kerogens: (a) is the siliceous rocks series (original kerogen is GY-8) and (b) is the mudstone series (original kerogen is GY-17). Peak identifications are shown in Table 2.

Fig. 4 is a ternary plot of the C_{27}–C_{29} regular sterane distributions for hydropyrolysates from two original samples and their thermally altered residues. For the GY-8 GY-17 series, the relative abundance of bound C_{29} 5α,14α,17α, 20R-ethylcholestane decreases, but C_{27} 5α,14α,17α, 20R-cholestane increases with increasing temperature. Nevertheless, the distributions of C_{27}–C_{29} regular steranes in hydropyrolysates are still similar to the original sample up to a special temperature (400 °C for both GY-8 and GY-17 series) because of the protection by the macromolecular network (Fig. 3). The only difference was their decreasing rate of bound C_{29} 5α,14α,17α, 20R-ethylcholestane. It seems the decreasing rate of bound C_{29} 5α,14α,17α, 20R-ethylcholestane for GY-8 series are faster than that for GY-17 series. Since the lithology of GY-8 sample (siliceous rocks) is different from that of GY-17 (mudstone), their maceral compositions should be also quite different. Thus, this may suggest that the degree of protection of the macrostructure on the bound steranes can differ with kerogen, particularly between kerogens with different maceral composition.

The distributions of bound C_{27}–C_{29} regular steranes in the thermally altered kerogens of GY-17 are quite different from those of the original kerogen (Fig. 4b). In contrast, the distributions of C_{27}–C_{29} regular steranes in the thermally altered kerogens of GY-8 are similar to those in the original kerogen, at least below the temperature of 430 °C. As already mentioned above, the original kerogen of GY-8 was extracted (benzene/acetone/methanol = 5:5:2, v:v:v) for two weeks, while the kerogen of GY-17 was not extracted. Thus, the free bitumen, especially the polar fraction containing hopanoids and steroids, was not removed from the kerogen concentrate of GY-17 and may have been incorporated into the kerogen during pyrolysis (cf. secondary reactions as per Vu et al., 2008). Some researchers have suggested that variable proportions of the steroid and hopanoid pools in geological samples are first incorporated into kerogen and later released as hopanes and steranes during catagenesis (Mycke et al., 1987; Sinninghe Damsté and de Leeuw, 1990). Therefore, the distributions of bound biomarkers within the kerogens of GY-17 at all temperatures may have been influenced by incorporation of free bitumen.

The ratios based on hopanes and tricyclic terpanes remain unified for all hydropyrolysates in each kerogen series (shown in Fig. 5). For example, Gam/H30 is in the range of 0.23–0.28 for the

Table 4
Biomarker assignments.

Peak	Compound
TT23	C_{23} tricyclic terpane
TT24	C_{24} tricyclic terpane
TT25	C_{25} tricyclic terpane
TT26	C_{26} tricyclic terpane
TT28	C_{28} tricyclic terpane
TT29	C_{29} tricyclic terpane
tT24	C_{24} tetracyclic terpane
H29	C_{29} 17α(H),21β(H)-hopane
H30	C_{30} 17α(H),21β(H)-hopane
H31 22S	C_{31} 17α(H),21β(H),22S-hopane
H31 22R	C_{31} 17α(H),21β(H),22R-hopane
H32	C_{32} 17α(H),21β(H)-hopane
H33	C_{33} 17α(H),21β(H)-hopane
Gam	Gammacerane
Mor	C_{30} 17β(H),21α(H)-hopane
Ts	C_{27} 17α-22,29,30-trisnorhopane
Tm	C_{27} 18α-22,29,30-trisnorhopane
C27	C_{27} 5α,14α,17α, 20R-cholestane
C28	C_{28} 5α,14α,17α, 20R-methylcholestane
C29	C_{29}-5α,14α,17α, 20R-ethylcholestane
C27 βαS	C_{27} 13β,17α,20S-diacholestane
C27 βαR	C_{27} 13β,17α,20R-diacholestane
S21	C_{21} sterane
S22	C_{22} sterane

GY-8 hydropyrolysates and in the range of 0.17–0.20 for the GY-17 hydropyrolysates (Fig. 5b, Table 6). The ratio of S21/S22 is also stable for the all hydropyrolysates in each kerogen series. S21/S22 is in the range 1.38–1.51 and 1.62–1.83 for hydropyrolysates of the GY-8 and GY-17 series, respectively (Fig. 5a, Table 6). However, most of the above biomarker ratios in the hydropyrolysates from the GY-8 series are similar to those in the original kerogen hydropyrolysate, while some biomarker ratios (such as the ratio of S21/S22 and H29/H30) in the hydropyrolysates from GY-17 series are quite different from those in the original kerogen hydropyrolysate (Table 6). This further confirms our previous speculation that the distributions of bound biomarkers within the kerogens of GY-17 at all temperatures may have been influenced by the incorporation of free bitumen.

Based on the above data, it is clear that ratios based on bound hopanes and tricyclic terpanes, such as H29/H30 and Gam/H30, are quite stable from 350 °C to 460 °C (Fig. 5), while the distribution of C_{27}–C_{29} regular steranes are thermally altered with increasing simulation temperature (Fig. 4). Thus the regular steranes should be more easily destroyed by thermal stress than hopanes and tricyclic terpanes. Additionally, the ratio S21/S22 is also based on steranes, but it is quite stable at all temperatures. The following discussion explains why the thermal evolution trend for S21/S22 differs from that of the C_{27}–C_{29} regular steranes.

3.3. Why biomarker parameters for bound hopanes and steranes differ

The results from anhydrous pyrolysis reveal that the thermal evolution of steranes and hopanes differ in the free fraction. Different thermal evolution trends between steranes and hopanes released by closed-system pyrolysis have been observed previously. Hydrous and anhydrous pyrolysis experiments by Lewan (1997) and Liang et al. (2015) reveal that C_{27}–C_{29} regular sterane are more easily altered by heating than hopane ratios such as Gam/H30 and H29/H30. Generally, the thermal stability of free biomarkers is controlled by their chemical structure. Most source-related biomarker parameters are the ratios of sterane or hopane homologs, because adjacent homologs show similar thermal stability (Peters et al., 2005). However, extensive thermal cracking can still influence those parameters, due to slight differences in degradation rates of biomarker homologs. Laboratory thermal alteration of triaromatic steroids by Beach et al. (1989) indicated that compounds with longer side chains show faster degradation than the shorter chain homologs. Thus, biomarkers with longer side chains should be more easily thermally degraded than those with shorter side chains. The C_{27}–C_{29} regular steranes have longer side chains than most commonly used biomarkers. By this line of reasoning, C_{27}–C_{29} regular sterane distributions are more easily thermally altered than parameters based on biomarkers with shorter branched chains (such as H29/H30 and Gam/H30) in the free fraction.

The influence of thermal stress on bound biomarkers is limited due to protection by the macromolecular structure (Tissot and Welte, 1978; Love et al., 1995, 2005). Sugden and Abbott (2002) reported that epimerization of bound hopanoids still occurs at C-17, C-21 and C-22 during closed system pyrolysis. Lockhart et al. (2008) also suggested that bound constituents undergo the same maturation reaction pathways as their free counterparts. However, the chemical structures of bound biomarkers are quite different from their corresponding free forms, since linkages via covalent bonds link the bound biomarker precursors to the kerogen. Thus, the incorporation of individual biomarkers in kerogen may also influence their thermal stability.

Previous labeling experiments with deuterium indicated that individual biomarkers are incorporated into the macromolecular network via functional groups in the biological precursors (Mycke and Michaelis, 1986; Richnow et al., 1992; Stalker et al., 1998). Bacteriohopanetetrol and similar highly functionalized compounds are precursors of hopanes (Rohmer et al., 1984;

Table 5
The biomarker parameters in pyrolysates of the thermal altered kerogen of GY-17.

Sample ID	GY-17 series				
Temp (°C)	350	380	400	430	460
$C_{27}/(C_{27}+C_{28}+C_{29})$	0.49	0.58	0.64	–	–
$C_{28}/(C_{27}+C_{28}+C_{29})$	0.30	0.21	0.19	–	–
$C_{29}/(C_{27}+C_{28}+C_{29})$	0.21	0.20	0.17	–	–
S21/S22	1.45	1.22	1.27	–	–
C_{27} βαR/C_{27}	0.22	0.15	0.17	–	–
C_{29} αββ/(αββ + ααα)	0.48	0.45	0.45	–	–
C_{29} 20S/(20S + 20R)	0.49	0.46	0.51	–	–
TT23/(TT23 + TT24)	0.84	0.78	0.73	–	–
Ts/(Ts + Tm)	0.42	0.40	0.45	–	–
TT23/H30	0.78	0.22	0.20	–	–
H29/H30	0.75	0.65	0.71	–	–
H31 22S/(22S + 22R)	0.60	0.62	0.59	–	–
Gam/H30	0.09	0.12	0.10	–	–

"–" = undetectable.

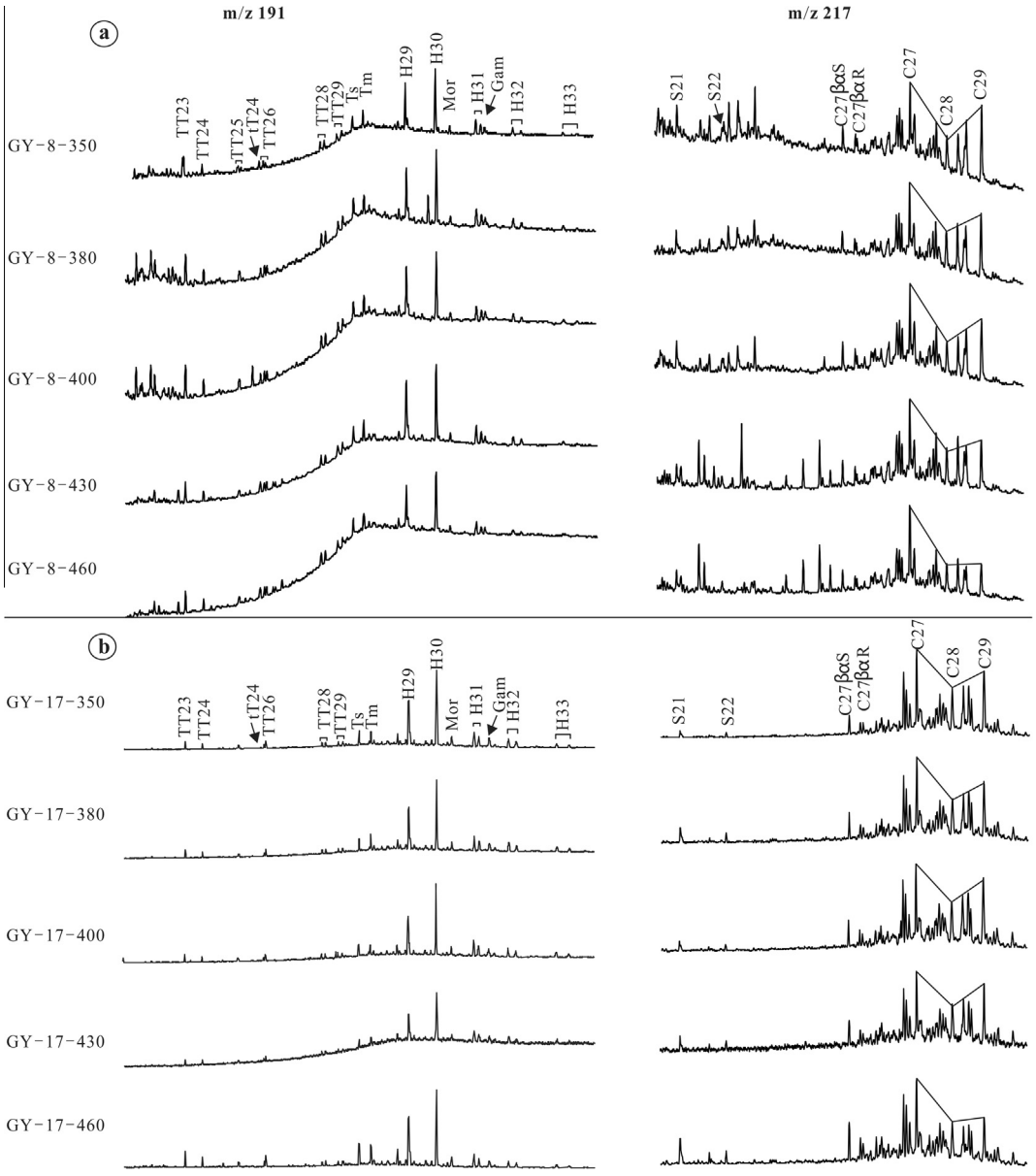

Fig. 3. Selected ion chromatograms (SIM) for *m*/*z* 191 and *m*/*z* 217 of the saturated fractions in hydropyrolysates of thermal altered kerogens: (a) is the siliceous rocks series (original kerogen is GY-8) and (b) is the mudstone series (original kerogen is GY-17). Peak identifications are shown in Table 2.

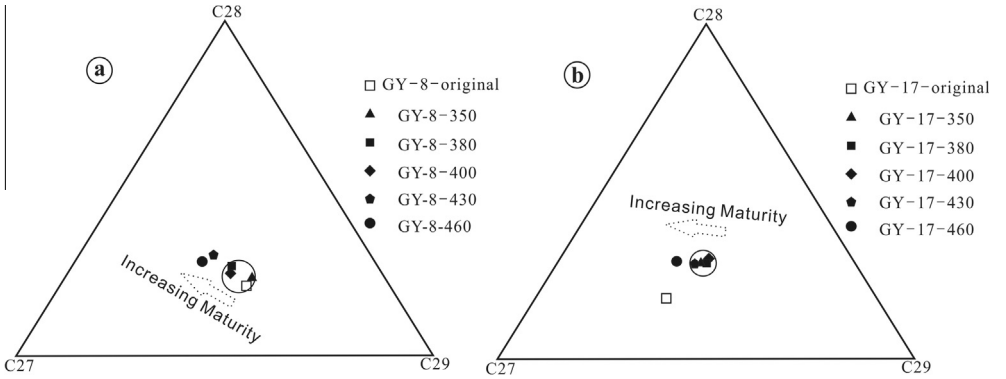

Fig. 4. Ternary plot of C_{27}–C_{29} ααα20R sterane distributions in the hydropyrolysate of the original sample and its thermal maturation residues: (a) is the series of GY-8 and (b) is the series of GY-17.

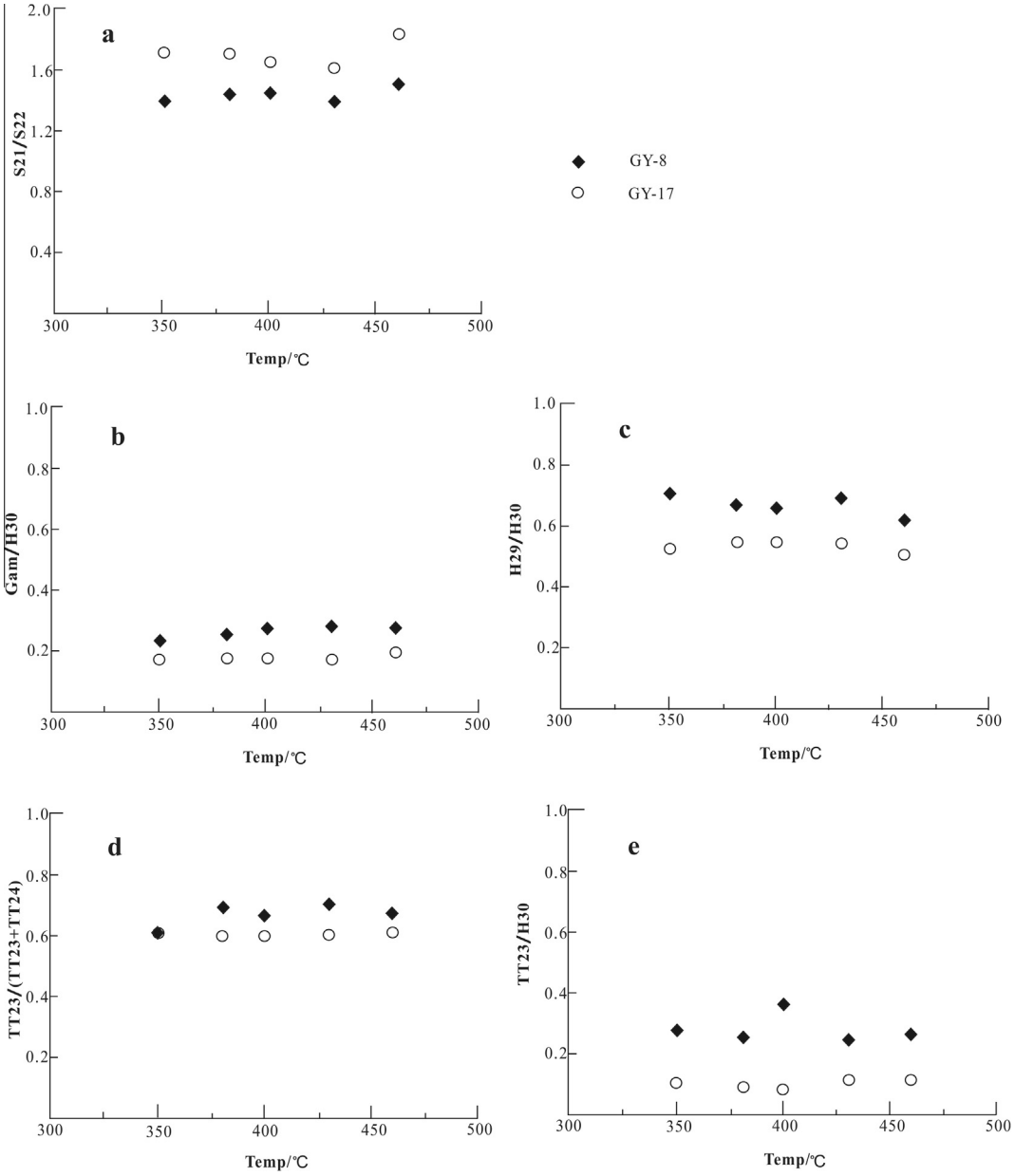

Fig. 5. Variations of source-related biomarker parameters in hydropyrolysates with increasing temperature.

Table 6
The biomarker parameters in hydropyrolysates of the thermal altered kerogens.

Sample ID	GY-8						GY-17					
Temp (°C)	Original	350	380	400	430	460	Original	350	380	400	430	460
$C_{27}/(C_{27}+C_{28}+C_{29})$	0.34	0.32	0.35	0.35	0.37	0.41	0.52	0.36	0.37	0.35	0.39	0.43
$C_{28}/(C_{27}+C_{28}+C_{29})$	0.21	0.23	0.27	0.26	0.30	0.29	0.16	0.26	0.28	0.30	0.38	0.29
$C_{29}/(C_{27}+C_{28}+C_{29})$	0.45	0.45	0.38	0.39	0.33	0.30	0.32	0.35	0.35	0.35	0.34	0.28
S21/S22	1.42	1.38	1.43	1.45	1.38	1.51	1.63	1.72	1.71	1.66	1.62	1.83
C_{27} βαR/C27	–	0.24	0.18	0.23	0.23	0.21	0.13	0.18	0.17	0.16	0.20	0.23
C_{29} αββ/(αββ + ααα)	0.42	0.50	0.51	0.50	0.51	0.53	0.48	0.37	0.40	0.39	0.37	0.38
C_{29} ααα20S/(20S + 20R)	0.50	0.39	0.42	0.39	0.43	0.4	0.47	0.42	0.44	0.42	0.44	0.41
TT23/(TT23 + TT24)	0.64	0.61	0.69	0.66	0.71	0.68	0.60	0.62	0.60	0.60	0.61	0.63
Ts/(Ts + Tm)	0.05	0.49	0.46	0.42	0.45	0.44	0.06	0.56	0.47	0.58	0.54	0.54
TT23/H30	0.12	0.28	0.25	0.36	0.24	0.32	0.27	0.11	0.09	0.08	0.12	0.12
H29/H30	0.73	0.70	0.67	0.66	0.69	0.62	0.93	0.53	0.55	0.55	0.54	0.51
H31 22S/(22S + 22R)	0.60	0.59	0.60	0.60	0.59	0.62	0.58	0.60	0.60	0.62	0.60	0.58
Gam/H30	–	0.23	0.25	0.27	0.28	0.27	–	0.17	0.18	0.18	0.17	0.20

Note: "–" mean undetectable, data for original samples cited from Wu et al. (2013).

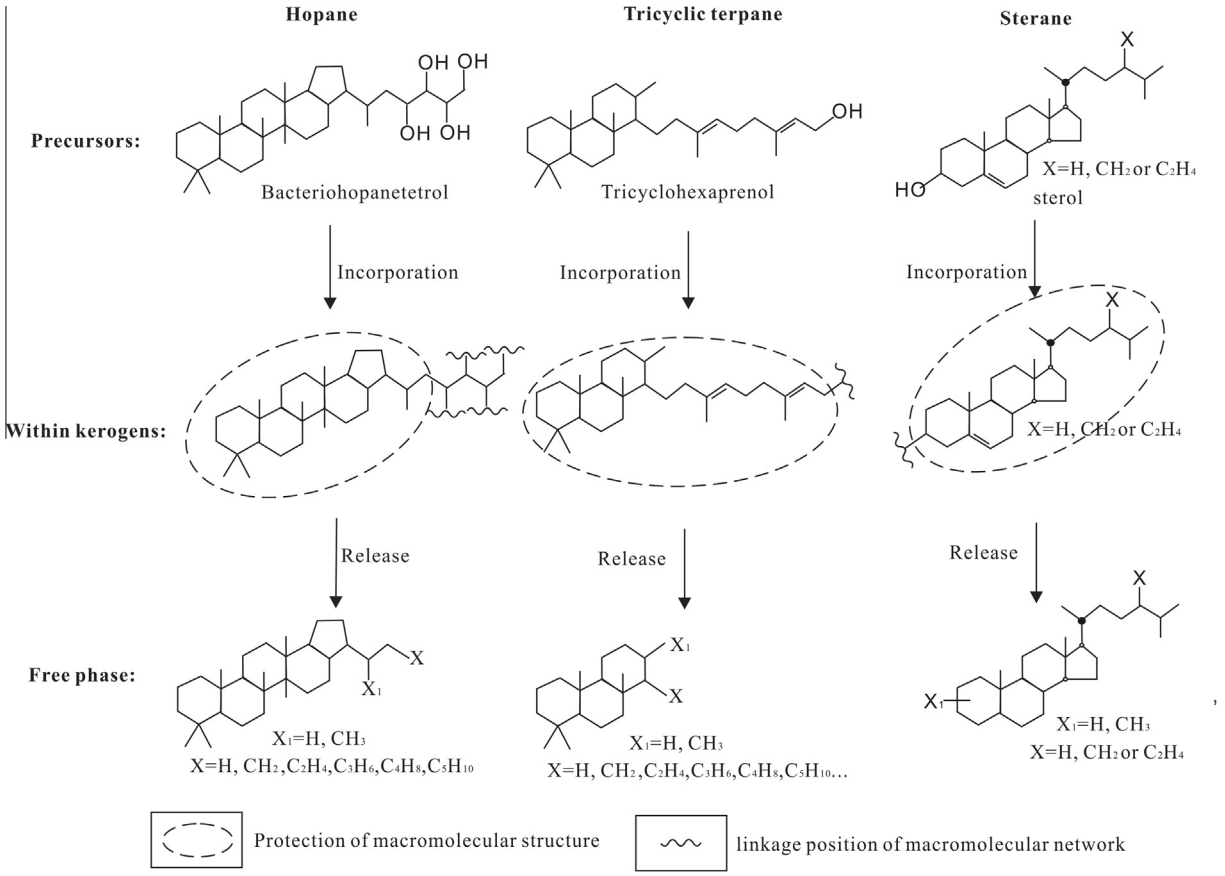

Fig. 6. Modes of incorporation of hopane and sterane precursors into macromolecular network (modified from Mycke and Michaelis, 1986; Richnow et al., 1992).

Rohmer, 1987; Richnow et al., 1992; Peters et al., 2005), while steranes originate from sterols (Rohmer, 1987; Richnow et al., 1992; Peters et al., 2005). The probable precursor for tricyclic terpanes is tricyclohexaprenol, which exists in microbial membrane lipids (Ourisson et al., 1982). Thus, hydroxyl groups exist in the long branched side chains of hopanes and tricyclic terpanes precursors, while they are directly linked to six-member rings of sterol precursors (Fig. 6). For hopanes and tricyclic terpanes, their long side chains are fixed into the kerogen through sulfur or oxygen bonds and are protected by the macromolecular structure. On the other hand, the sterols are incorporated into kerogen through short bonds to their six-member A-ring, while their long side chain is exposed to the thermal stress (Fig. 6). When long branched chain cracking occurs, thermally altered hopanes or tricyclic terpanes will be released from the kerogen because they are incorporated into kerogen through long branched chain, whereas part of the thermally altered steranes may remain in kerogen because the cracking of long branched chain cannot break their linkage into kerogen. For example, as cracking products of regular steranes, C_{21} and C_{22} steranes can be released from kerogen or solid bitumen (Wu et al., 2012, 2013; Fang et al., 2014). Thus, the thermal stress has little influence on the original distributions of hopanes or tricyclic terpanes, but will change the distribution of steranes within kerogen. This may also explain why the ratio of TT23/(TT23 + TT24) is stable in bound fractions at all simulation temperatures (Fig. 5d), although TT23 and TT24 also have long side chains. Moreover, the C_{21} and C_{22} steranes do not have long branched chains, so the ratio S21/S22 is as stable as hopane ratios in the hydropyrolysate at all temperatures. Therefore, biomarker parameters based on bound hopanes and tricyclic terpanes are more stable than those based on bound steranes.

4. Conclusions

Two kerogens (GY-8 and GY-17) isolated from different outcrop lithology of the Dalong Formation were subjected to by anhydrous pyrolysis at various temperatures. The bound hopanes and steranes within the original samples were released from the thermally altered kerogens by HyPy. The results from the anhydrous pyrolysis and HyPy experiments indicate that hopanes and tricyclic terpanes show greater thermal stability than steranes in both the free and bound fraction. Because of differences in the length of branched side chains and the mode of incorporation into kerogen, the thermal evolution of steranes is quite different from that of hopanes and tricyclic terpanes in both free and bound fractions. The source-related biomarker parameters based on hopanes and steranes have quite different thermal evolution trends in both free and bound fractions. For the investigated Permian Dalong Formation kerogen, bound regular sterane distributions are thermally altered above a simulation temperature of 430 °C (Easy% Ro = 2.27), but many hopane ratios and S21/S22 remain stable even at 460 °C. Therefore, ratios based on bound hopane and tricyclic terpane homologs seem to be very reliable source-related biomarker parameters even at 460 °C (Easy%Ro = 2.86). However, more studies are needed to confirm the maturity range in which bound hopanes and steranes might be invalid, because the results from artificial simulation experiment are not directly analogous to natural samples.

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