

Genesis study of high abundant 17 α (H)-diahopanes in Lower Cretaceous lacustrine source rocks of the Lishu Fault Depression, Songliao Basin, Northeast China

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Abstract Relatively abundant 17 α (H)-diahopanes have been detected in the lower cretaceous lacustrine source rocks from the Lishu Fault Depression in the Songliao Basin Northeast China. Rich long chain tricyclic terpanes (carbon number up to C₃₅) and gammacerane have been observed in those source rocks with relatively abundant 17 α (H)-diahopanes, which is rarely seen in previous reports. In this paper, the formation of 17 α (H)-diahopanes has been discussed from three aspects including maturity, oxidation-reduction nature of depositional environment and parent material composition by the GC/MS analyses. The results reveal that maturity and oxidation-reduction nature of depositional environment have little effect on the formation of 17 α (H)-diahopanes in the investigated area. However, the positive correlation between long-chain tricyclic terpanes and 17 α (H)-diahopanes argues strongly for a common origin, and the origin is related to the algae in saline water environment. The algae in saline water environment may be a kind of origin of 17 α (H)-diahopanes.

Key words diahopanes; long-chain tricyclic terpanes; oxidation-reduction nature; parent material composition; Lishu Fault Depression

1 Introduction

Rearranged hopanes have several homologues series in oils and rock extracts, the 17 α (H)-diahopane series are one of them. Similar to the distribution of 17 α (H)-hopane series, C₃₀ member (C₃₀^{*}) is usually the dominant peak of 17 α (H)-hopane series. C₃₀^{*} has been widely observed in earlier studies (Philp and Gilbert, 1986). But Moldowan et al. (1991) determined its structure and observed a pseudohomologous series of C₂₉–C₃₄ 17 α (H)-hopanes by X-ray crystallography and GC–MS–MS. Since then, the 17 α (H)-hopane series have received increasing attention.

So far, there are about three ideas: some suggested that C₃₀ 17 α (H)-diahopane may be formed by clay-mediated acidic catalysis under oxic or suboxic

conditions (Philip et al., 1986; Moldowan et al., 1991; Peters et al., 1993; Huang et al., 1994; Farrimond and Teln, 1996; Wang et al., 2000; Zhu et al., 2007; Zhang et al., 2007); some believed that it is useful for the formation of 17 α (H)-diahopanes by clay catalysis under moderately alkaline conditions (Xiao et al., 2004); others inferred that C₃₀ 17 α (H)-diahopane may be originated from red alga (Zhang et al., 2007). Above all, they focused on depositional environment, diagenetic conditions, maturity, and parent material sources, etc. But its origin and genesis is yet unclear (Zhang, 2013). Based on previous researches, the controlling factors has been discussed from three aspects including maturity, oxidation-reduction nature of depositional environment and parent material composition, which should be significative for precise

oil-source correlation and the identification of chief hydrocarbon source rocks in the lower cretaceous lacustrine source rocks from the Lishu Fault Depression, Songliao Basin.

2 Geological setting

The Lishu Fault Depression is located in the southern part of the Southeast Uplift of the Songliao Basin Northeast China, which developed at Late Jurassic to Early Cretaceous, and belongs to an independent hydrocarbon-generating depression. It develops many sets of source rocks vertically: from bottom to up exhibits successively Huoshiling Formation, Shahezi Formation, Yingcheng Formation and Denglouku Formation, the lithology is mainly composed of mudstone and coal-bearing strata (coal, carbonaceous mudstone and mudstone). The Shahezi and Yingcheng formations are the main hydrocarbon source rock sections in the research area, and deposited in strand shallow lake or delta environments.

3 Samples and methods

Forty dark mudstones were collected from Yingcheng and Shahezi formations and analyzed especially for this research. The mudstones show variable TOC (total organic carbon) values, ranging from 0.55% to 5.03%, mostly over 1.0%, averaging 1.86%. Their S1+S2 (hydrocarbon-generating potential) values vary between 0.13 and 10.03 mg/g, with an average of 3.87mg/g. Chloroform extract yields of the mudstones change in the range of 0.03%–2.92%, averaging 0.76%. The mudstones contain type II-III kerogen, and have the measured vitrinite reflectance in the sections of 0.66%–1.27%, indicative of marginally mature to the peak oil generation conditions.

All of the mudstones were firstly analyzed by a Rock-Eval II instrument. Eighteen of them were selected and extracted using dichloromethane in a Soxhlet apparatus for 72 h. After precipitation of asphaltene from the rock extracts, the saturated hydrocarbon fractions were obtained using column chromatography. The saturated hydrocarbon fractions were obtained.

Chromatogram and mass spectrum conditions: A HP 5973 mass spectrometer coupled with a HP 6890 GC and equipped with a 30 m (0.25 mm i.d., 0.25 μ m in film thicknesses). And HP-5MS fused silica capillary column was used for GC-MS analysis. The GC for the analysis was temperature-programmed to be heated for 1 minute at 50°C, then the temperature raise from 50 to 100°C at a rate of 20°C/min, and from 100 to 315°C at a rate of 3°C/min and then was held for 18 minutes at 315°C. Helium was used as the carrier gas with a rate of 1.0 mL/min and the ionization source operated at 70 eV.

4 Geochemical characteristics of hydrocarbon source rocks

The mudstones have Pr/Ph ratios from 0.29–2.43, and most of them show a strong phytane-over-pristane predominance, which suggests that the source rocks deposited under highly reducing environment. In addition, the gammacerane contents are generally high, gammacerane/C₃₀ 17 α (H)-hopane ratios of most samples are greater than 0.2, and some samples even have the dominant peak for gammacerane, indicating that the hydrocarbon source rocks developed in brackish-salty depositional environments (Moldowan et al., 1991). The molecular composition of steranes in the samples is generally marked by a predominance of C₂₉ sterane over C₂₇ and C₂₈ steranes. The C₂₇/C₂₉ regular sterane ratios ranged between 0.07–0.90, implying a strong contribution of higher land plants.

As shown in Fig. 1, rearranged hopanes were observed in variable abundance in these samples. The samples from SN65, SN203 and SN92 well have higher C₃₀^{*}/C₃₀ hopane ratios (up to 0.26–1.09) and C₂₉Ts/C₂₉ hopane ratios (0.23–1.75). The carbon number distribution of 17 α (H)-diahopane series range from C₂₇ and C₂₉–C₃₅, with the dominant peak for C₃₀ member (C₃₀^{*}). While the contents of 17 α (H)-diahopane and C₂₉Ts, Ts in the rest samples (e.g. the sample from SN55 Well) are low, diahopanes peaks can barely be seen in the m/z 191 mass chromatograms.

5 Results and discussion

5.1 Sample maturity

The vitrinite reflectance (R_o) values of studied samples range from 0.65% to 1.27%, their C₂₉ $\alpha\alpha\alpha$ sterane 20S/(20S+20R) ratios distribute between 0.4 to 0.6, indicating that all samples have entered mature stage. Fig. 2 is plotted in order to understand the relationship between C₃₀^{*}/C₃₀ hopane and maturity parameters [R_o and C₂₉ $\alpha\alpha\alpha$ sterane 20S/(20S+20R), respectively]. It is clear that Fig. 2 does not show a good correlation between the C₃₀^{*}/C₃₀ hopane index and the maturity indexes, and displays similar maturity with different abundance of C₃₀^{*}. In Fig. 2(a), both high and low values of diahopanes have appeared when R_o is about at 0.80%, and even low ratios of C₃₀^{*}/C₃₀ hopane occurs in the largest R_o value. A similar phenomenon turns up in Fig. 2(b), showing the formation of diahopanes does not depend on thermal evolution. However, it is noticed that higher values of C₃₀^{*}/C₃₀ hopane appear in such a maturity range ($R_o \geq 0.80\%$ and C₂₉ $\alpha\alpha\alpha$ sterane 20S/(20S+20R) ≥ 0.45), illustrating that maturity still plays a certain role on the formation of diahopanes.

5.2 Oxidation reduction nature of depositional environments

From the perspective of sedimentology, the source rocks from Yingcheng and Shahezi formations of Lishu Fault Depression in Songliao Basin mainly

developed in strand shallow lake or delta environments, whose sedimentary water is brackish-salty. The source rocks with high concentrations of C_{30}^* in Lishu Fault Depression are observed in the strand shallow lake environments, and the source rocks with low C_{30}^* content are found in the delta facies.

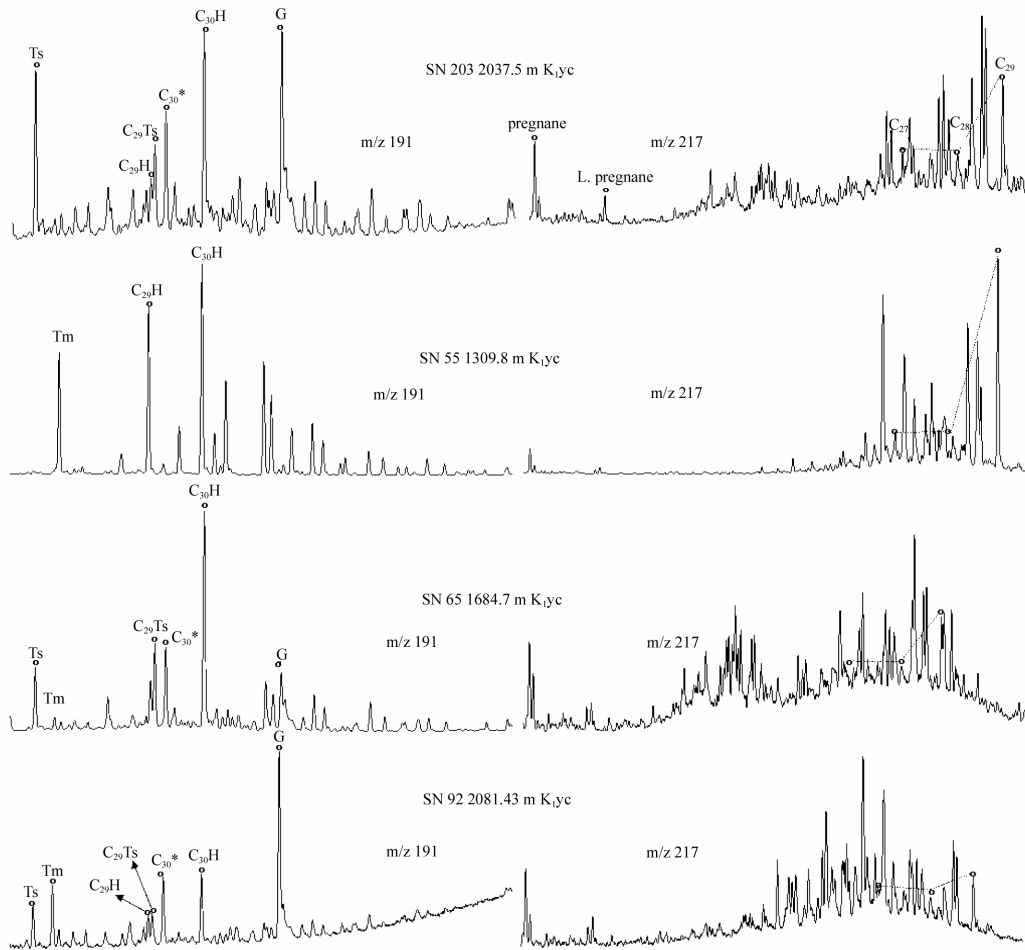


Fig. 1. Distribution of steranes and terpanes in representative source rocks in Lishu Fault Depression (m/z 191 and m/z 217).

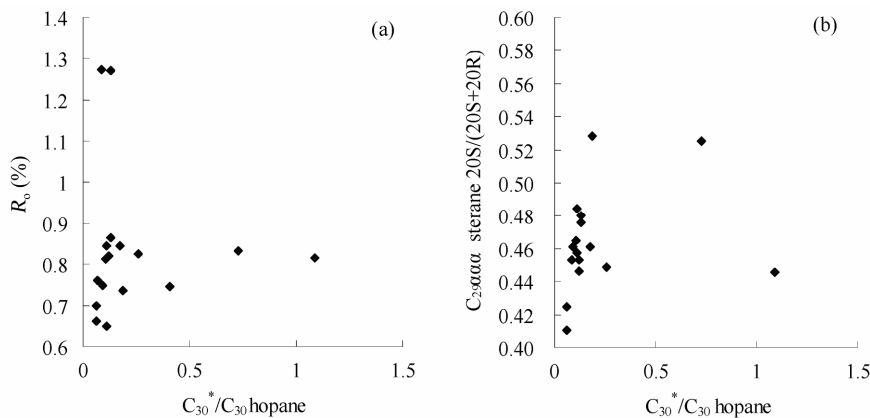


Fig. 2. Correlogram of C_{30}^*/C_{30} hopane and R_0 , C_{29} sterane $20S/(20S+20R)$ of source rocks in Lishu Fault Depression.

Table 1 Geochemical parameters for the lower cretaceous source rocks from the Lishu Fault Depression

Well No.	Depth (m)	Formation	1	2	3	4	5	6	7	8
SN 118	1303.8	K _{1yc}	0.11	0.74	0.650	0.48	1.98	0.14	0.14	0.47
SN 55	1309.8	K _{1yc}	0.06	0.04	0.662	0.41	4.27	0.03	0.05	0.09
SN 22	1333.8	K _{1yc}	0.06	0.03	0.700	0.42	3.79	0.02	0.00	0.07
SN 203	1496	K _{1yc}	0.19	0.70	0.735	0.53	0.79	0.94	0.50	0.63
SN 65	1684.7	K _{1yc}	0.41	1.75	0.747	0.60	1.17	0.27	0.93	0.29
SN 153	1520.6	K _{1sh}	0.09	0.37	0.749	0.46	0.54	–	0.45	0.50
SN 146	1778.56	K _{1sh}	0.07	0.10	0.761	0.40	0.81	0.09	0.17	0.43
SN 64	1862.48	K _{1yc}	0.11	0.30	0.812	0.47	0.32	0.19	0.38	0.75
SN 92	2081.43	K _{1yc}	1.09	1.29	0.815	0.45	0.88	2.77	3.36	0.50
SN 105	2093.56	K _{1sh}	0.12	0.34	0.820	0.45	0.84	0.17	0.43	0.48
SW 6	1987.46	K _{1yc}	0.12	0.53	0.821	0.45	0.58	0.33	0.47	0.83
SN 152	2276.76	K _{1sh}	0.26	0.23	0.825	0.45	1.37	0.07	0.37	0.49
SN 203	2037.5	K _{1sh}	0.73	1.60	0.834	0.53	0.95	1.14	1.86	0.35
SN 148	2023.82	K _{1sh}	0.17	0.15	0.844	0.46	2.43	0.06	0.32	0.51
SN 18	2232	K _{1yc}	0.11	0.42	0.845	0.46	0.54	0.29	0.25	0.90
SN 203	2191.5	K _{1sh}	0.13	0.43	0.866	0.48	0.70	0.30	0.55	0.78
SN 52	2871.3	K _{1yc}	0.13	0.40	1.271	0.48	0.59	0.21	0.80	0.76
SN 52	3234.2	K _{1sh}	0.09	0.27	1.274	0.45	0.33	0.23	0.70	0.48

Note: 1. C_{30}^*/C_{30} hopane; 2. $C_{29}Ts/C_{29}$ hopane; 3. R_o (%); 4. $\alpha\alpha C_{29}-20S/(20S+20R)$; 5. Pr/Ph; 6. gammacerane/ C_{30} hopane; 7. $(C_{28}+C_{29})$ tricyclic terpanes/ C_{29} norhopane; 8. C_{27}/C_{29} regular steranes.

The pristane/phytane (Pr/Ph) parameter is a relatively effective indicator for the redox conditions of the depositional environment. As seen from Fig. 3, low C_{30}^* values are mainly distributed in the Pr/Ph of 0–4.5, and the Pr/Ph ratios corresponding to high C_{30}^* values range over 0.8–1.3, while the literatures about terrestrial source rocks in Kuqa Depression were reported that Pr/Ph ratios corresponding to high C_{30}^* values are between 1.70–3.00 (Zhang and Zhu, 1996), indicating that high C_{30}^* values have not always appeared in source rocks with higher ratios of Pr/Ph. Besides, the source rock samples from the SN 65, SN 203 (from Shahezi Formation) and SN 92 well, depositing in the strand shallow lake facies, have similar redox environment condition but different relative abundance of C_{30}^* , and their relative abundance of C_{30}^* even decreases along with the enhancement of oxidation (Fig. 5). Moreover, C_{30}^* content of the samples from SN22 and SN55 well that developed in strong oxidizing braided river delta front facies is very low (Fig. 2). It suggests that the formation of diahopanes is incompletely controlled by oxidation reduction nature of depositional environments.

There is no direct relationship between rearranged hopanes and gammacerane in terms of genetic and parent material sources. Gammacerane is generally believed to be an indicator for deposition salinity, but to some extent also indicates redox of depositional environment. As shown in Fig. 5, the gammacerane index and C_{30}^*/C_{30} hopane index showed some positive correlation. Nevertheless, the rearrangement mechanisms of C_{30}^* demonstrate that a strong reducing environment is not conducive to its formation, which is a further support for the conclusion that oxi-

duction reduction nature of depositional environments is not the main controlling factor of the formation of C_{30}^* , and such changes of the relative abundance of C_{30}^* along with gammacerane may be affected by salinity.

5.3 Composition of source rocks

In regard to source material of rearranged hopanes, some scholars believed that all rearranged hopanes are derived from bacterial hopane precursors, others thought that the relative abundance of C_{30}^* may be related to terrigenous organisms (Philip et al., 1986), red algae (Zhang et al., 2007) and other biological materials.

As already mentioned above, the distribution of steranes is indicative of a strong contribution of higher plants with a certain amount of aquatic organisms input. Combining with generally lower pristane/phytane ratios of source rocks (less than 1.50), it is considered that C_{29} sterane predominance may related to the input of bacteria and algae (Chen, 2009).

Fig. 4 is m/z191 mass chromatograms of source rock samples from different depths of SN 203 well. It should be noted that the sample containing high abundance of C_{30}^* at 2037.5 m of SN 203 well is simultaneously rich in long chain tricyclic terpanes. And samples with low C_{30}^* content are lack of long chain tricyclic terpanes. It also occurred in other samples. Tricyclic terpanes series, in particular the C_{26}^+ long-chain tricyclic terpane members, are commonly used as indicators of the contribution from lower organisms algae (Mackenzie, 1984).

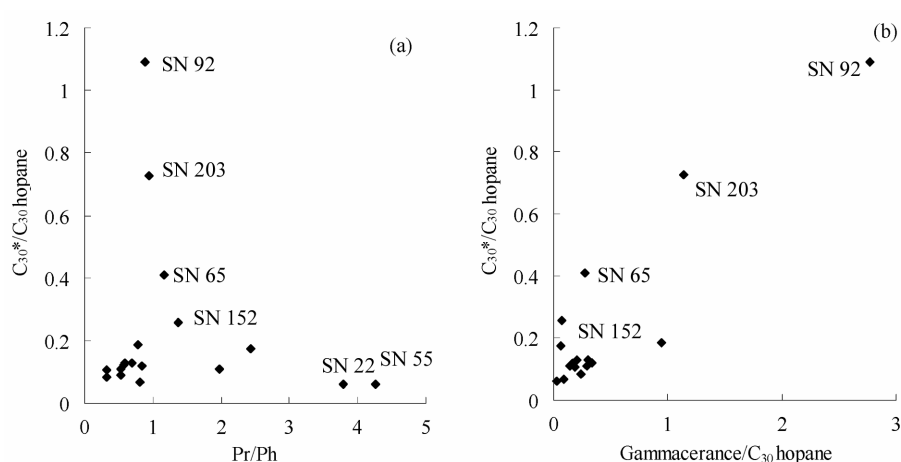


Fig. 3. Relation graph of C_{30}^*/C_{30} hopane respectively with Pr/Ph and gammacerane/ C_{30} hopane of source rocks in Lishu Fault Depression.

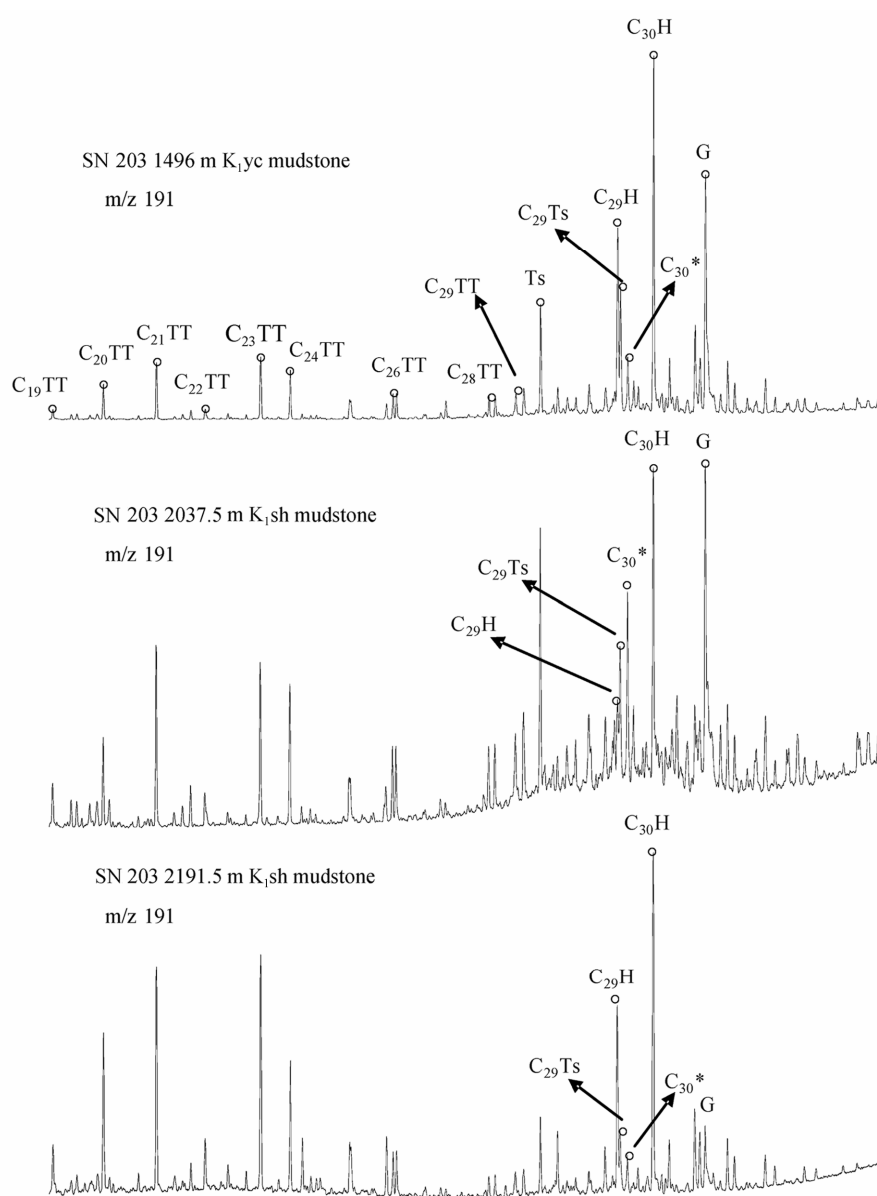


Fig. 4. Distribution of terpanes in the source rocks from SN 203 well in Lishu Fault Depression (m/z 191).

In order to investigate the connection between long chain tricyclic terpanes and rearranged hopanes compounds, C_{30}^*/C_{30} hopane index and corresponding $(C_{28}+C_{29})$ tricyclic terpanes/ C_{29} norhopane index of all analysed samples were plotted as a relation graph. It can be seen from Fig. 5 that a good positive correlation between C_{30}^*/C_{30} hopane and $(C_{28}+C_{29})TT/C_{29}$ hopane ratios indicated C_{30}^* and long chain tricyclic terpanes may have a common origin, and its formation is relevant with contribution of algae under brackish environments.

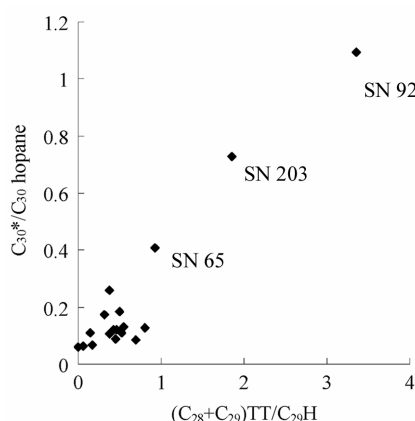


Fig. 5. Relation graph of $(C_{28}+C_{29})$ tricyclic terpanes/ C_{29} norhopane and C_{30}^*/C_{30} hopane of source rocks in Lishu Fault Depression.

6 Conclusions

(1) The vitrinite reflectance (R_o) values of studied samples range from 0.65% to 1.27%, all in lower-mature or mature stage. There is no good correlation between the diahopane index and maturity indexes. Even the samples with similar maturity have obvious different abundance of C_{30}^* , indicating the formation of rearranged hopanes incompletely depends on thermal evolution.

(2) The relationship between relative abundance of C_{30}^* and Pr/Ph ratios revealed that not the stronger oxidation is, the more rearranged hopanes becomes. C_{30}^* content of source rock samples from SN 22 and SN 55 well that developed in strong oxidizing deposited in braided river delta front is very low. It suggests that the formations of diahopanes are incompletely controlled by oxidation reduction nature of depositional environments.

(3) Source rocks containing high C_{30}^* content are simultaneously rich in long chain tricyclic terpanes, and both present good positive correlation, indicating both of them have a common origin, which is related to the contribution of bacteria and algae under brackish environments.

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