Distribution of sterane maturity parameters in a lacustrine basin and their control factors: A case study from the Dongying Sag, East China

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Abstract: Fifty samples from the source rocks in Member 3 and Member 4 of the Paleogene Shahejie Formation in the Bohai Bay Basin, East China, were analyzed to investigate the distribution, evolution of the molecular maturity ratios $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ and $C_{29}20S/(20S+20R)$ and their control factors in the natural geological profile and sequence. The results showed that progressive changes in molecular maturity parameters are associated with major changes in thermal evolution of related biomarkers. Increases in the $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ and $C_{29}20S/(20S+20R)$ ratios result from the difference in the relative rate between generation and thermal degradation of isomers involved. The samples from a hyper-saline environment below 3.5 km in which evaporitic rocks deposited shows high response of Sr/Ba, Sr/Ca, Fe/Mn, Pr/n-C₁₇, Ph/n-C₁₈ and gammacerane and low response of Pr/Ph. There presents negative reversal of biomarker maturity $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$, $C_{29}20S/(20S+20R)$ and Ts/(Ts+Tm) in the samples from hypersaline environment, reflecting that the gypsum-halite have negative effect on the isomerization of biomarker and thermal evolution of organic matter. The minerals in evaporites also retard the conventional thermal indicators including vitrinite reflectance (R_o) and pyrolysis peak temperature T_{max} at the depth below 3.4 km (i.e. >3.4 km), and these parameters also show the inhibition from overpressure in the range of 2.4–3.4 km. This result will be helpful in the interpretation and application of molecular maturity parameters for similar saline lacustrine basins.

Key words: C_{29} 24-ethyl cholestane, biomarker, thermal maturity parameters, saline basins, Dongying Sag

1 Introduction

Quantitative study of biomarker transformation and trend in the distribution of biomarker maturity ratios with increasing burial depth are rarely found in literature. The reason is mainly the lack of suitable set of samples. However, this kind of study is essential for understanding related biomarkers and the distribution of biomarker maturity ratios, which are widely used in petroleum exploration.

In this study, four types of C_{29} 24-ethyl cholestanes isomers were detected: $5\alpha,14\alpha,17\alpha$ - C_{29} cholestane (20S), is referred to as $C_{29}S\alpha\alpha$; $5\alpha,14\beta,17\beta$ - C_{29} cholestane (20S), is referred to as $C_{29}S\beta\beta$; $5\alpha,14\alpha,17\alpha$ - C_{29} cholestane (20R), is referred to as $C_{29}R\alpha\alpha$; and $5\alpha,14\beta,17\beta$ - C_{29} cholestane (20R), is referred to as $C_{29}R\beta\beta$.

The $C_{29}20S/(20S+20R)$ ratio is based on the relative enrichment of the 20S isomer compared with the biologically-inherited 20R isomer to reach an equilibrium end-point of 0.50–0.55 (Mackenzie and Mckenzie, 1983). Preferential

generation of the 20S isomer and preferential loss of the 20R isomer are identified as the dominant controls on this $C_{29}20S/(20S+20R)$ ratio (Dzou et al, 1995; Requejo, 1994). Other factors such as rock matrix (or organic matter) effects are used to explain the difference in the 20S content between coals and shales with equivalent geothermal histories (Strachan et al, 1989).

The parameters $C_{29}20S/(20S+20R)$ and $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ have been widely used in petroleum geochemistry as indicators of thermal maturity. Profiles of these ratios versus depth are widely used for describing the thermal maturity of source rocks or oils (Seifert and Moldowan, 1986). These ratios are mainly used in oil/gas evolution beyond the oil window (Farrimond et al, 1998), although they are known to give anomalous values dependent upon organic facies (Rullkötter and Marzi, 1988), which is perhaps related to specific precursors (ten Haven et al, 1986).

Biomarker maturity parameters generally increase with increasing burial depth before they reach an equilibrium value. However, a number of molecular maturity parameters exhibit a significant maturity reduction or “reversal” after they reach equilibrium, such as the two parameters $C_{29}20S/$

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Received November 16, 2010

(20S+20R) and $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ for C_{29} 24-ethyl cholestane, the thermal reversal of which has been recorded both in the laboratory and also in sedimentary basins (Mackenzie et al, 1980; ten Haven et al, 1986; Peters et al, 1990; Strachan, et al, 1989; Chen, 1997; Wang et al, 2006).

Most of previous investigations of biomarker maturity parameters have been conducted in the laboratory, including hydrous pyrolysis experiments or other types of pyrolysis experiment in closed system. However, laboratory experiments may not simulate the actual burial-related maturation which is controlled by a wide range of geological factors (Lewis, 1993). Quantitative studies of biomarker ratio evolution using data from natural depositional sequences are rare (Requejo, 1994; Farrimond et al, 1998).

Requejo (1994) investigated nine samples, which have uniform lithologies and organic facies, from the Upper Devonian Duvernay Formation (Western Canada Basin), covering a maturity range from immature to overmature with respect to hydrocarbon generation. He found that different maturity parameters are controlled at different extents by isomerization progress and by the relative rate between the generation and thermal degradation of isomers. Farrimond et al (1998) quantitatively studied biomarkers from the Tertiary section (1,400-3,000 m) of a well located in the Barents Sea, and analysed 27 samples covering a maturity range from immature to mature with respect to hydrocarbon generation. The results showed the importance of the relative rate between generation and thermal degradation of isomers, and suggested that increased concentration of individual isomer was the result of biomarker generation from kerogen and other macromolecular/polar fractions.

Further investigations are necessary. We studied the

maturity ratios $C_{29}20S/(20S+20R)$ and $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ in Paleogene lacustrine source rocks in the Dongying sag, a lacustrine rift basin in East China. The source rocks are present in Members 4 and 3 of the Shahejie Formation (Zhu et al, 2004; Chen et al, 2004), and are comprised of dark mudstones and some evaporites over 1,000 m thick. These source rocks have been previously investigated by our lab team (Chen et al, 2004, 2005, 2008, 2009; Chen and Zha, 2006, 2007, 2008). Samples came from wells Feng-8, Fengshen-1, Shi-121 and Shi-126 over a depth range of 2,800 m to 4,000 m and cover most of the oil window.

2 Regional geological setting

The Dongying sag is a typical rift basin located in the southern Bohai Bay Basin, covering an area of about 5,700 km². The Paleogene succession is dominated by mudstone with interbedded carbonates, gypsum-evaporite rocks and sandstones. The main source rocks comprise the upper part of Member 4 (Es_4) and lower part of Member 3 (Es_3) of the Shahejie Formation.

During early Es_4 deposition, chemical sediments began to be deposited in response to the hot and dry climatic conditions. Some 400-600 m of grey mudstones with evaporite and gypsum intervals were deposited in the centre of the lacustrine basin (Zhu et al, 2003; Chen et al, 2009). Tectonic subsidence then increased significantly and a large-scale rift basin formed (Zhu et al, 2004) under a hot and dry climate. Large volumes of water evaporated with a resulting increase in salinity. Evaporites and mudstones thus dominate the middle part of the Es_4 member (Fig. 1). The overlying Member 3 of the Shahejie Formation (Es_3) is dominated by

Fig. 1 Distribution of the co-sedimentary system of evaporites and source rocks in the middle part of Member 4 of the Shahejie Formation in the Dongying Sag
1. halite, gypsum; 2. limestone, dolomite; 3. mudstone; 4. wells; 5. faults; 6. boundary of different sedimentary systems; 7. the wells for the samples coring

dark mudstones with some oil shales and thin sandstones.

The dark mudstones and evaporites in the upper to middle parts of Es_4 and the middle to lower parts of Es_3 constitute the main source rock intervals in the depression (Chen et al, 2004; Chen and Zha, 2006). Theoretical investigations and exploration data show that the threshold of oil generation occurs at around 2,800 m (Chen et al, 2005).

3 Experimental methods

We analyzed 50 source rock samples (Table 1) from

the Dongying Sag in Bohai Bay Basin, East China. The rock samples were cored from Es_3 and Es_4 of the Paleogene Shahejie Formation in the Wells Feng-8, Fs-1, Shi-121, Shi-126, Niu-11, Li-91, Tuo-102 and Tuo-103. These wells are located around the Lijin sub-sag which is recognized as the main oil source in Dongying Sag (Fig. 1). The middle part of the Es_4 member around Lijin sub-sag is dominated by evaporites and mudstones. The Es_3 samples are dark mud and dark-gray mud, and the Es_4 samples are dark mud, dark-gray mud, and gypsum-mud.

Table 1 The relative contents of molecular biomarkers (%) and their ratios

Well	Depth, m	Strata	S $\alpha\alpha$	R $\beta\beta$	S $\beta\beta$	R $\alpha\alpha$	Ts	Tm	H ₃₀ (17a)	R ₃₀	Ts/(Ts+Tm)	C ₂₉ 20S/(20S+20R)	C ₂₉ $\beta\beta$ /($\beta\beta$ + $\alpha\alpha$)	R ₃₀ /H ₃₀
FS-1	2870	Es_3	3.22	7.35	1.17	19.90	2.21	3.53	27.11	1.90	0.38	0.14	0.27	0.070
Niu-11	3318	Es_3	7.11	6.50	4.76	9.89	3.19	2.21	27.30	1.25	0.59	0.42	0.40	0.046
Shi-121	3289.6	Es_3	7.16	5.62	4.01	9.29	3.68	2.66	26.32	2.77	0.58	0.43	0.37	0.105
Shi-121	3521.8	Es_3	2.92	7.27	5.91	4.25	4.10	1.66	27.91	1.38	0.71	0.43	0.65	0.049
Shi-121	3561.9	Es_3	3.80	7.12	6.74	4.58	4.31	2.03	25.30	1.26	0.68	0.47	0.62	0.050
Shi-121	3563	Es_3	4.22	7.50	7.01	4.68	4.26	2.08	25.58	1.12	0.67	0.48	0.62	0.044
Shi-121	3563.5	Es_3	2.74	8.53	6.81	4.00	5.87	1.23	27.83	1.13	0.83	0.43	0.69	0.041
Shi-121	3565.9	Es_3	3.86	6.40	6.13	4.72	4.54	1.59	28.66	1.49	0.74	0.47	0.59	0.052
Shi-121	3568.5	Es_3	3.35	7.72	5.66	4.08	4.88	1.58	29.24	1.09	0.76	0.43	0.64	0.037
Shi-121	3569.25	Es_3	3.22	8.31	6.17	3.84	6.64	1.26	27.17	1.57	0.84	0.44	0.67	0.058
Shi-121	3572.8	Es_3	2.78	8.04	5.50	3.61	5.58	1.36	27.99	1.36	0.80	0.42	0.68	0.048
Shi-121	3575.8	Es_3	4.07	9.35	6.88	5.37	5.04	1.80	28.16	1.11	0.74	0.43	0.63	0.040
Shi-121	3577.2	Es_3	3.85	7.62	6.63	4.69	5.50	1.34	27.23	1.29	0.80	0.46	0.63	0.047
Shi-121	3578.5	Es_3	3.88	9.25	6.87	4.97	3.85	1.77	26.25	1.31	0.69	0.43	0.65	0.050
Shi-121	3580.8	Es_3	4.02	11.08	7.23	5.39	4.39	2.00	25.94	1.35	0.69	0.41	0.66	0.052
Shi-121	3582.1	Es_3	4.03	11.26	7.44	5.13	4.14	1.84	25.92	1.40	0.69	0.41	0.67	0.054
Shi-121	3582.7	Es_3	3.92	9.56	6.73	4.60	4.54	1.75	25.90	1.37	0.72	0.43	0.66	0.053
Shi-121	3585	Es_3	3.90	10.84	6.77	4.73	4.73	1.91	26.57	1.24	0.71	0.41	0.67	0.047
Shi-126	3521.9	Es_3	5.73	13.72	6.35	6.91	3.42	2.35	29.16	1.14	0.59	0.37	0.61	0.039
Shi-126	3525.6	Es_3	4.38	7.72	7.07	5.18	4.07	1.68	25.22	1.45	0.71	0.47	0.61	0.057
Tuo-103	2806	Es_3	3.60	5.87	1.40	20.80	1.47	2.53	41.55	1.92	0.37	0.16	0.23	0.046
Tuo-104	2963.7	Es_3	3.85	5.34	0.92	13.12	1.96	3.72	26.86	2.24	0.34	0.21	0.27	0.083
Tuo-104	2966.2	Es_3	6.98	5.54	3.11	11.69	1.68	3.20	28.15	1.76	0.34	0.37	0.32	0.062
Tuo-104	3185.5	Es_3	4.25	5.18	3.08	10.21	2.41	3.03	25.00	1.25	0.44	0.32	0.36	0.050
Tuo-104	3432.4	Es_3	5.22	4.61	2.94	5.31	3.44	3.57	23.03	3.88	0.49	0.45	0.42	0.168
Fan-1	3311.7	Es_4	7.86	16.18	8.94	7.88	6.97	3.78	23.31	2.51	0.65	0.41	0.61	0.108
Feng-8	3050	Es_4	6.75	7.59	2.11	17.70	1.84	3.55	26.22	1.71	0.34	0.26	0.28	0.065
Feng-8	3164	Es_4	10.49	7.71	4.23	16.76	1.80	3.01	25.38	0.95	0.37	0.38	0.30	0.038
Feng-8	3166	Es_4	10.82	7.73	4.51	15.78	2.07	3.40	24.92	1.10	0.38	0.39	0.32	0.044
Feng-8	3403	Es_4	11.09	10.36	8.46	11.79	2.08	2.85	27.15	4.26	0.42	0.47	0.45	0.157
Feng-8	3403.4	Es_4	9.89	8.32	7.44	11.61	1.89	2.44	28.26	3.99	0.44	0.47	0.42	0.141

(Continued)

Well	Depth, m	Strata	S $\alpha\alpha$	R $\beta\beta$	S $\beta\beta$	R $\alpha\alpha$	Ts	Tm	H ₃₀ (17a)	R ₃₀	Ts/ (Ts+Tm)	C ₂₉ 20S/ (20S+20R)	C ₂₉ $\beta\beta$ / ($\beta\beta$ + $\alpha\alpha$)	R ₃₀ /H ₃₀
Feng-8	3816.3	Es ₄	4.71	9.77	6.99	5.94	5.26	3.01	10.86	14.12	0.64	0.43	0.61	1.300
Feng-8	3818	Es ₄	5.41	10.73	7.47	6.59	4.50	2.57	14.67	10.45	0.64	0.43	0.60	0.712
Feng-8	3947	Es ₄	2.65	6.04	4.13	3.58	6.07	1.27	24.16	2.53	0.83	0.41	0.62	0.105
Fs-1	3440	Es ₄	9.11	10.97	8.60	10.21	2.12	2.53	27.75	5.28	0.46	0.46	0.50	0.190
Fs-1	3685.6	Es ₄	9.92	10.66	8.33	9.56	5.44	2.53	26.28	4.56	0.68	0.47	0.49	0.173
Fs-1	3686.3	Es ₄	9.39	11.17	8.15	10.27	5.15	2.55	25.58	4.61	0.67	0.45	0.50	0.180
G u a n - 118	3000	Es ₄	9.04	7.18	4.60	12.57	0.83	2.05	25.34	4.11	0.29	0.41	0.35	0.162
Li-91	3030	Es ₄	6.35	8.25	5.08	7.08	2.37	2.80	29.28	2.24	0.46	0.43	0.50	0.076
Tuo-102	3467.8	Es ₄	5.51	5.01	4.60	5.26	1.98	3.11	27.18	2.33	0.39	0.50	0.47	0.086
Tuo-102	3565	Es ₄	4.01	5.12	5.35	5.01	4.06	2.00	28.69	1.80	0.67	0.48	0.54	0.063
Tuo-102	3656.7	Es ₄	4.92	4.82	4.88	3.72	3.37	2.25	22.68	1.76	0.60	0.53	0.53	0.078
Tuo-103	3339.7	Es ₄	3.06	6.38	3.45	4.72	3.35	2.69	27.54	1.47	0.56	0.37	0.56	0.053
Tuo-103	2993.4	Es ₄	4.90	4.97	2.72	12.01	1.98	2.91	30.70	1.31	0.40	0.31	0.31	0.043
Tuo-103	3108.4	Es ₄	4.32	6.33	2.65	8.80	2.19	3.21	24.10	1.51	0.41	0.32	0.41	0.063
Tuo-103	3169.8	Es ₄	5.74	4.73	3.79	8.02	2.81	2.17	33.20	1.27	0.56	0.43	0.38	0.038
Tuo-104	3431.4	Es ₄	6.70	4.08	3.82	5.16	2.26	2.73	27.38	1.72	0.45	0.53	0.40	0.063
Tuo-104	3533.2	Es ₄	3.37	5.80	2.25	3.15	3.64	2.71	22.98	0.98	0.57	0.39	0.55	0.043
Tuo-104	3537.6	Es ₄	4.26	2.86	3.46	3.71	2.73	2.91	26.85	2.57	0.48	0.54	0.44	0.096
Wang-46	3788	Es ₄	5.77	7.48	3.16	12.05	1.65	2.83	23.16	6.34	0.37	0.31	0.37	0.274

Notes: S $\alpha\alpha$, R $\beta\beta$, S $\beta\beta$, R $\alpha\alpha$ are $\alpha\alpha$ C₂₉(20S), $\alpha\beta$ C₂₉(20R), $\alpha\beta$ C₂₉(20S), $\alpha\alpha$ C₂₉(20R) respectively, and their relative contents are the ratios of their concentrations compared to the total concentrations in the m/z 217; Ts, Tm, H₃₀(17a) and R₃₀ are 18 α -C₂₇Hopane, 17 α -C₂₇Hopane, 17 α -21 β -C₃₀Hopane and gammacerane respectively, and their relative contents are the ratios of their concentrations compared to the total concentrations in the m/z 191.

Chloroform was used as solvent for 72 hours of continuous extraction at a constant temperature of 70 °C in a Soxhlet apparatus and then evaporated to dryness. 10-15 mg of extractant was dissolved by adding petroleum ether, then repeatedly washed and moved in a flask, standing for 24 h (about 100 mL of petroleum ether in flask), and then filtered. The insoluble part was asphaltene; the soluble part was a mixture of saturated hydrocarbons, aromatic hydrocarbons and non-hydrocarbons.

A silica-alumina column was prepared. The alumina was activated for 5 h at 450 °C, and the silica was activated for 8 h at 150 °C. The silica and alumina was filled into the column at a silica/alumina ratio of 3:1 in volume with silica above alumina. After wetting the column with petroleum ether, a sample of the filtrate was poured into the column. Washing with petroleum ether, dichloromethane and diethyl ether, separately, we obtained saturated hydrocarbons, aromatic hydrocarbons and non-hydrocarbons, respectively.

An HP-Chemistation GC-MS analyzer was used (Model HP-5890 II for the GC, HP-5890A for the MS; Column: DB5-MS; Column length: 60 m; internal diameter: 0.25 mm). The temperature was elevated from an initial 100 °C to the final 320 °C at a heating rate of 4.0 °C/min. The temperature of the

gasification and transmission line was 310 °C, the ion source temperature 250 °C, and the pre-column pressure was 170 kPa. The split ratio was 20:1, and the carrier gas was helium. Electron energy was 70 eV, the scan rate was 0.46 can/s, with electron-impact ionization.

Biomarkers were identified by using the mass fragmentogram and relative retention time in comparison with standard sample. Quantification of biomarker was performed by peak area response in specific mass chromatograms (m/z 191 and m/z 217). For some samples from Es₄ member, the relative contents of C₂₉ 24-ethyl cholestane isomers were calculated from the mass chromatogram combined with the mass spectrogram to eliminate or reduce the effect of coprostan.

Thirty samples (Table 2) were separately crushed in a rotary mill, and their aliquots were submitted to Rock-Eval pyrolysis for determination of total organic carbon (TOC) content, residual soluble hydrocarbon (S₁), pyrolysed hydrocarbon (S₂), production index (PI) (The production index (PI) is the ratio of already generated hydrocarbon to potential hydrocarbon), hydrogen index (I_H), temperature of maximum kerogen pyrolysate yield (T_{max}) and so on. Vitrinite reflectance (R_o) analyses were performed on randomly

oriented grains using conventional microphotometric methods. The instruments were calibrated with known standard.

The contents of inorganic elements were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (AAS) in the well drilling.

4 Results and discussion

4.1 Distribution of the molecular parameters from 2.8-3.57 km

At a depth of 2.8-3.57 km, the environment of the formation was a fresh to brackish depositional system. The distribution of the biomarkers maturity parameters $C_{29}20S/(20S+20R)$ and $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ reflects the process of the molecular parameters with thermal maturation.

Results indicate that in the depth range of 2.8-3.57 km, the relative contents of the C_{29} isomers, $C_{29}S\alpha\alpha$ and $C_{29}S\beta\beta$, increase with increasing thermal evolution. At around 3.57 km, these two isomers appear to reach equilibrium, and then exhibit a decrease trend. By contrast, the isomers $C_{29}R\alpha\alpha$,

$C_{29}R\beta\beta$ decrease in relative content with increasing thermal evolution before equilibrium, and their trends then change in the opposite direction (Fig. 2). The $C_{29}20S$ cholestane isomers thus in general follow the same evolution path. For the $C_{29}20R$ isomers, $C_{29}R\beta\beta$ shows smaller changes with increasing depth than $C_{29}R\alpha\alpha$. Before reaching thermal equilibrium, the relative contents of the total $\beta\beta$ ($S\beta\beta+R\beta\beta$) and total S-type ($S\alpha\alpha+S\beta\beta$) increase with thermal evolution, while the relative contents of the total $\alpha\alpha$ ($S\alpha\alpha+R\alpha\alpha$) and total R-type ($R\alpha\alpha+R\beta\beta$) decline with thermal evolution. After thermal equilibrium, all the isomers show the opposite evolutionary trends to their original profiles.

For Member 3 and Member 4, the biomarkers maturity parameters $C_{29}20S/(20S+20R)$ and $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ are consistent in terms of their overall distribution. Ratios increase with increasing burial depth in the interval 2.8-3.57 km before equilibrium; After thermal equilibrium, ratios then decline with further increase in burial depth (Fig. 3). The study result shows that the equilibrium value of $C_{29}20S/(20S+20R)$ ratio for Es_3 and Es_4 is 0.5 and 0.55 respectively, and the equilibrium value of $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ ratio for the two sequences is 0.7 and 0.6 respectively. This is mostly consistent with the results reported by Seifert and Moldowan

Fig. 2 Distribution of biomarker isomers related to C_{29} 24-ethyl sterane in Member 3 and Member 4 profile of the Shahejie Formation in the Dongying Sag. The relative contents of $S\alpha\alpha$, $S\beta\beta$, $R\alpha\alpha$ and $R\beta\beta$ is the percentage of total C_{29} 24-ethyl sterane

Fig. 3 Distribution of the parameters $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ and $C_{29}20S/(20S+20R)$ in profiles from Member 3 and Member 4 of the Shahejie Formation in the Dongying Sag

(1986). They proposed that isomerization at C-20 of 5α , $14a$, $17a(H)$ - C_{29} cholestanes causes $C_{29}20S/(20S+20R)$ to increase from 0 to around 0.5, and isomerization at C-14 and C-17 of $C_{29}20S$ and $20R$ regular cholestanes causes an increase in the $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ ratio from around zero to around 0.7, with increasing thermal maturity. They obtained equilibrium values of $C_{29}20S/(20S+20R)$ and $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ of 0.52-0.55 and 0.61-0.71, respectively.

The distribution and evolution process of the molecular parameters $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$, $C_{29}20S/(20S+20R)$ and relative isomers from 2.8 km to 3.57 km are controlled by thermal maturation. In this interval depth, with increasing thermal maturation, the relative content of $S\alpha\alpha$ and $S\beta\beta$ in C_{29} 24-ethyl cholestanes increases, the relative content of $R\alpha\alpha$ and $R\beta\beta$ decreases, and $R\alpha\alpha$ shows a stronger decline than $R\beta\beta$. This result shows that between hydrocarbon generation and thermal equilibrium, the transformation of $20R$ is faster than that of $20S$, including some transformation from $20R$ to $20S$ (mainly $C_{29}R\alpha\alpha$), and the transformation of the $\alpha\alpha$ structure is faster than that of the $\beta\beta$ structure. The rate of transformation follows the order: $C_{29}R\alpha\alpha > C_{29}R\beta\beta > C_{29}S\alpha\alpha > C_{29}S\beta\beta$. The relative rates of both generation and degradation of the two isomers may control the $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ and $C_{29}20S/(20S+20R)$ ratios, consistent with the result by Farrimond et al (1998). The point is that the evolution of the molecular parameters $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ and $C_{29}20S/(20S+20R)$ is mainly controlled by the different rate of their thermal degradation due to the difference in their thermal stability, and the different rate of thermal degradation results in the change of relative content of isomers. In this process, some transformations take place between isomers because of isomerization, but they are not the main controlling factor.

4.2 Reversal of maturity parameters at 3.57-4.0 km

Reversal of molecular parameters at high maturities has been known for some time. The $C_{29}20S/(20S+20R)$ and $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ ratios are the most commonly reported biomarker maturity parameters related to this reversal. Lewan et al (1986) found that the $C_{29}20S/(20S+20R)$ ratio increases with increasing temperatures up to 330 °C in hydro-pyrolysis experiments for samples of the Phosphoria Shale, and that the trend is then reversed after reaching a thermal equilibrium (at 0.55). In the hydrous pyrolysis experiments with immature Phosphoria Shale samples, which are rich in dolomite and phosphate, from the Santa Maria Basin, Peters et al (1990) found that after equilibrium (330 °C), the $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ and $C_{29}20S/(20S+20R)$ ratios shows a reversal trend, which is consistent with the experimental results of Lewan (1986). But in the experiments with samples rich in clay minerals (Peters et al, 1990), the values of $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ and $C_{29}20S/(20S+20R)$ ratios continue to increase without reversal occurring. This suggests that different mineral compositions are likely to be an important controlling factor for isomerization at low temperature; while at high temperature, differences in thermal stability between different isomers are the main controlling factor. In a pyrolysis of Jurassic black shales from the Cape Range 2 Well in the Carnarvon Basin, Strachan et al (1989) found that at 2,850 m, the $C_{29}20S/(20S+20R)$ ratio reaches an equilibrium value of 0.55, but there is then a reversal trend. This phenomenon was suggested to be associated with the different cracking rate, as the thermal stability of the $20S$ and $20R$ configuration is different. It may also be associated with high abundances of organic matter and low content of minerals, which contribute to the lag of cracking in the process. In the Pingluoba region of the Sichuan Basin, and

Chande region of the Songliao Basin in China, the R_o of the source rocks is $>1.65\%$, while the $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ and $C_{29}20S/(20S+20R)$ ratios show abnormal low values; these values suggests that they are resulted from the different cracking rates between different isomers (Chen, 1997).

Causes of the reversal in biomarkers ratios distribution are complex. But this study shows that minerals have a larger effect on the reversal than other factors. The reversal of the related biomarker parameters is accordance with a significant increase in the content of evaporitic rocks.

Regional geological data shows that at a shallower burial depth (<3.5 km), the main source rocks are calcareous shales and mudstone; at a deeper burial depth (>3.5 km), the content of evaporites (gypsum and halite) increases significantly, and the evaporites and mudstones formed into a single sedimentary system (i.e. co-sedimentary system), as shown in the Haoke-1 Well in Fig. 4. In the co-sedimentary system, the contents of elements such as calcium and sodium greatly increase, and the Sr/Ba, Sr/Ca and Fe/Mn ratios display significant high-value response (Fig. 4), indicating a typical

Fig. 4 Distribution of contents and ratios of mineral elements in the Paleogene system profile from Haoke-1 Well in the Dongying Sag
1. mudstone; 2. silty mudstone; 3. oil shale; 4. calcic mudstone; 5. argillaceous dolomite; 6. halite; 7. gypsum and halite

high-saline environment (Chen and zha, 2008). The deep Es_3 can also be affected by the high salinity in Es_4 through formation water migration along faults or other channels. Furthermore, the high response of gammacerane also shows a hypersaline depositional environment and the marked stratification in the saline water environment with a halocline (Peters and Moldowan, 1993; Sinninghe Damsté et al, 1995; Wang, 2002) (Fig. 5, Fig. 6). In Fig. 5 the long-chain homohopanes display the characteristics of C_{35} hopane $> C_{34}$ hopane $> C_{33}$ hopane, and this also reflects the characteristics of biomarkers in the depositional environment with high salinity (Seifert and Moldowan, 1979, 1981; Tissot and welte, 1984; zhu et al, 2004).

Among the 50 samples, 30 samples were tested by Rock-Eval pyrolysis and chromatograph. Three data from Feng-8 Well (3816.3 m, 3818 m, 3947 m) show higher Pr/n- C_{17} , Ph/n- C_{18} and lower Pr/Ph values compared to the other data (Table 2). The distributions of pristine/phytane (Pr/Ph) and gammacerane/ $C_{30}17\alpha$ -Hopane are well differentiated by the two class of samples, and the samples from the evaporated system in the Member 4 show the dominance of phytane

Fig. 5 Distribution of a typical response of gammacerane and the hopane series in the m/z191 of the evaporite system in the Dongying Sag

Fig. 6 High response of gammacerane and gammacerane/17 α -hopane in the deep hypersaline source rocks of Paleogene System in the Dongying Sag

(Pr/Ph<1.0) and high gammacerane response (gammacerane/ C_{30} Hopane>0.065) (Fig. 7). Such high gammacerane indices and low pristine/phytane of the samples from the evaporite system reflect increased water salinity during deposition. This result is in accordance with the understanding of ten Haven et al (1987) and Schwark et al (1998). ten Haven et al (1987)

Fig. 7 Distribution of Pr/Ph and $\gamma/C_{30}H$ of the source rocks from the evaporite system of Member 4 and non-evaporite system of Member 3 in Dongying depression. This data was from 32 samples that were analyzed with GC and GCMS

recommended that low Pr/Ph (<1) is typical of hypersaline environments, and the Pr/Ph ratio has a relationship with the salinity that halophilic bacteria depend on. Likewise, Schwark et al (1998) noted a general decrease in Pr/Ph during deposition of the Permian Kupferschiefer sequence in Germany, and they interpreted it as increasing paleosalinity. Although the validity of the Pr/Ph ratio is limited in accurately describing the paleoenvironments, which are also related to other factors, including variable source rock inputs, different rates of early generation, variations at higher maturity and analytical uncertainty (Peters and Moldowan, 1993), the relationship between Pr/Ph and gammacerane index reinforces the relationship of Pr/Ph and salinity.

The statistical analysis of 30 samples on the relationship between commonly-used maturity indicators, vitrinite reflectance (R_o), and the $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ and $C_{29}20S/(20S+20R)$ ratios show positive correlations between them. However, the three samples (3816.3 m, 3818 m, 3947 m of the Well Feng-8) from a hypersaline environment in Es_4 depart from the normal distribution trend, indicating that with increasing R_o , the $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ of the three samples increases very little and even decreases in $C_{29}20S/(20S+20R)$ (Fig. 8), which implied that the biomarker maturity parameters $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ and $C_{29}20S/(20S+20R)$ are more negatively affected by hypersaline environment than by R_o .

In the Es_4 hypersaline environment (>3.5 km), the relative contents of isomers $S\alpha\alpha$ and $S\beta\beta$ decrease, and the relative contents of isomers $R\alpha\alpha$ and $R\beta\beta$ increase with increasing burial depth. The relative contents of total $\beta\beta$ ($S\beta\beta+R\beta\beta$) and total S-type ($S\alpha\alpha+S\beta\beta$) decrease with thermal evolution, and

Table 2 The general geochemical properties of some samples

Well	Strata	Depth m	R_o	T_{max}	TOC	OEP	CPI	$C_{21}+C_{22}/$ $C_{28}+C_{29}$	$\Sigma C_{21}^- /$ ΣC_{22}^+	IH	Pr/ n-C ₁₇	Ph/ n-C ₁₈	Pr/Ph	R_{30}/H_{30}	$C_{29}\beta\beta /$ $(\beta\beta+\alpha\alpha)$	$C_{29}20S /$ $(20S+20R)$
FS-1	Es ₃	2870	0.49	436	1.21	1.55	1.69	1.34	0.94	382.4	0.9	1.27	0.96	0.070	0.27	0.14
Shi-121	Es ₃	3289.6	0.6	443	0.96	1.34	1.29	1.19	0.49	93.5	1.16	0.52	2.13	0.105	0.37	0.43
Shi-121	Es ₃	3318	0.6	439	0.76	1.27	1.37	2.21	1.01	173.5	0.49	0.39	1.25	0.046	0.40	0.42
Shi-121	Es ₃	3521.8	0.64	441	0.88	1.17	1.24	1.7	0.77	236.4	0.63	0.46	1.4	0.049	0.65	0.43
Shi-121	Es ₃	3561.9	0.66	443	2.76	1.09	1.13	2.44	0.89	272.9	0.29	0.21	1.24	0.050	0.62	0.47
Shi-121	Es ₃	3563	0.66	443	2.82	1.1	1.14	2.43	0.91	349.0	0.29	0.2	1.26	0.044	0.62	0.48
Shi-121	Es ₃	3563.5	0.66	442	1.29	1.17	1.21	2.56	0.96	215.8	0.48	0.36	1.32	0.041	0.69	0.43
Shi-121	Es ₃	3565.9	0.7	440	0.58	1.14	1.2	1.86	0.87	239.8	0.63	0.49	1.25	0.052	0.59	0.47
Shi-121	Es ₃	3568.5	0.72	444	1.32	1.13	1.2	1.66	0.84	440.9	0.59	0.38	1.51	0.037	0.64	0.43
Shi-121	Es ₃	3569.25	0.7	443	1.63	1.14	1.17	2.16	0.92	417.4	0.43	0.37	1.05	0.058	0.67	0.44
Shi-121	Es ₃	3572.8	0.68	442	1.59	1.14	1.19	2.14	0.97	305.4	0.44	0.3	1.46	0.048	0.68	0.42
Shi-121	Es ₃	3575.8	0.7	446	0.92	1.13	1.23	1.63	0.92	217.2	0.71	0.4	1.85	0.040	0.63	0.43
Shi-121	Es ₃	3577.2	0.72	442	1.71	1.15	1.2	1.95	0.92	288.6	0.49	0.35	1.32	0.047	0.63	0.46
Shi-121	Es ₃	3578.5	0.7	441	1.39	1.1	1.15	1.7	0.87	342.3	0.45	0.37	1.17	0.050	0.65	0.43
Shi-121	Es ₃	3580.8	0.68	446	2.17	1.07	1.11	1.66	0.87	302.5	0.32	0.27	1.2	0.052	0.66	0.41
Shi-121	Es ₃	3582.1	0.68	434	2.43	1.06	1.1	1.64	0.82	192.4	0.32	0.27	1.19	0.054	0.67	0.41
Shi-121	Es ₃	3582.7	0.7	443	2.13	1.06	1.09	1.77	0.87	275.4	0.31	0.26	1.2	0.053	0.66	0.43
Shi-121	Es ₃	3585	0.66	442	2.57	1.07	1.1	1.76	0.83	302.9	0.33	0.28	1.15	0.047	0.67	0.41
Shi-126	Es ₃	3521.9	0.62	446	1.87	1.12	1.2	2.44	1.47	301.8	0.46	0.4	1.28	0.039	0.61	0.37
Shi-126	Es ₃	3525.6	0.63	446	3.02	1.09	1.1	1.63	0.79	271.6	0.4	0.32	1.23	0.057	0.61	0.47
Feng-8	Es ₄	3050	0.57	439	1.87	1.15	1.25	1.52	1	385.9	0.59	0.72	0.95	0.065	0.28	0.26
Feng-8	Es ₄	3164	0.52	441	1.99	1.15	1.22	1.49	0.87	401.4	0.5	0.44	1.2	0.038	0.30	0.38
Feng-8	Es ₄	3166	0.58	446	2.17	1.23	1.32	2.32	1.04	543.2	0.5	0.45	1.21	0.044	0.32	0.39
Feng-8	Es ₄	3403	0.65	442	4.42	1.04	1.1	1.1	0.71	126.5	0.62	0.93	0.71	0.157	0.45	0.47
Feng-8	Es ₄	3816.3	0.86	427	1.23	1.02	1.05	2.29	1.12	397.2	0.93	1.75	0.54	1.300	0.61	0.43
Feng-8	Es ₄	3818	0.85	424	1.13	1	1.04	2.03	0.82	402.3	0.96	1.78	0.49	0.712	0.60	0.43
Feng-8	Es ₄	3947	0.92	419	0.49	1.09	1.09	1.62	1.35	302.7	1.16	1.46	0.68	0.105	0.62	0.41
FS-1	Es ₄	3440	0.56	443	1.66	1.1	1.17	1.45	0.73	53.9	0.52	0.77	0.71	0.190	0.50	0.46
FS-1	Es ₄	3685.6	0.66	446	2.29	1.03	1.05	1.68	1.15	405.5	0.35	0.35	1.07	0.173	0.49	0.47
FS-1	Es ₄	3686.3	0.7	449	1.99	1.01	1.05	1.41	0.9	377.0	0.33	0.34	1.03	0.180	0.50	0.45

the relative contents of total $\alpha\alpha$ ($S\alpha\alpha+R\alpha\alpha$) and total R-type ($R\alpha\alpha+R\beta\beta$) decrease. This indicates that the transformation of 20R and $\alpha\alpha$ structure was retarded or inhibited compared to that of 20S and $\beta\beta$ structure.

The negative reversal of C_{29} 24-ethyl cholestane isomers and the $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ and $C_{29}20S/(20S+20R)$ ratios in hypersaline environments reflects the negative effect of gypsum-halite on isomerization and thermal evolution of organic matter.

This negative effect of gypsum-halite on the biomarker maturity parameters is supported by the distributions of

maturity-related biomarker parameters Ts/Tm and $Ts/(Ts+Tm)$, which display negative reversal similar to $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ and $C_{29}20S/(20S+20R)$ (Fig. 9). The reversal of the $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ and $C_{29}20S/(20S+20R)$ ratios is associated with specific lithologies such as carbonates or evaporitic rocks other than the result of isomerisation, a process commonly interpreted as the controlling factor for the relative contents of biomarkers (and thus molecular maturity parameters). Also, such inhibition or retardation by carbonate minerals is found in some evaporite systems, and supported by some immature to low-matured oils discovered in high carbonate evaporite

Fig. 8 Relationship between $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$, $C_{29}20S/(20S+20R)$ and R_o for the 32 samples from the Paleogene system in the Dongying Sag. The three abnormal data are from the hypersaline source rocks from Member 4 (3816.3 m, 3818 m, 3947 m in the Feng-8 well)

Fig. 9 Distribution of the parameters Ts/Tm and $Ts/(Ts+Tm)$ in profile from the Member 4 of Shahejie Formation in the Paleogene system in the Dongying sag

system. The retarding effect is proposed to mainly due to the absence of catalysis of clay minerals (Tuo et al, 1994), for the calcites in the gypsum-halite play little or no role in the transformation of kerogen. The low content of clay and sometimes even deficiency in gypsum-halite rocks may result in the retardation of thermal evolution in evaporite systems. This is supported by thermal simulation experiments, which shows the effect of different substrates on the hydrocarbon generation process. Carbonate rocks play an anti-catalytic role in hydrocarbon generation from kerogen, more evident as the temperature increases (Zhao et al, 2005). Such negative effect of carbonate minerals even occurs in the formation of

diamonoids. Wei et al (2006) suggest that clay minerals have a significant catalysis effect on the formation of diamonoids, and may catalyze the diamonoid synthesis via carbonium ion mechanisms resulting from Lewis acid sites available on their surface; In contrast, $CaCO_3$ has an inhibitory effect on the generation of diamonoids, as well as on diamonoid maturity parameters such as MAI and MDI. This inhibitory effect may be related to the mode of organic matter present in carbonate minerals, since in evaporite systems, the organic matter is mainly present within cryptocrystalline or fine-grained carbonate minerals and may not be easily released as a result (Xie et al, 2000).

The thermal retardation in the evaporite system is not only reflected by biomarker parameters but also displayed in the distribution of conventional thermal indicators including vitrinite reflectance (R_o) and pyrolysis peak temperature (T_{max}) (Fig. 10), which shows a similar negative reversal in evaporite rocks. But some differences are also apparent. For the R_o and T_{max} data, distinct negative anomalies begin to appear at the depth of around 2400 m, which corresponds to the overpressure of this area. Around 3400 m, R_o and T_{max} values show a stronger negative departure in their distribution. Such results indicate that two types of inhibition or retardation act on R_o and T_{max} . The overpressure in the Dongying Sag is distributed in mudstones of the middle and lower parts of E_{s3} and gypsum-salt layer of E_{s4} (Chen and Zha, 2008). The negative departure of R_o and T_{max} in the overpressured interval (high overpressure, the pressure coefficient reaches 1.8) from 2,400 m to 3,400 m suggests the inhibition of thermal evolution in response to overpressure. The stronger decline of R_o and T_{max} in the hypersaline interval from 3,400 m to 4,000 m indicates similar retardation due to the presence of carbonate minerals, as with the related biomarker maturity ratios.

Fig. 10 Distribution of R_o and T_{max} in profile in the Paleogene system of the Dongying Sag

5 Conclusions

1) Progressive changes in molecular maturity ratios are associated with major thermal evolutions of the biomarkers concerned. Increase in the ratios $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ and $C_{29}20S/(20S+20R)$ result from differences in the relative rates of generation and thermal degradation of these isomers. Transformation of the 20R isomers occurs more rapidly than 20S isomer, including some transformation from 20R to 20S. $\alpha\alpha$ type C_{29} 24-ethyl cholestanes degrade more rapidly than $\beta\beta$ type C_{29} 24-ethyl cholestanes.

2) Below 3.5 km of the Paleogene system in Dongying

sag in which evaporitic rocks deposited was a hyper-saline environment generally. In this environment high responses of Sr/Ba, Sr/Ca, Fe/Mn, Pr/n- C_{17} , Ph/n- C_{18} , gammacerane and low response of Pr/Ph were observed.

3) The reversal of the molecular maturity ratios $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$, $C_{29}20S/(20S+20R)$, Ts/(Ts+Tm) demonstrated the negative effects of gypsum-halite on isomerization of biomarkers isomers and organic matter thermal evolution.

Acknowledgements

This study was supported by the National Natural Science Foundation of China (40802026) and “the Fundamental Research Funds for the Central Universities”. We acknowledge collaboration with and enthusiastic support from Shenli Oilfield (CPCC), and the assistance from Christopher Tiratsoo in having revised the paper with the English language presentation. We also thank the helpful reviewers and editor Yang Lei who gave valuable amendments for the manuscript.

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(Edited by Zhu Xiuqin)