

Carbon isotopic compositions of 1,2,3,4-tetramethylbenzene in marine oil asphaltenes from the Tarim Basin: Evidence for the source formed in a strongly reducing environment

JIA WangLu^{1†}, PENG PingAn¹ & XIAO ZhongYao²¹ State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China;² Tarim Oilfield Company, PetroChina, Korla 841000, China

Although 1-alkyl-2,3,6-trimethylbenzenes and a high relative amount of 1,2,3,4-tetramethylbenzene have been detected in marine oils and oil asphaltenes from Tabei uplift in the Tarim Basin, their biological sources are not determined. This paper deals with the molecular characteristics of typical marine oil asphaltenes from Tabei and Tazhong uplift in the Tarim Basin and the stable carbon isotopic signatures of individual compounds in the pyrolysates of these asphaltenes using flash pyrolysis-gas chromatograph-mass spectrometer (PY-GC-MS) and gas chromatograph-stable isotope ratio mass spectrometer (GC-C-IRMS), respectively. Relatively abundant 1,2,3,4-tetramethylbenzene is detected in the pyrolysates of these marine oil asphaltenes from the Tarim Basin. $\delta^{13}\text{C}$ values of 1,2,3,4-tetramethylbenzene in the pyrolysates of oil asphaltenes vary from -19.6‰ to -24.0‰ , while those of *n*-alkanes in the pyrolysates show a range from -33.2‰ to -35.1‰ . The 1,2,3,4-tetramethylbenzene in the pyrolysates of oil asphaltenes proves to be significantly enriched in ^{13}C relative to *n*-alkanes in the pyrolysates and oil asphaltenes by 10.8‰ – 15.2‰ and 8.4‰ – 13.4‰ , respectively. This result indicates a contribution from photosynthetic green sulfur bacteria *Chlorobiaceae* to relatively abundant 1,2,3,4-tetramethylbenzene in marine oil asphaltenes from the Tarim Basin. Hence, it can be speculated that the source of most marine oil asphaltenes from the Tarim Basin was formed in a strongly reducing water body enriched in H_2S under euxinic conditions.

1,2,3,4-tetramethylbenzene, asphaltenes, marine oils, the Tarim Basin, carbon isotopic composition

Although exploitation and production of marine oils in the Tarim Basin has continued for more than twenty years, the source rocks for the main industrial petroleum are still in debate, even though a theory has been proposed that they may be resulted from growth of numerous petroleum source rocks, multiple stages of hydrocarbon generation and tectogenesis in this old basin [1]. Results from detailed molecular geochemical study suggest the Middle-Upper Ordovician marls deposited at the slope of the margin are the source of marine oils in the Tarim Basin [2]. However, 1,2,3,4-tetramethylben-

zene and 1-alkyl-2,3,6-trimethylbenzenes were detected in the pyrolysates of oil asphaltenes and oils from Tabei uplift of the Tarim Basin^{1,2}, [3,4], while these compounds

Received May 22, 2007; accepted November 28, 2007

doi: 10.1007/s11430-008-0030-7

†Corresponding author (email: wljia@gig.ac.cn)

Supported by the National Natural Science Foundation of China (Grant No. 40403005)

1) Peng P A, Lu X X. Diversity of sources, reservoir formation periods and crudes in Lunnan area. Study Report on the Project on "Formation and Distribution As Well As Enrichment Rules for Oil and Gas in Superimposed Basins in China". Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. 2002

2) Wang T G, Wang C J, Zhang W B, et al. Geochemical study on formation of the Ordovician oil/gas reservoirs in Tahe oil field. Study Report of National Tenth Five Key Science and Technology Research Program. Sinopec Xinjing Northwest China Branch, 2003

are usually considered to be derived from green sulfur bacteria Chlorobiaceae living in the strong reducing water body enriched in H₂S. So a strongly reducing water body was suggested as the sedimentary environment for marine oil source rocks in the Tarim Basin. Based on this conclusion and results from studies of hydrocarbon generation and source rocks, several suites of source rocks deposited in strongly reducing environment were suggested to be the source of marine oils from the Tarim Basin, including the Middle-Upper Ordovician mudstones of the Shaergan Formation^[5,6], the Lower-Middle Ordovician mudstones of the Heituo Formation^[6,7] and Cambrian-Lower Ordovician marls^[4,7]. However, detection of 1,2,3,4-tetramethylbenzene in the pyrolysates of oil asphaltenes and 1-alkyl-2,3,6-trimethylbenzenes in the oils from Tabei uplift could not sufficiently determine a contribution from green sulfur bacteria Chlorobiaceae, because 1,2,3,4-tetramethylbenzene and 1-alkyl-2,3,6-trimethylbenzenes could be derived from other bacteria or algae^[8–10]. As several studies show, the stable carbon isotopic signatures of 1,2,3,4-tetramethylbenzene and 1-alkyl-2,3,6-trimethylbenzenes were critical to determining their biological sources^[8,9]. The reverse tricarboxylic acid cycle by which green sulfur bacteria Chlorobiaceae fix carbon would lead to unusually high contents of ¹³C in the biosynthetic products^[11]. Hence, 1,2,3,4-tetramethylbenzene and 1-alkyl-2,3,6-trimethylbenzenes derived from Chlorobiaceae would have much heavier carbon isotopic compositions than those compounds from other biological sources (by about 10‰–15‰^[12]). Only one oil asphaltene sample of the Well Lunnan1 from Tabei uplift in the Tarim Basin was presented with carbon isotopic data up to date^[13], and the carbon isotopic characteristics of oils or oil asphaltenes from most wells in Tazhong uplift and Tabei uplift, which are the main oil fields in the Tarim Basin, were not reported yet.

The pyrolysates of oil asphaltenes from several typical oil wells in both Tabei and Tazhong uplift of the Tarim Basin were investigated in this paper, and the carbon isotopic signatures of the pyrolysates were also determined. Relatively abundant 1,2,3,4-tetramethylbenzene was generally detected in the pyrolysates of most marine oil asphaltenes from the Tarim Basin, and 1,2,3,4-tetramethylbenzene are characterized by significantly high enrichment of ¹³C relative to oil asphaltenes and *n*-alkanes in the pyrolysates of oil asphaltenes. The

results support a contribution from green sulfur bacteria Chlorobiaceae to relatively high amount of 1,2,3,4-tetramethylbenzene detected in the pyrolysates of most marine oil asphaltenes from the Tarim Basin, and a strongly reducing water body under euxinic conditions for formation of the source rocks for oil asphaltenes.

1 Samples and experiments

1.1 Samples

Oil asphaltenes were selected to be investigated for the following reasons: first, oil asphaltenes were produced in the early maturation stage of organic matter and have a structure more similar to that of kerogen than other components in the oils^[14]; secondly, compared with other components in the oils, oil asphaltenes are hardly affected by biodegradation and water washing^[15]; thirdly, the changes in physical phase during oil mixing, such as precipitation of asphaltenes, have little effect on the molecular structure of oil asphaltenes^[16]; and finally, molecular structures of oil asphaltenes show little variations during oil transfer^[17]. However, the above factors may have significant effects on the low molecular biomarkers and may be the main cause that can account for the debate on the oil/source correlations in the Tarim Basin^[1]. Moreover, determination of carbon isotopic characteristics of those long chain 1-alkyl-2,3,6-trimethylbenzenes cannot be easily carried out due to the low relative abundances of the compounds in the oils, and interferences from the background of samples and co-elution. The oil asphaltenes in the Tarim Basin usually show relatively high amount of 1,2,3,4-tetramethylbenzene^[13], and thus determination of carbon isotopic characteristics of 1,2,3,4-tetramethylbenzene would be easily performed.

1.2 Experiments

Oil samples were collected from Tabei and Tazhong uplift where most marine oils were produced (Table 1). The extraction and purification, determination of carbon isotopic compositions and on-line pyrolysis of oil asphaltenes were carried out using the reported methods^[13].

About 50 mg asphaltenes was loaded into a gold tube. The tube was sealed under protection of argon and subject to pyrolysis in an oven at 320 °C (±1 °C) for 72 h. After cooling, the gold tube was opened and the pyrolysates were ultrasonically extracted with hexane. The concentrated extracts were separated into saturates and

Table 1 Sample list of marine oils from the Tarim Basin

Well	Horizon	Depth (m)	Location	$\delta^{13}\text{C}$ (‰)		
				<i>n</i> -alkanes ^{a)}	asphaltenes	1,2,3,4-tetramethylbenzene
TZ401	C	3244–3247	Tazhong	–34.8	–33.8	–22.0
TZ402	C	3705–3708	Tazhong	–35.1	–33.5	–20.9
TZ2	C	3870–3883	Tazhong	–34.9	–33.3	–19.9
TZ40	C	4317–4324	Tazhong	–33.6	–32.7	–20.5
TZ4	C	3610–3669	Tazhong	–33.3	–33.8	–22.4
TZ16	C	3812–3819	Tazhong	–34.8	–32.4	–24.0
TZ16	O	4128–4260	Tazhong	–33.2	–33.5	–22.3
TZ10	C	4227–4234	Tazhong	–34.2	–32.5	–20.3
HD11	C	5125	Tabei	–34.7	–33.1	–20.1
DH4	C	6068–6085	Tabei	–34.6	–33.1	–19.6
YM2	O	5940–5953	Tabei	–35.1	–33.7	–19.9
YW2	O	5460–5463	Tabei	–34.1	–32.2	–20.2
LN2-22	T		Tabei	–34.3	–33.0	–20.5
LN58	T		Tabei	–34.6	–31.7	–20.1

a) average $\delta^{13}\text{C}$ values of *n*-alkanes.

aromatics by column chromatography, and the saturates were further purified by urea adduction to get *n*-alkanes. The stable carbon isotopic signatures of the saturates and aromatics from the pyrolysates of oil asphaltenes were determined by an Isoprime isotope ratio mass spectrometer (GV Instruments, UK) to which an Agilent 6890 gas chromatograph was coupled. A typical *m/z*44 ion currents chromatograph of *n*-alkanes and aromatics in the isotopic analysis is shown in Figure 1. A careful inspection of the *m/z*(45/44) chromatograph of the aromatics demonstrates that the isotopic measurements of 1,2,3,4-tetramethylbenzene were not disturbed by other compounds (e.g., methyl-indane).

A national reference material (black carbon, $\delta^{13}\text{C}$ =–36.91‰) and a mixing standard of *n*-alkanes (derived from Indiana University) were measured to monitor the precision of the total carbon isotopic analysis and the carbon isotopic analysis of individual compounds, respectively. The precision was better than $\pm 0.2\%$ and $\pm 0.4\%$ for the total carbon isotopic analysis and for the carbon isotopic analysis of individual compounds, respectively. Every sample was analyzed twice, and the deviation of two runs was usually no more than 0.3‰ for the total carbon isotopic analysis and 0.6‰ for the carbon isotopic analysis of individual compounds. The average value of two runs was accepted as the isotopic result of a given sample.

2 Results and discussion

The pyrolysates of asphaltenes in marine oils from the Tarim Basin display similar characteristics, indicating

that the molecular structures of these oil asphaltenes are similar (Figure 2). The most abundant compounds identified from the pyrolysates of oil asphaltenes are *n*-alkanes/1-*n*-alkenes doublets, which suggest significant contributions from non-saponifiable, highly aliphatic biopolymers in algae^[18]. Relatively abundant 1,2,3,4-tetramethylbenzene is generally detected in the pyrolysates of oil asphaltenes, and the relative intensities of 1,2,3,4-tetramethylbenzene are the highest besides those of *n*-alkanes/1-*n*-alkenes and C₁-C₂ benzenes in the pyrolysates.

Relatively abundant 1,2,3,4-tetramethylbenzene detected in the pyrolysates of some geological macromolecules, such as kerogens and asphaltenes, was produced by cracking of aromatic carotenoids bonded to the structures of macromolecules, which might indicate contributions from photosynthetic green sulfur bacteria Chlorobiaceae^[19]. However, several studies have shown that detection of relatively abundant 1,2,3,4-tetramethylbenzene in macromolecules alone is not sufficient to infer a contribution from green sulfur bacteria Chlorobiaceae^[8–10], because 1,2,3,4-tetramethylbenzene and 1-alkyl-2,3,6-trimethylbenzenes may be derived partly from algae^[8]. Moreover, the pigments of other photosynthetic bacteria (e.g., purple sulfur bacteria)^[10] and the aromatization products of β -carotene in algae^[9] could give 1,2,3,4-tetramethylbenzene upon pyrolysis, too. Stable carbon isotopic characteristics of 1,2,3,4-tetramethylbenzene are the key to determining if it was resulted from green sulfur bacteria Chlorobiaceae^[8,9]. Different from other bacteria and algae, green sulfur

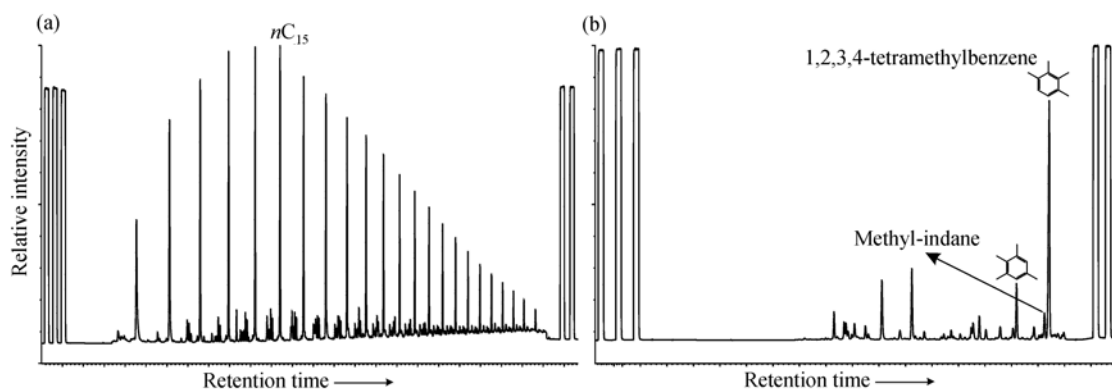


Figure 1 $m/z44$ ion current chromatograph for carbon isotopic analysis of the pyrolysates of oil asphaltenes. (a) n -alkanes; (b) aromatics.

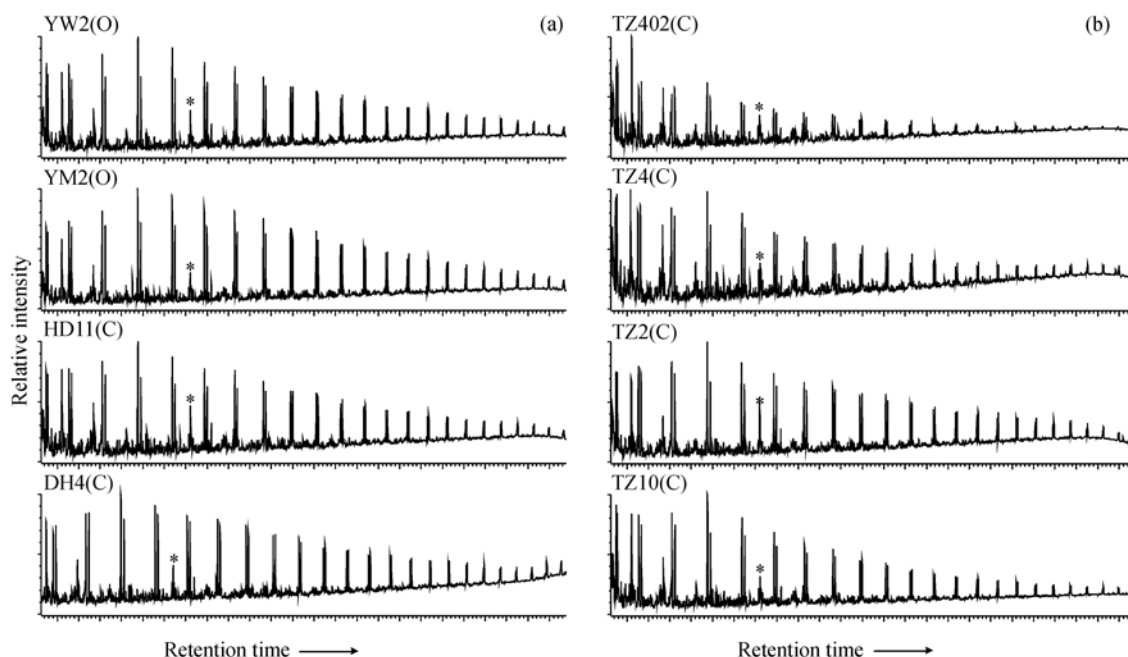


Figure 2 Total ion currents chromatograph for the products by flash pyrolysis of marine oil asphaltenes from the Tarim Basin. (a) Tabei uplift; (b) Tazhong uplift. * stands for 1,2,3,4-tetramethylbenzene.

bacteria Chlorobiaceae carries out the photosynthesis through a reverse tricarboxylic acid cycle, which can lead to unusual enrichment of ^{13}C in the biosynthetic products of Chlorobiaceae. Hence, the 1,2,3,4-tetramethylbenzene and 1-alkyl-2,3,6-trimethylbenzenes derived from Chlorobiaceae should be enriched in ^{13}C significantly relative to those compounds from algae or other bacteria in such macromolecules as kerogen and asphaltenes.

The $\delta^{13}\text{C}$ values of 1,2,3,4-tetramethylbenzene in the pyrolysates of oil asphaltenes from Tabei uplift vary from -19.6‰ to -20.5‰ , while the average $\delta^{13}\text{C}$ values of n -alkanes and $\delta^{13}\text{C}$ values of oil asphaltenes range

from -34.1‰ to -35.1‰ and from -31.7‰ to -33.7‰ , respectively. Thus 1,2,3,4-tetramethylbenzene is more enriched in ^{13}C than n -alkanes and oil asphaltenes by $13.8\text{‰} - 15.2\text{‰}$ and $11.6\text{‰} - 13.8\text{‰}$, respectively (Table 1, Figure 3). Similar to the case of oil asphaltenes from Tabei uplift, 1,2,3,4-tetramethylbenzene in the pyrolysates of oil asphaltenes from Tazhong uplift is also enriched in ^{13}C significantly relative to n -alkanes and oil asphaltenes. The average $\delta^{13}\text{C}$ values of n -alkanes and $\delta^{13}\text{C}$ values of oil asphaltenes from Tazhong uplift range from -33.2‰ to -35.1‰ and from -32.4‰ to -33.8‰ , respectively, and the $\delta^{13}\text{C}$ values of 1,2,3,4-tetramethylbenzene in the pyrolysates have a range from

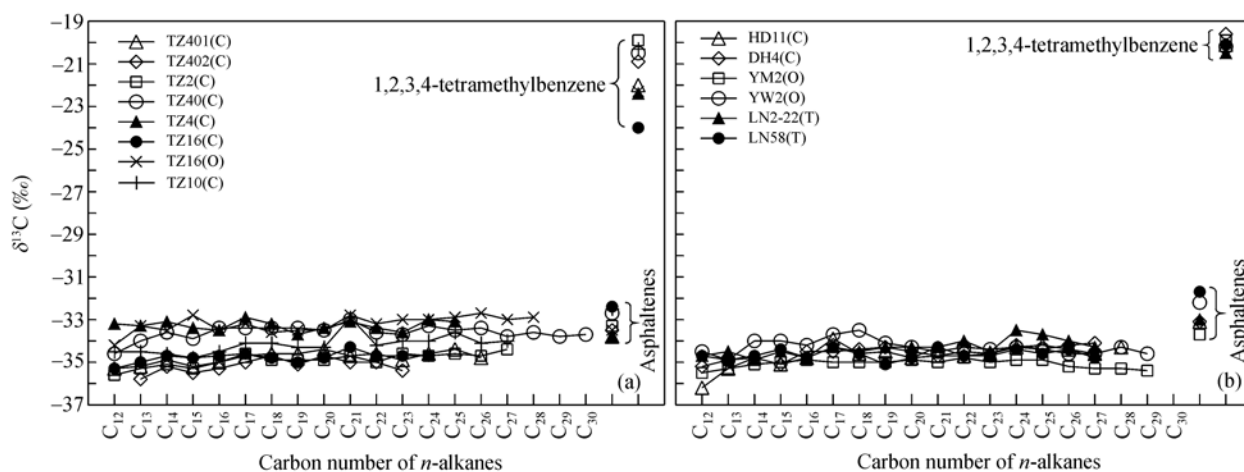


Figure 3 Stable carbon isotopic compositions of the pyrolysates of marine oil asphaltenes from the Tarim Basin. (a) Tazhong uplift; (b) Tabei uplift.

−19.9‰ to −24.0‰. 1,2,3,4-tetramethylbenzene is more enriched in ^{13}C than n -alkanes and oil asphaltenes from Tazhong uplift by 10.8‰–15.0‰ and 8.4‰–13.4‰, respectively (Table 1, Figure 3). Based on literature data, those 1,2,3,4-tetramethylbenzene and 1-alkyl-2,3,6-trimethylbenzenes derived from Chlorobiaceae should be more enriched in ^{13}C by 12‰–16‰ relative to those compounds from algae or other bacteria [10,20–22]. Hence, relatively abundant 1,2,3,4-tetramethylbenzene detected in most oil asphaltenes from the Tarim Basin indicates contribution from aromatic carotenoids of green sulfur bacteria Chlorobiaceae.

The 1,2,3,4-tetramethylbenzene in some asphaltene samples from Tazhong uplift ($\delta^{13}\text{C}$ values range from −22.0‰ to −24.0‰), e.g., well TZ4, well TZ16, exhibits relatively lighter carbon isotopic compositions when compared with that in most samples from the Tarim Basin ($\delta^{13}\text{C}$ values range from −19.6‰ to −20.5‰), and the differences in $\delta^{13}\text{C}$ values between 1,2,3,4-tetramethylbenzene and n -alkanes in asphaltenes from well TZ4 and TZ16 are also relatively small when compared with those for most other samples. This phenomenon may suggest a slight mixing of some oils from Tazhong uplift.

3 Conclusions

Results of pyrolysis of oil asphaltenes from the Tarim Basin in closed system suggest that carbon isotopic signatures of individual compounds in the pyrolysates of asphaltenes could be used to perform oil/oil correlations and to study mixing of oils.

The pyrolysates of oil asphaltenes from Tabei and Tazhong uplifts in the Tarim Basin display similar characteristics, and relatively abundant 1,2,3,4-tetramethylbenzene is detected in the pyrolysates. The carbon isotopic characteristics of 1,2,3,4-tetramethylbenzene in oil asphaltenes support a contribution from green sulfur bacteria Chlorobiaceae, which suggests that the source for most oil asphaltenes from the Tarim Basin should be formed in a strongly reducing water body under euxinic conditions.

Based on results from the studies on source rocks, it can be inferred that the sedimentary environment for the Lower-Middle Cambrian marls, the Middle-Upper Ordovician and Lower-Middle Ordovician mudstone may be consistent with that for marine oil asphaltenes in Tarim Basin. Further work, e.g., studies of hydrocarbon generation history, should be considered in eventual determination of the main source rocks for marine oils from the Tarim Basin.

- 1 Wang Z M, Xiao Z Y. A comprehensive review concerning the problem of marine crudes sources in the Tarim Basin. *Chin Sci Bull*, 2004, 49(Suppl 1): 1–9
- 2 Zhang S C, Hanson A D, Moldowan J M, et al. Paleozoic oil-source rock correlations in the the Tarim Basin, NW China. *Org Geochem*, 2000, 31(4): 273–286 [DOI]
- 3 Sun Y, Xu S, Lu H, et al. Source facies of the Paleozoic petroleum systems in the Tabei uplift, the Tarim Basin, NW China. *Org Geochem*, 2003,34(4): 629–634 [DOI]
- 4 Shi H X, Xu Z M, Lin F, et al. Oil source analysis and exploration prospect of Lunnan Field in the Tarim Basin. *Xinjiang Petrol Geol* (in Chinese), 2005, 26(6): 623–626

- 5 Jin Z J. New progresses in research of China's typical superimposed basins and reservoiring of hydrocarbons (Part II). *Oil Gas Geol* (in Chinese), 2006, 27(3): 281–294
- 6 Zhao Z J, Jia C Z, Zhou X Y, et al. Key factors of oil-gas reservoir-forming and exploration targets in Ordovician in Tazhong area, the Tarim Basin. *China Petrol Explor* (in Chinese), 2006, 11(4): 6–16
- 7 Zhao Z J, Zhou X Y, Zheng X P, et al. Evidences of chief source rock in the Tarim Basin. *Acta Petrol Sin* (in Chinese), 2005, 26(3): 10–15
- 8 Hoefs M J L, van Heemst J D H, Gelin F, et al. Alternative biological sources for 1,2,3,4-tetramethylbenzene in flash pyrolyzate of kerogen. *Org Geochem*, 1995, 23(10): 975–979[DOI]
- 9 Koopmans M P, Schouten S, Kohnen M E L. Restricted utility of aryl isoprenoids as indicators for photic zone anoxia. *Geochim Cosmochim Acta*, 1996, 60(23): 4873–4876[DOI]
- 10 Pedentchouk N, Freeman K H, Harris N B, et al. Sources of alkylbenzenes in Lower Cretaceous lacustrine source rocks, West African rift basins. *Org Geochem*, 2004, 35(1): 33–45[DOI]
- 11 Quandt L, Gottschalk G, Ziegler H, et al. Isotope discrimination by photosynthetic bacteria. *FEMS Microbiol Lett*, 1977, 1(3): 125–128[DOI]
- 12 Sinninghe Dasmté J S, Köster J. A euxinic southern North Atlantic Ocean during the Cenomanian/Turonian oceanic anoxic event. *Earth Planet Sci Lett*, 1998, 158(3-4): 165–173[DOI]
- 13 Jia W L. Molecular structure and its application study of oil asphaltenes from Lunnan area, Tarim basin. Dissertation for the Doctoral Degree (in Chinese). Guangzhou: Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 2004. 10–21
- 14 Behar F, Pelet R, Roucache J. Geochemistry of asphaltenes. *Org Geochem*, 1984, 6: 587–595[DOI]
- 15 Rubinstein I, Spyckerelle C, Strausz O P. Pyrolysis of asphaltenes: A source of geochemical information. *Geochim Cosmochim Acta*, 1979, 43(1): 1–6[DOI]
- 16 Jia W L, Peng P A. Asphaltene structure in reservoir affected by discharge of secondary condensate oil: Laboratory simulation. *Petrol Explor Develop* (in Chinese), 2003, 30(6): 112–116
- 17 Nali M, Caccialanza G, Ghiselli C, et al. Tmax of asphaltenes: a parameter for oil maturity assessment. *Org Geochem*, 2000, 31(12): 1325–1332[DOI]
- 18 del Rio J C, Martin F, Gonzalez-Vila F J, et al. Chemical structure investigation of asphaltenes and kerogens by pyrolysis-methylation. *Org Geochem*, 1995, 23(11-12): 1009–1022[DOI]
- 19 Hartgers W A, Sinninghe Damste J S, De Leeuw J W. Geochemical significance of alkylbenzene distribution in flash pyrolysates of kerogens, coals, and asphaltenes. *Geochim Cosmochim Acta*, 1994, 58(7): 1759–1775[DOI]
- 20 Grice K, Schaeffer P, Schwark L, et al. Molecular indicators of palaeoenvironmental conditions in an immature Permian shale (Kupferschiefer, Lower Rhine Basin, north-west Germany) from free and S-bound lipids. *Org Geochem*, 1996, 25(3-4): 131–147[DOI]
- 21 Grice K, Schaeffe P, Schwark L, et al. Changes in palaeoenvironmental conditions during deposition of the Permian Kupferschiefer (Low Rhine Basin, northwest Germany) inferred from molecular and isotopic compositions of biomarker components. *Org Geochem*, 1997, 26(11-12): 677–690[DOI]
- 22 Hartgers W A, Sinninghe Damsté J S, Requejo A G, et al. Evidence for only minor contributions from bacteria to sedimentary organic carbon. *Nature*, 1994, 369(6477): 224–226[DOI]