



Original Paper

Identification and geochemical significance of unusual C₂₄ tetracyclic terpanes in Shahejie Formation source rocks in the Bozhong subbasin, Bohai Bay Basin



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ARTICLE INFO

Article history:

Received 7 August 2021

Accepted 25 February 2022

Available online 2 April 2022

Edited by Jie Hao

Keywords:

Unusual tetracyclic terpanes

10β(H)-des-A-oleanane

10β(H)-des-A-lupane

Geochemical significance

Shahejie Formation

Bozhong subbasin

ABSTRACT

C₂₄ tetracyclic terpanes are common compounds in source rocks and crude oils, and C₂₄ 17,21-secohopane is the most common and widely used source-related indicator. In this study, three unusual C₂₄ tetracyclic terpanes were detected on the *m/z* 191 chromatogram of saturated hydrocarbons in the Shahejie Formation source rocks in the Bozhong subbasin. Based on the mass spectra characteristics, diagnostic ion fragments, retention time and comparisons with published literature, three unusual C₂₄ tetracyclic terpanes were identified as 10β(H)-des-A-oleanane, 10β(H)-des-A-lupane and C₂₄ des-A-hopane. To the best of our knowledge, this is the first study to detect and publicly report these three compounds in source rock samples from the Shahejie Formation of the Bozhong subbasin, Bohai Bay Basin. The results indicated that 10β(H)-des-A-oleanane and 10β(H)-des-A-lupane likely originated from terrestrial angiosperms, while C₂₄ des-A-hopane likely originated from prokaryotic organisms. Terrestrial angiosperms provide the material basis for the generation of compounds A and B, and the distribution and concentration of these two compounds are affected by thermal maturity. In the low maturity stage (0.5% < *R*_o < 0.7%), compounds A and B are relatively enriched in the source rocks.

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1. Introduction

C₂₄ tetracyclic terpanes are widely found in sediments and crude oils (Peters et al., 2005; Bao et al., 2018). The formation of C₂₄ tetracyclic terpanes in sediments occurs mainly in two ways: one is related to the cleavage of the C-17 and C-21 bonds on the E-rings of hopanes or hopanoids caused by microbial activity or thermal effects (Ekweozor et al., 1981; Connan et al., 1986), and the other is related to the decyclization of the E-rings or A-rings of terrestrial triterpenes mediated by microorganisms (Woolhouse et al., 1992; Samuel et al., 2010; Bao et al., 2018). The tetracyclic terpane formed by the former mechanism is also known as 17,21-secohopane (Trendel et al., 1982; Lu et al., 2009). Most of these compounds occur as single C₂₄ 17,21-secohopane compounds (Hu, 1991; Zhang

et al., 2003) or as a C₂₄–C₂₇ 17,21-secohopane homolog series in sediments and crude oils (Aquino et al., 1983; Woolhouse et al., 1992). In addition, the C₂₈–C₃₀ 17,21-secohopane homolog series was also detected in evaporitic sediments in the Bohai Bay Basin (Lu et al., 2009). In general, C₂₄ 17,21-secohopane is the most typical compound in these series and is especially enriched in carbonate and evaporative sedimentary environments (Palacas et al., 1984; Lu et al., 2009; Chattopadhyay and Dutta, 2014). However, C₂₄ 17,21-secohopane is also widely found in source rocks deposited in various sedimentary environments, such as marine/lacustrine shale/mudstone and terrestrial coal seam environments (Ekweozor et al., 1981; Woolhouse et al., 1992; Kruge et al., 1996; Bao et al., 1999; Samuel et al., 2010). This kind of C₂₄ tetracyclic terpanes (C₂₄ 17,21-secohopane) has been widely used in oil-source correlations (Woolhouse et al., 1992; Peters et al., 2005; Samuel et al., 2010), and C₂₄ 17,21-secohopane (C₂₄TeT)/hopane, C₂₄TeT/C₂₃ tricyclic terpane (TT) and C₂₄TeT/C₂₆TT ratios are common source-related indicators (Peters et al., 2005).

With the in-depth study of tetracyclic terpanes, some novel C₂₄

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tetracyclic terpanes have been detected and identified in crude oils in addition to C₂₄ 17,21-secohopane. These C₂₄ tetracyclic terpanes are believed to be formed by the decyclization of the E-ring or A-ring of terrestrial triterpenes mediated by microorganisms (Woolhouse et al., 1992; Samuel et al., 2010; Bao et al., 2018). These A/E-ring degraded tetracyclic terpanes usually contain des-A-oleanane, des-A-lupane, des-A-ursane, and des-E-lupane (Woolhouse et al., 1992; Chattopadhyay and Dutta, 2014). Woolhouse et al. (1992) first detected a series of ring-degraded C₂₄ tetracyclic terpanes in crude oils and tentatively identified them as 10β(H)-des-A-oleanane, 10β(H)-des-A-lupane, and 10β(H)-des-A-ursane. Subsequently, 10β(H)-des-A-oleanane was also detected in organic-rich Holocene sediment extracts (Bechtel et al., 2007), Tertiary crude oils from the Niger Delta (Samuel et al., 2010) and Eocene coal-bearing sediments from India (Chattopadhyay and Dutta, 2014). These novel C₂₄ tetracyclic terpanes have also been detected in some domestic crude oil and source rock extracts since 2014, although all of these sources were from the Pearl River Mouth Basin (Ma et al., 2014; Zhu et al., 2015; Bao et al., 2018). To date, few reports have focused on these novel tetracyclic terpane compounds in the source rocks of other sedimentary basins in China.

In this study, four C₂₄ tetracyclic terpanes, including three unusual C₂₄ tetracyclic terpanes, were detected in the Shahejie Formation source rocks in the Bozhong subbasin, Bohai Bay Basin. These unusual C₂₄ tetracyclic terpanes have not been previously reported in the study area. In this study, we systematically analyzed the distribution patterns of these three unusual C₂₄ tetracyclic terpanes in source rocks to investigate possible factors affecting the unusual C₂₄ tetracyclic terpanes generated and concentrated in source rocks and their potential geochemical significance. The results are expected to help geochemists better understand the geochemical significance of these unusual C₂₄ tetracyclic terpanes.

2. Geological setting

The Bohai Bay Basin is a Meso-Cenozoic extensional rift basin located in northeastern China (Yang and Xu, 2004; Xu et al., 2019) that experienced two major tectonic movements during the Cenozoic (Gong et al., 2007) and formed seven subbasins: Jiyang, Linqing, Jizhong, Huanghua, Liaohe, Liaodong Bay and Bozhong (Fig. 1a). The Bozhong subbasin is one of the important petroleum-producing areas and favorable exploration areas in the Bohai Bay Basin (Yin et al., 2020). In recent years, an increasing number of oil and gas resources have been discovered in the Bozhong subbasin. A 100 billion cubic meter gas field (BZ19–6) was successfully discovered in the Bozhong subbasin in 2019 (Xu et al., 2019). More recently, another large-scale oil and gas (BZ13–2) field was discovered in the Bozhong subbasin, which has proven geological reserves of 100 million tons of oil and gas equivalent (Shi et al., 2021).

The Bozhong subbasin contains two main sags and several uplifts in the southwest, namely, the Bozhong sag, Huanghekou sag, Shaleitian uplift, Shijiutuo uplift, Bonan lower uplift and Bodong lower uplift (Fig. 1b). A succession of fluvial-lacustrine sediments, including the Kongdian, Shahejie and Dongying formations, was deposited during the Paleogene in the Bozhong and Huanghekou sags (Fig. 1c). Among them, the Shahejie Formation can be divided into four members from top to bottom: E₂S₁, E₂S₂, E₂S₃ and E₂S₄. E₂S₁ and E₂S₃ are mainly composed of mudstones and silty mudstones, which are important source rocks in the Bozhong subbasin (Hao et al., 2011). Previous studies indicated that terrestrial higher plants, phytoplankton and algae were the main biological sources of E₂S₁ and E₂S₃ (Hao et al., 2011; Yin et al., 2020), and E₂S₁ and E₂S₃ were deposited in highly saline and fresh lacustrine environments, respectively (Hao et al., 2011; Jiang et al., 2019).

3. Samples and methods

A total of 25 mudstone/shale core samples were collected from the Bozhong and Huanghekou sags, with nineteen samples taken from E₂S₃ at depths from ~3356 m to ~3684 m and the remaining six samples taken from E₂S₁ at depths from 3034 m to 3297.5 m (Table 1).

All samples were washed using deionized water and then crushed to < 100 mesh after drying. The powder samples were extracted using Soxhlet extraction for 48 h with dichloromethane. Isolated extracts were fractionated by column chromatography after the asphaltene was precipitated by adding excessive petroleum ether. The remaining saturated, aromatic and resin fractions were separated by a column filled with active silica gel and alumina with appropriate elution solvents. The elution solvents were *n*-hexane, dichloromethane:petroleum ether (2:1) and dichloromethane:methyl alcohol (93:7).

Gas chromatography-mass spectrometry (GC-MS) analyses of the saturated hydrocarbons were conducted on an Agilent-6890N gas chromatograph coupled with an Agilent-5975 mass spectrometer. The Agilent-6890N gas chromatograph was equipped with an HP-5MS fused silica capillary column (30 m × 0.25 mm × 0.25 μm), and the carrier gas was helium. The initial temperature of the GC oven for saturated analysis was 50 °C (held for 1 min); then, the temperature was increased to 120 °C at a rate of 20 °C per minute and finally increased to 310 °C at a rate of 20 °C per minute and held for 25 min.

4. Results and discussion

4.1. Basic geological information of the studied samples

Before discussing the main factors controlling the abundance of these three unusual compounds in geological samples, it is necessary to investigate the basic geological information of the studied E₂S₁ and E₂S₃ source rock samples, such as the thermal maturity, sedimentary environment and organic matter sources.

The maximum pyrolysis temperatures (T_{max}) of the E₂S₁ and E₂S₃ samples vary from 436 °C to 447 °C and 429 °C to 447 °C, respectively (Table 1), suggesting a low maturity to maturity stage. The sterane isomer ratios C₂₉ααα-20S/(20S+20R) and C₂₉αββ/(αββ+ααα), which represent the degree of biological configuration transformation to geological configuration, are widely used to evaluate the thermal maturity of source rocks (Seifert and Moldowan, 1986; Peters et al., 2005). The C₂₉ααα-20S/(20S+20R) and C₂₉αββ/(αββ+ααα) ratios of E₂S₁ are in the range of 0.29–0.45 (mean of 0.41) and 0.30–0.35 (mean of 0.32) (Table 1), respectively, suggesting a low maturity stage. The C₂₉ααα-20S/(20S+20R) and C₂₉αββ/(αββ+ααα) values of E₂S₃ are higher than those of the E₂S₁ samples, indicating a low maturity-maturity stage (Seifert and Moldowan, 1986; Peters et al., 2005).

The ratio of pristane to phytane (Pr/Ph) is often used to evaluate redox conditions in bottom water (Didyk et al., 1978). Generally, anoxic conditions are conducive to the formation of Ph, while oxic conditions promote the formation of Pr, resulting in a lower Pr/Ph ratio under anoxic conditions (Didyk et al., 1978; Shanmugam, 1985). The E₂S₁ source rock samples exhibit relatively lower Pr/Ph values (0.84–1.4) than those of the E₂S₃ source rock samples (1.13–2.12), suggesting that E₂S₁ was deposited under more anoxic conditions than E₂S₃ (Table 1). The high abundance of gammacerane in source rock samples is usually associated with high salinity water conditions (Moldowan et al., 1985; Summons et al., 2008). Except for the two samples, most of the gammacerane indices (gammacerane/C₃₀ hopane) of the E₂S₃ source rock samples are in the range of 0.03–0.07 (Table 1), indicating freshwater conditions.

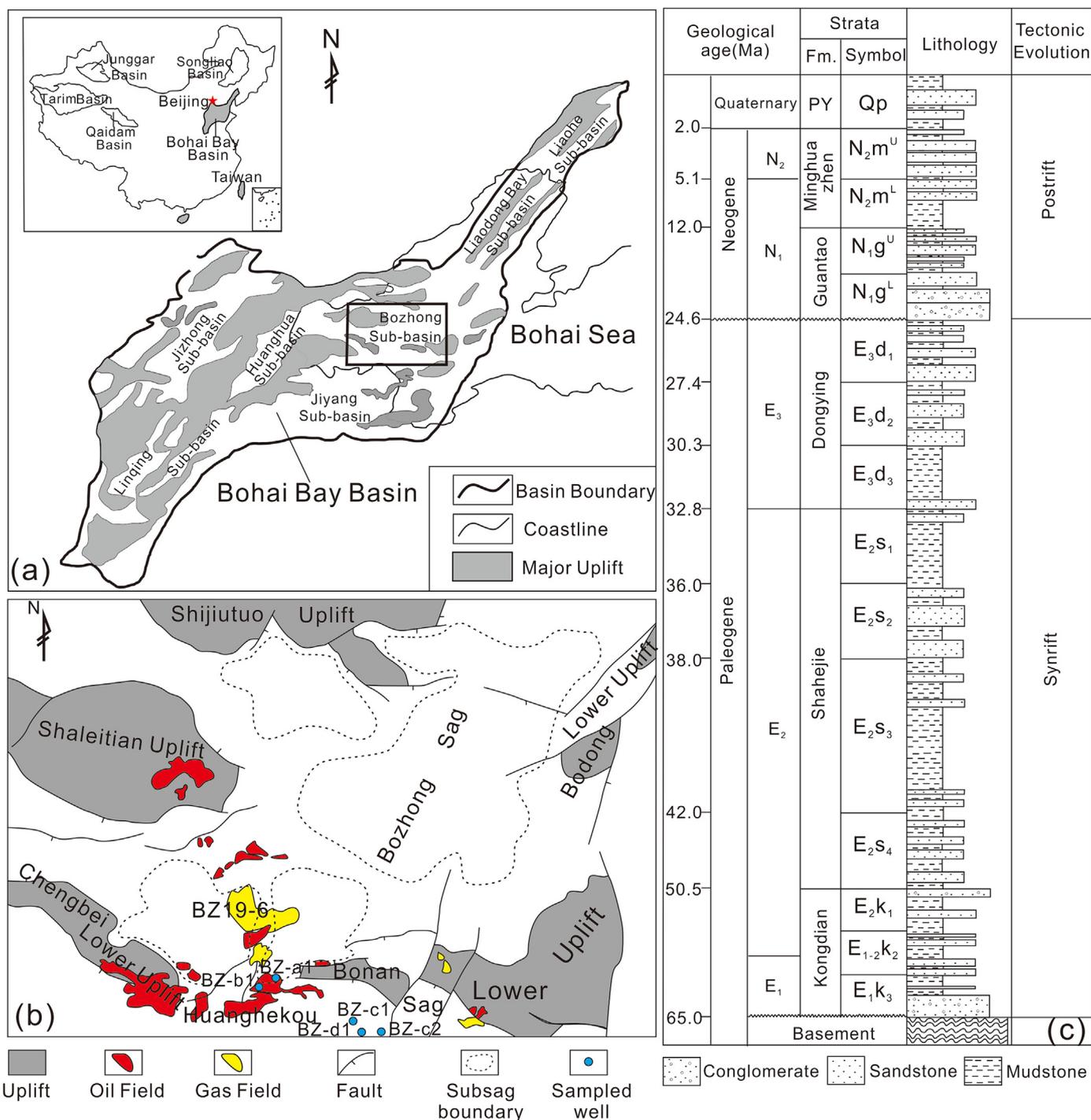


Fig. 1. (a) The location of the Bohai Bay Basin and its sub-basin classification (according to Liu et al., 2016); (b) Simplified structural map showing the tectonic units and sampling well in the Bozhong sub-basin (modified after Yin et al., 2020); (c) Generalized stratigraphic column of the Paleogene-Quaternary in the Bohai Bay Basin (modified after Liu et al., 2016).

The E₂s₁ source rock samples have wide ranges of gammacerane index values, suggesting a great variation in water salinity.

The relative abundances of C₂₇–C₂₉ regular steranes are effective indices to reflect the origin of organic matter, especially the contribution of eukaryotes (Gaskell and Eglinton, 1973; Peters, 2005). A previous study proposed that C₂₇ regular steranes in sediments are related to the contribution of phytoplankton or algae while C₂₉ regular steranes mainly originate from terrestrial higher plants (Volkman et al., 2005). The average proportion of C₂₇ regular

steranes among the C₂₇–C₂₉ regular steranes is ~38% in the E₂s₃ source rock samples, which is slightly lower than that of the C₂₉ regular steranes (Table 1), suggesting the mixed input of phytoplankton, algae and terrestrial higher plants to E₂s₃ organic matter. In addition, 4-methylsteranes are also detected in the E₂s₃ source rock samples, which are believed to have originated from dinoflagellates in the Bohai Bay Basin (Zhang et al., 2005; Hao et al., 2011). However, the E₂s₁ samples contain a high abundance of C₂₉ regular steranes compared to C₂₇ and C₂₈ regular steranes

Table 1
The relevant biomarker parameters of the studied E₂S₁ and E₂S₃ samples in the study area.

No.	Well	Depth, m	Stratum	T _{max} , °C	Ga/C ₃₀ H	C ₂₇ %	C ₂₈ %	C ₂₉ %	I	II	III	IV	C ₃₀ H/C ₂₃ TT	A/C ₂₃ TT	B/C ₂₃ TT	C/C ₂₃ TT	A%	B%	C%
1	BZ-a1	3356	E ₂ S ₃	439	0.43	44.8	18.4	36.8	1.37	0.23	0.31	0.41	17.5	0.12	0.00	0.06	65.4	0.0	34.6
2	BZ-a1	3357	E ₂ S ₃	434	0.42	45.6	16.7	37.8	1.41	0.27	0.32	0.42	16.4	0.08	0.00	0.04	63.4	3.8	32.8
3	BZ-a1	3359.2	E ₂ S ₃	437	0.05	38.6	20.2	41.2	1.24	0.12	0.51	0.42	67.2	0.75	0.05	0.50	57.9	3.8	38.4
4	BZ-a1	3412.6	E ₂ S ₃	434	0.05	37.5	17.0	45.4	1.42	0.14	0.37	0.48	58.3	0.38	0.03	0.07	78.7	6.2	15.1
5	BZ-a1	3414.2	E ₂ S ₃	435	0.04	36.0	19.7	44.2	1.61	0.18	0.42	0.47	61.6	0.50	0.02	0.12	77.7	3.6	18.7
6	BZ-a1	3416.4	E ₂ S ₃	431	0.05	36.6	21.3	42.2	1.63	0.24	0.42	0.50	78.7	0.98	0.04	0.13	85.0	3.7	11.3
7	BZ-a1	3419.9	E ₂ S ₃	436	0.05	36.0	18.8	45.3	1.55	0.24	0.43	0.47	63.3	0.83	0.03	0.07	88.7	3.6	7.6
8	BZ-a1	3422.7	E ₂ S ₃	/	0.05	35.9	15.5	48.5	1.59	0.21	0.44	0.45	59.1	0.72	0.03	0.10	84.6	3.6	11.8
9	BZ-a1	3423.9	E ₂ S ₃	436	0.05	36.7	18.1	45.2	1.66	0.24	0.44	0.47	44.6	0.87	0.03	0.09	88.3	2.9	8.8
10	BZ-a1	3426.4	E ₂ S ₃	436	0.05	34.4	22.6	43.0	1.13	0.30	0.45	0.52	52.1	1.36	0.04	0.05	93.9	2.5	3.6
11	BZ-a1	3665.2	E ₂ S ₃	447	0.05	45.3	22.0	32.7	1.79	0.63	0.53	0.54	14.3	0.84	0.00	0.04	95.2	0.0	4.8
12	BZ-b1	3543.8	E ₂ S ₃	435	0.06	37.1	21.3	41.6	1.14	0.09	0.41	0.43	29.4	0.42	0.00	0.34	55.7	0.0	44.3
13	BZ-b1	3545.7	E ₂ S ₃	439	0.07	38.8	20.9	40.4	1.17	0.10	0.45	0.41	49.5	0.44	0.05	0.29	56.8	6.6	36.6
14	BZ-b1	3657.4	E ₂ S ₃	429	0.07	39.6	22.4	38.0	1.28	0.17	0.42	0.49	16.7	0.23	0.00	0.07	75.6	0.0	24.4
15	BZ-b1	3658.8	E ₂ S ₃	440	0.07	37.5	25.8	36.8	1.66	0.17	0.38	0.50	25.0	0.24	0.00	0.09	73.4	0.0	26.6
16	BZ-b1	3660.6	E ₂ S ₃	441	0.05	38.0	24.0	38.0	1.44	0.17	0.43	0.48	23.2	0.27	0.00	0.09	75.3	0.0	24.7
17	BZ-b1	3677.5	E ₂ S ₃	437	0.03	33.5	27.3	39.1	1.69	0.31	0.40	0.53	65.0	0.27	0.00	0.09	75.7	0.0	24.3
18	BZ-b1	3683.5	E ₂ S ₃	443	0.05	35.6	25.0	39.5	2.12	0.19	0.42	0.49	27.9	0.90	0.00	0.11	88.8	0.0	11.2
19	BZ-b1	3684.5	E ₂ S ₃	442	0.03	38.1	24.0	38.0	1.66	0.18	0.43	0.52	26.2	0.37	0.00	0.09	80.5	0.0	19.5
20	BZ-c1	3276.65	E ₂ S ₁	441	0.42	26.4	19.3	54.3	1.70	0.80	0.47	0.33	22.1	6.20	0.70	0.22	87.1	9.8	3.1
21	BZ-c2	3276	E ₂ S ₁	447	0.75	37.6	22.0	40.5	0.85	0.54	0.41	0.35	28.3	2.95	0.45	0.05	85.7	12.9	1.4
22	BZ-c2	3281.4	E ₂ S ₁	441	0.10	28.4	17.5	54.1	0.84	0.71	0.45	0.31	9.6	0.29	0.03	0.10	70.1	6.6	23.3
23	BZ-c2	3287	E ₂ S ₁	445	0.06	36.1	19.7	44.2	1.40	0.18	0.38	0.33	90.4	2.48	0.18	0.82	71.3	5.1	23.6
24	BZ-c2	3297.5	E ₂ S ₁	444	0.06	19.8	16.3	63.9	1.33	0.83	0.46	0.30	23.8	5.12	0.33	0.24	90.1	5.8	4.1
25	BZ-d1	3035	E ₂ S ₁	436	0.36	54.3	18.6	27.1	1.30	0.33	0.29	0.32	6.3	0.21	0.03	0.04	76.0	10.8	13.2

Note: Ga = gammacerane; C₃₀H = C₃₀-hopane; C₂₇% = C₂₇ regular steranes/(C₂₇+C₂₈+C₂₉) regular steranes; I = pristane/phytane; II = oleanane/(oleanane+C₂₉ hopane); III = C₂₉ααα-20S/(20S+20R); IV = C₂₉αββ/(αββ+ααα).

(Table 1), indicating a significant input of terrestrial higher plants. The dominant contribution of higher plants to E₂S₁ samples is also confirmed by the relatively high content of oleanane (Table 1). The relatively high abundance of hopane series biomarkers in both the E₂S₁ and E₂S₃ samples suggests a large amount of prokaryotic organism input. In summary, the organic matter in the E₂S₁ and E₂S₃ samples was derived from a variety of organisms, including primary producers, such as algae/phytoplankton, terrestrial higher plants and prokaryotic organisms, e.g., bacteria. However, the contribution ratios of different kinds of organisms to E₂S₁ and E₂S₃ organic matter are different. The E₂S₁ source rocks are dominated by terrigenous higher plant inputs, while the E₂S₃ source rocks are characterized by typical mixed organic matter sources.

4.2. Occurrence and identification of unusual C₂₄ tetracyclic terpanes

Three uncommon compounds in geological samples were detected on the *m/z* 191 chromatogram of saturated hydrocarbons from the studied samples, which are termed A, B and C (Fig. 2). In addition, C₂₄ 17,21-secohopane (C₂₄TeT), which is widely present in sedimentary organic matter, can also be clearly identified in all E₂S₃ and E₂S₁ samples. Compounds A, B and C elute midway between tricyclic terpanes C₂₄ and C₂₅ in the order of increasing elution time (Fig. 2). The relative contents of compound A, which ranges from ~57% to ~95%, is dominant among the three C₂₄ tetracyclic terpanes (Table 1). In some E₂S₁ source rock samples, the relative abundance of compound A is even higher than that of C₁₉–C₂₉TT (Fig. 2). Compound B is present in relatively lower abundance in the *m/z* 191 chromatogram, and its concentration is even below the detection level in some E₂S₃ source rock samples. However, the relative abundance of compound C varies greatly in different samples. In some studied samples, its relative content is as high as 44% among the three compounds, while in other source rock samples, its content is lower than 2% (Table 1).

The molecular structures of compounds A, B and C were further determined by analysis of ion fragments and retention time and

comparison with published literature, which is a common method of determining the molecular structure of unknown compounds (Li et al., 2015). The representative mass spectra of the three C₂₄ tetracyclic terpanes after subtracting the background mass spectra are shown in Fig. 3.

For compound A, the base peak and molecular ion peak occur at *m/z* 191 and 330, respectively, and relatively high contents of ion fragments occur at *m/z* 109, 177 and 206 (Fig. 3a), indicating that this is a C₂₄ tetracyclic terpane with a molecular formula of C₂₄H₄₂. Furthermore, the mass spectra of compound A in this study are almost identical to the published mass spectra of 10β(H)-des-A-oleanane (Woolhouse et al., 1992; Samuel et al., 2010; Bao et al., 2018). The retention time of compound A is also identical to that of 10β(H)-des-A-oleanane reported in previous studies (Woolhouse et al., 1992; Samuel et al., 2010; Bao et al., 2018). Thus, compound A is classified as 10β(H)-des-A-oleanane based on the analysis of the retention time and mass spectra. The mass spectra of compound B present a relatively high content of the characteristic ion fragment at *m/z* 287, which is obviously different from that of compound A (Fig. 3b). The presence of this fragment is usually associated with the cleavage of an isopropyl from the terminal five-membered ring (Woolhouse et al., 1992). In addition, the base peak and molecular ion peak are at *m/z* 123 and 330, respectively. All of these mass spectral characteristics of compound B are similar to those of 10β(H)-des-A-lupane reported in previous literature (Trendel et al., 1989; Woolhouse et al., 1992; Bao et al., 2018), indicating that compound B can be identified as 10β(H)-des-A-lupane. This finding is also supported by the identical elution order and relative retention time of compound B and 10β(H)-des-A-lupane (Bao et al., 2018). Compound C also has an ion fragment at *m/z* 287 and a molecular ion at *m/z* 330, indicating that this is a C₂₄ tetracyclic terpane with an isopropyl substituent group in its molecular structure. However, the different base peak ion fragments and retention times indicate that the molecular structure of compound C is different from that of compound B. The identical mass spectrum to compound C has been reported by Zhu et al. (2015), although the molecular structure is still unknown. Subsequently, Bao et al. (2018)

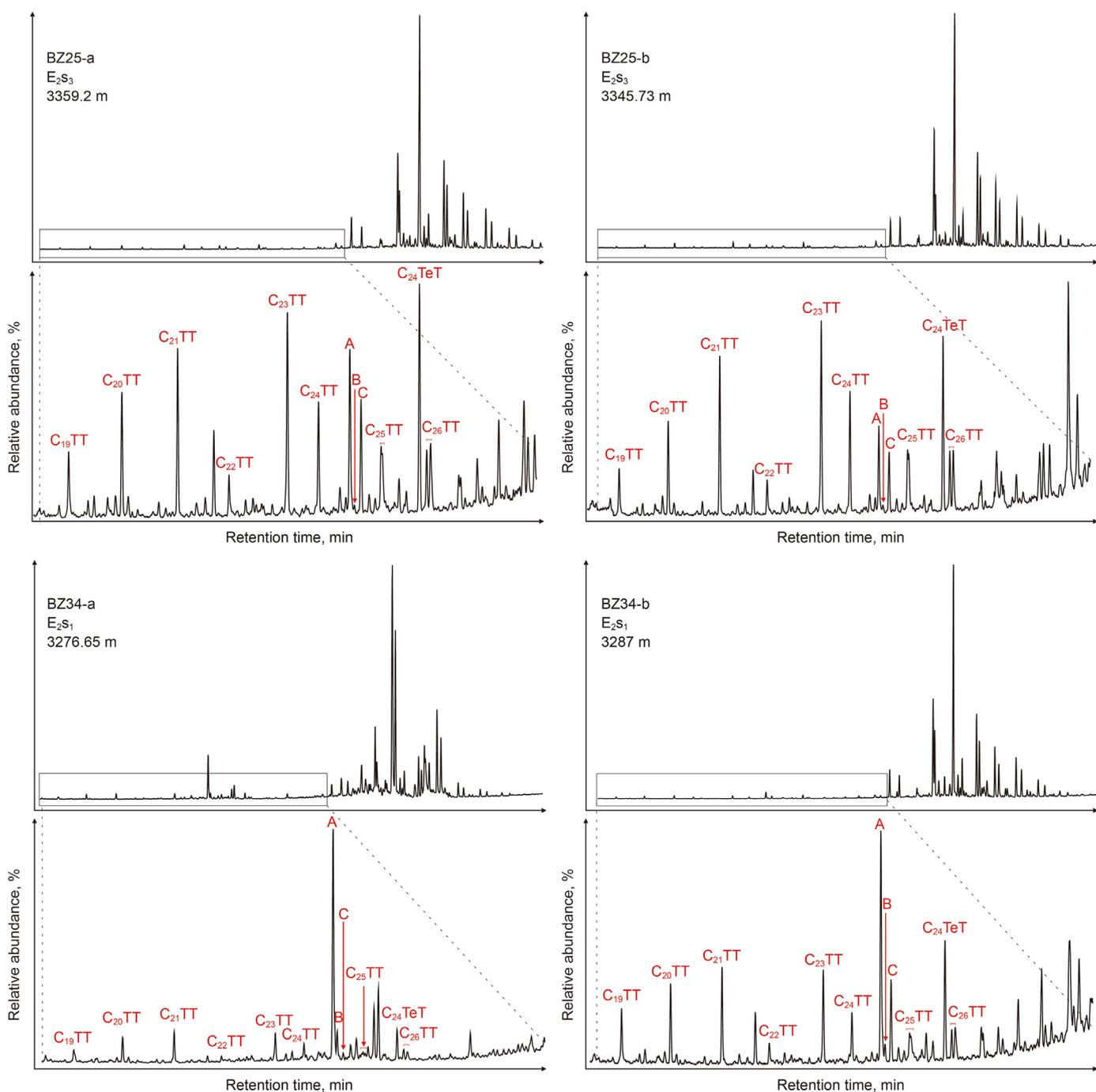


Fig. 2. Representative m/z 191 chromatograms of saturated hydrocarbons showing the distribution of novel tetracyclic terpenes from the E_{2S1} and E_{2S3} in the Bozhong sub-basin. TT = tricyclic terpene; TeT = tetracyclic terpene.

detected tetracyclic terpene C_{24} in crude oils from the Pearl River Mouth Basin, and its mass spectrum was identical to that of compound C in this study and the unknown structural compound discovered by Zhu et al. (2015). Based on the diagnostic ion fragment at m/z 287 and 191, Bao et al. (2018) identified this compound as C_{24} des-A-hopane. In this study, the research results of Bao et al. (2018) are accepted; thus, compound C is tentatively identified as C_{24} des-A-hopane. In summary, compounds A, B and C are classified as 10β (H)-des-A-oleanane, 10β (H)-des-A-lupane and C_{24} des-A-hopane based on diagnostic ion fragments and the retention time.

4.3. Origin of the unusual C_{24} tetracyclic terpenes

The above analyses show that compounds A and B are 10β (H)-des-A-oleanane and 10β (H)-des-A-lupane, respectively, indicating that they are degraded products of oleanane and lupane. In addition, higher A/ C_{23} TT and B/ C_{23} TT ratios are generally observed in the E_{2S1} source rocks, where terrigenous higher plants are important biological sources, while relatively lower A/ C_{23} TT and B/ C_{23} TT ratios are observed in the E_{2S3} source rocks, where mixed organic matter is an important source (Table 1). Based on the above analyses, we propose that the precursors of compounds A and B may be

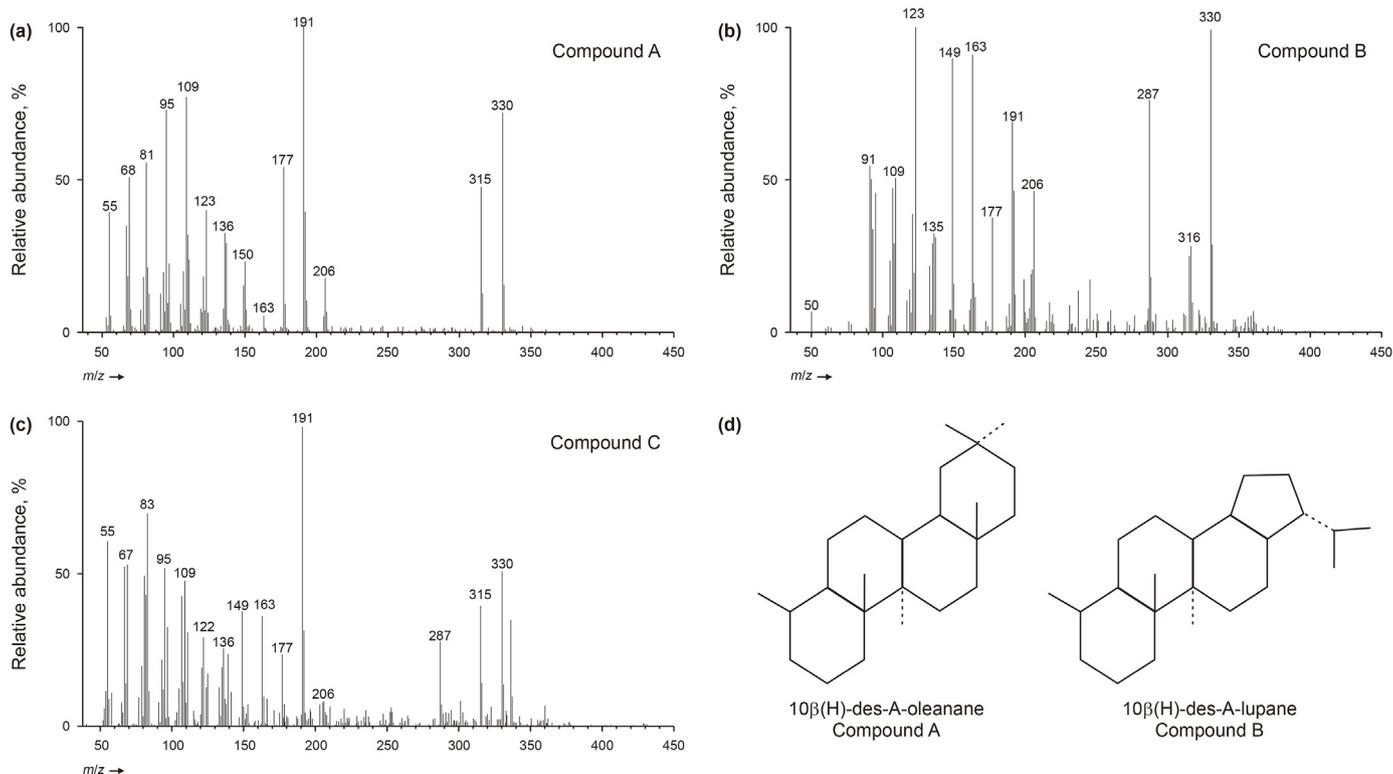


Fig. 3. Representative mass spectra of compounds A, B and C, and molecular structures of compounds A and B.

the same as those of oleanane and lupane. Previous studies have suggested that oleanane and lupane originate from angiosperms; thus, they are widely used as source indicators of terrigenous angiosperms (Ekweozor and Telnae, 1990; Peters et al., 2005). The possibility that compounds A and B may originate from terrestrial angiosperms is therefore proposed in this study.

A biosynthetic pathway for the formation of compounds A and B further supports that these two unusual tetracyclic terpanes originate from terrestrial angiosperms (Fig. 4). β-amyrin and betulin are two natural constituents of terrigenous angiosperms that can be oxidized to corresponding ketones (β-amyrone and lupanone) under certain conditions (reaction processes of 1, 5, and 6 in Fig. 4; Corbet et al., 1980; Samuel et al., 2010). Under anoxic conditions with the participation of microorganisms, the A-ring of these ketones are

degraded and form corresponding 3,4-seco-triterpenoid acids (reaction processes of 2 and 7 in Fig. 4; Trendel et al., 1989; Huang et al., 2008). This reaction process can also occur through photochemical alteration reactions under nonreducing conditions (Simoneit et al., 2009). The reaction of A ring degradation and 3,4-seco-triterpenoid acid formation may have occurred before deposition in the precursor plant material or during the deposition stage because 3,4-seco-triterpenoid acids have been detected in immature sediments and some higher plants (Devon and Scott, 1975; Schmitter et al., 1981; Huang et al., 1996). With increasing burial depth, 3,4-seco-olean-12-en-3-oic acid and 3,4-seco-lup-3-oic acid can further decarboxylate and finally form 10β(H)-des-A-oleanane and 10β(H)-des-A-lupane (reaction processes of 3, 4, and 8 in Fig. 4; Samuel et al., 2010). The intermediate products of this process have

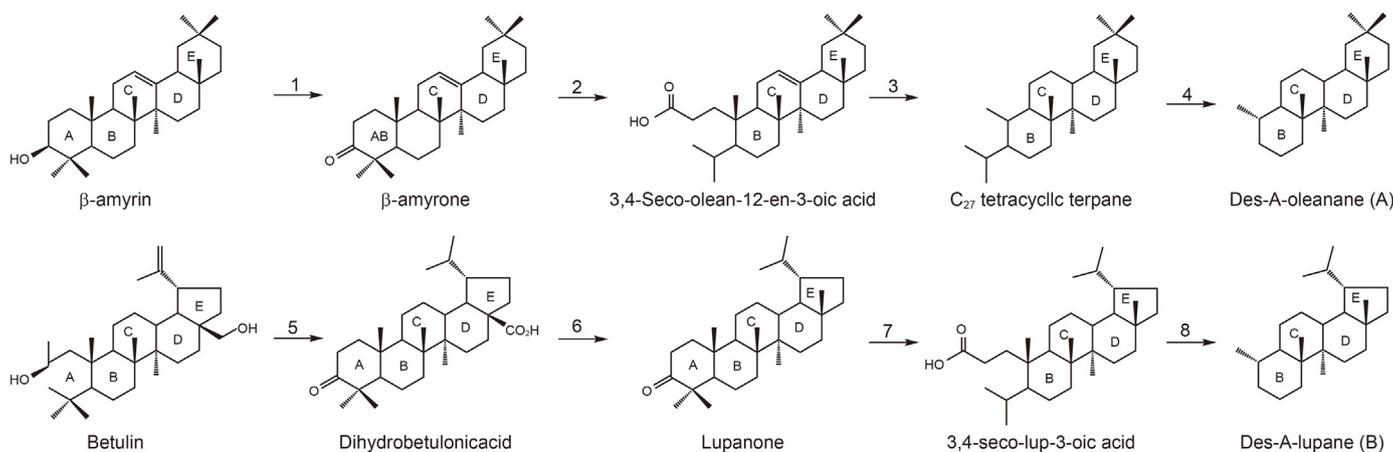


Fig. 4. Proposed formation pathway of compounds A and B (modified after Corbet et al., 1980; Trendel et al., 1989; Huang et al., 2008; Samuel et al., 2010).

been detected in sediments and crude oils, which further suggests that this biosynthetic pathway may occur under geological conditions (Schmitter et al., 1981; Huang et al., 1996). Based on the above analysis, compounds A and B can be generated by the transformation of related ketones and alcohols in higher angiosperms. The proposed formation pathways of compounds A and B are shown in Fig. 4.

Compound C (C_{24} des-A-hopane) has no obvious correlation with compounds A and B, indicating that they may have different biological sources. However, the relative content of compound C (calculated as C/C_{23} TT) in the studied samples exhibited a positive relationship with the relative abundance of hopane (calculated as C_{30} hopane/ C_{23} TT) (Fig. 5d). In addition, Bao et al. (2018) proposed that compound C formed under certain sedimentary and diagenetic conditions by the degradation of the A-ring of hopane or its precursors, such as diploptene and diplopterol. Considering that hopane series compounds originate from prokaryotic organisms (Ourisson et al., 1979; Peters et al., 2005; Zhao et al., 2021), a similar origin of compound C is inferred in this study.

4.4. Possible factors affecting the unusual C_{24} tetracyclic terpanes generated and concentrated in source rocks

The relative contents of these three tetracyclic terpanes vary greatly in different E_{2S1} and E_{2S3} source rock samples. Generally, the concentration of a certain compound in sediments is related to three factors: biological origin, sedimentary environment and thermal maturity. A positive relationship between the relative content of compound A and oleanane has been observed in previous crude oil studies (Samuel et al., 2010; Zhu et al., 2015; Bao et al.,

2018). Based on this, researchers propose that the input of higher plants is significantly correlated with the content of compound A in samples (Samuel et al., 2010; Zhu et al., 2015; Bao et al., 2018). In this study, the values of A/C_{23} TT in the E_{2S1} and E_{2S3} source rocks range from 0.08 to 1.36 and 0.29 to 6.2, respectively, indicating that the relative content of compound A in the E_{2S1} samples is higher than that in the E_{2S3} source rocks. This is consistent with the higher input of terrigenous higher plants in the E_{2S1} source rocks. However, the A/C_{23} TT, B/C_{23} TT and C/C_{23} TT ratios have no significant correlation with the oleanane contents in most of the E_{2S1} and E_{2S3} samples (Fig. 5a–c), suggesting that there are other factors affecting the contents of compounds A and B in addition to terrigenous higher plant input. However, the positive correlation between C/C_{23} TT and $C_{30}H/C_{23}$ TT ratios indicates that the concentration of compound C may be related to $C_{30}H$.

A previous study suggested that an oxidized depositional environment may be more conducive to the formation and preservation of compounds A, B and C (Samuel et al., 2010; Zhu et al., 2015; Bao et al., 2018). However, the results of this study do not seem to support this conclusion. The relationship between the relative contents of the three compounds and the Pr/Ph ratios of the E_{2S1} and E_{2S3} source rock samples is shown graphically in Fig. 6a–c. Overall, the relative contents of the three compounds in source rock samples do not show systematic variations with changes in Pr/Ph ratios, indicating that the redox condition has a limited effect on the concentration of these three compounds. In addition, the relative contents of these three compounds are also independent of the variation in the gammacerane index (Ga/C_{30} hopane) (Fig. 6d–f).

The formation pathways of compounds A and B, indicate that the degree of thermal maturity plays an important role in

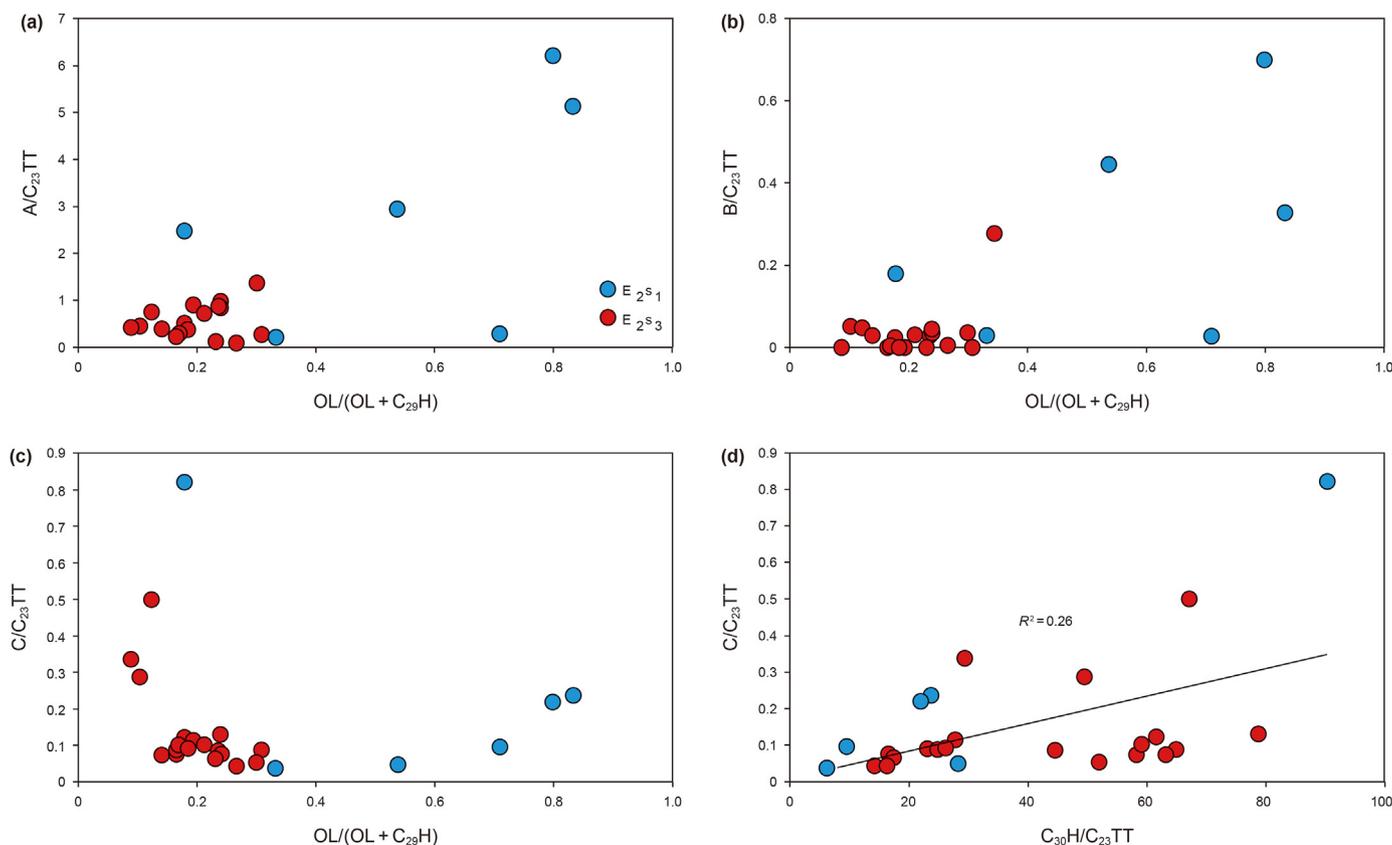


Fig. 5. Crossplot of A/C_{23} TT versus $OL/(OL+C_{29}H)$ (a), B/C_{23} TT versus $OL/(OL+C_{29}H)$ (b), C/C_{23} TT versus $OL/(OL+C_{29}H)$ (c) and C/C_{23} TT versus $C_{30}H/C_{23}$ TT (d) of E_{2S1} and E_{2S3} source rock samples in study area. OL = oleanane; $C_{29}H$ = C_{29} hopane.

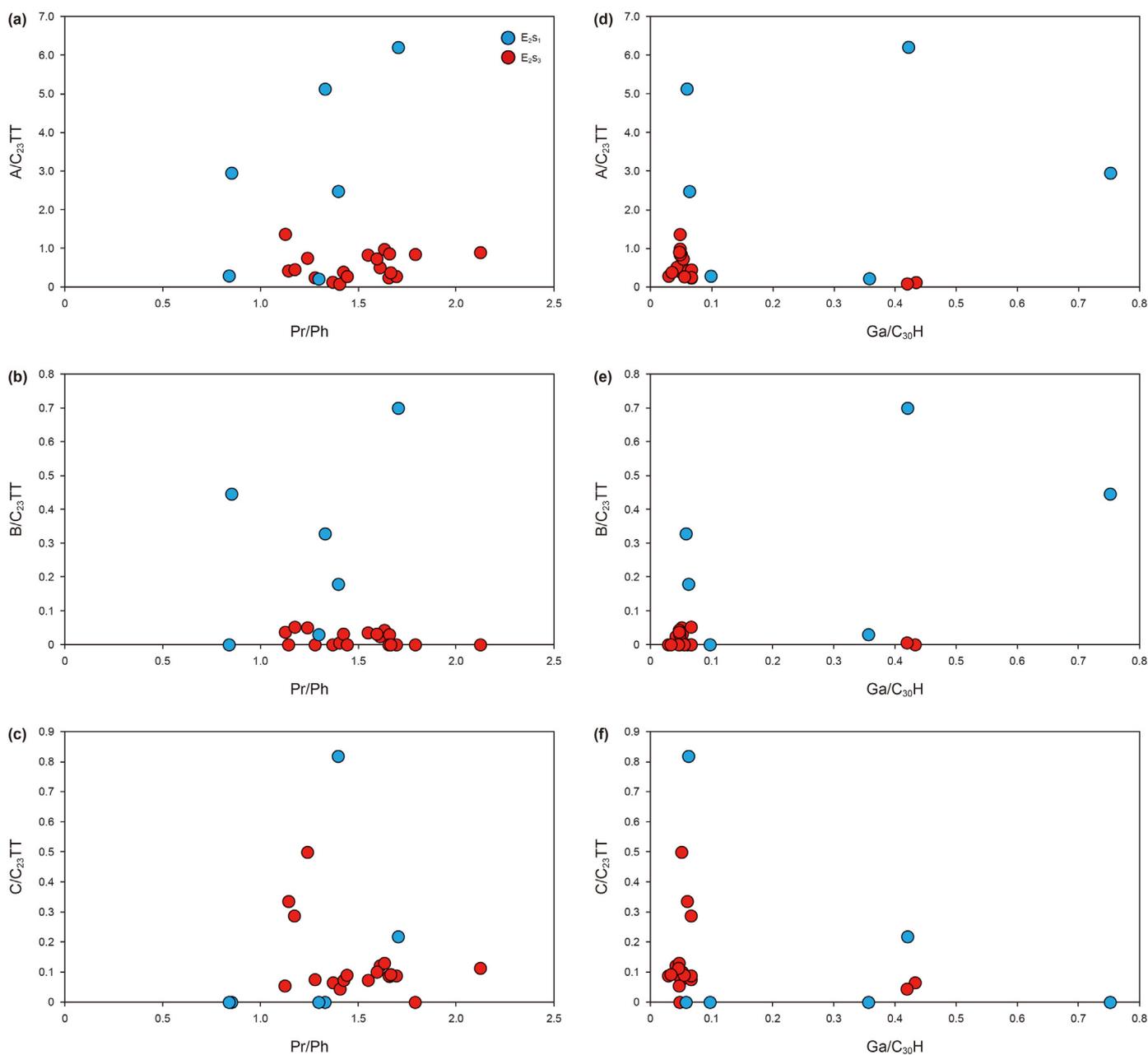


Fig. 6. Crossplot of A/C₂₃TT versus Pr/Ph (a), B/C₂₃TT versus Pr/Ph (b), C/C₂₃TT versus Pr/Ph (c), A/C₂₃TT versus Ga/C₃₀H (d), B/C₂₃TT versus Ga/C₃₀H (e) and C/C₂₃TT versus Ga/C₃₀H (f) of E₂S₃ and E₂S₁ source rock samples in study area.

controlling the formation of the two compounds. Two important pathways in the formation of compounds A and B, the degradation of the A ring of β -amrone and lupanone and the deacidification of 3,4-seco-olean-12-en-3-oic acid and 3,4-seco-lup-3-oic acid, are all controlled by the degree of thermal maturity. Thermal maturity is an important factor controlling the concentration of compounds A and B, which is also supported by the data analysis in this study. The relationship between the relative contents of the two compounds and the $C_{29}\alpha\alpha\alpha-20S/(20S+20R)$ of the E₂S₁ and E₂S₃ source rock samples is shown graphically in Fig. 7a–d. When the $C_{29}\alpha\alpha\alpha-20S/(20S+20R)$ ratio is less than 0.4, the contents of compounds A and B in the E₂S₃ source rock samples are relatively low, increase with the increase of the $C_{29}\alpha\alpha\alpha-20S/(20S+20R)$ ratio, reach a maximum when the $C_{29}\alpha\alpha\alpha-20S/(20S+20R)$ ratio is approximately 0.45, and finally decrease with the increase of the $C_{29}\alpha\alpha\alpha-20S/(20S+20R)$

ratio. An identical correlation between the $C_{29}\alpha\alpha\alpha-20S/(20S+20R)$ ratio and the contents of compounds A and B is also observed in the E₂S₁ source rock samples. However, due to the lack of samples with higher thermal maturity in the E₂S₁ source rock samples, when the $C_{29}\alpha\alpha\alpha-20S/(20S+20R)$ ratio is greater than 0.5, the covariant relationship between the $C_{29}\alpha\alpha\alpha-20S/(20S+20R)$ ratio and the contents of compounds A and B cannot be established. According to the correlation between the $C_{29}\alpha\alpha\alpha-20S/(20S+20R)$ ratio and vitrinite reflectance (R_o) established by Peters et al. (2005), when the $C_{29}\alpha\alpha\alpha-20S/(20S+20R)$ ratios are 0.4 and 0.5, the corresponding R_o values are approximately 0.5% and 0.7%, respectively. The above analysis indicated that compounds A and B in source rocks began to generate in large quantities when R_o was 0.5%, and the concentration of these two compounds reached the maximum when R_o was ~0.6%. With the increase of the thermal maturity degree, the

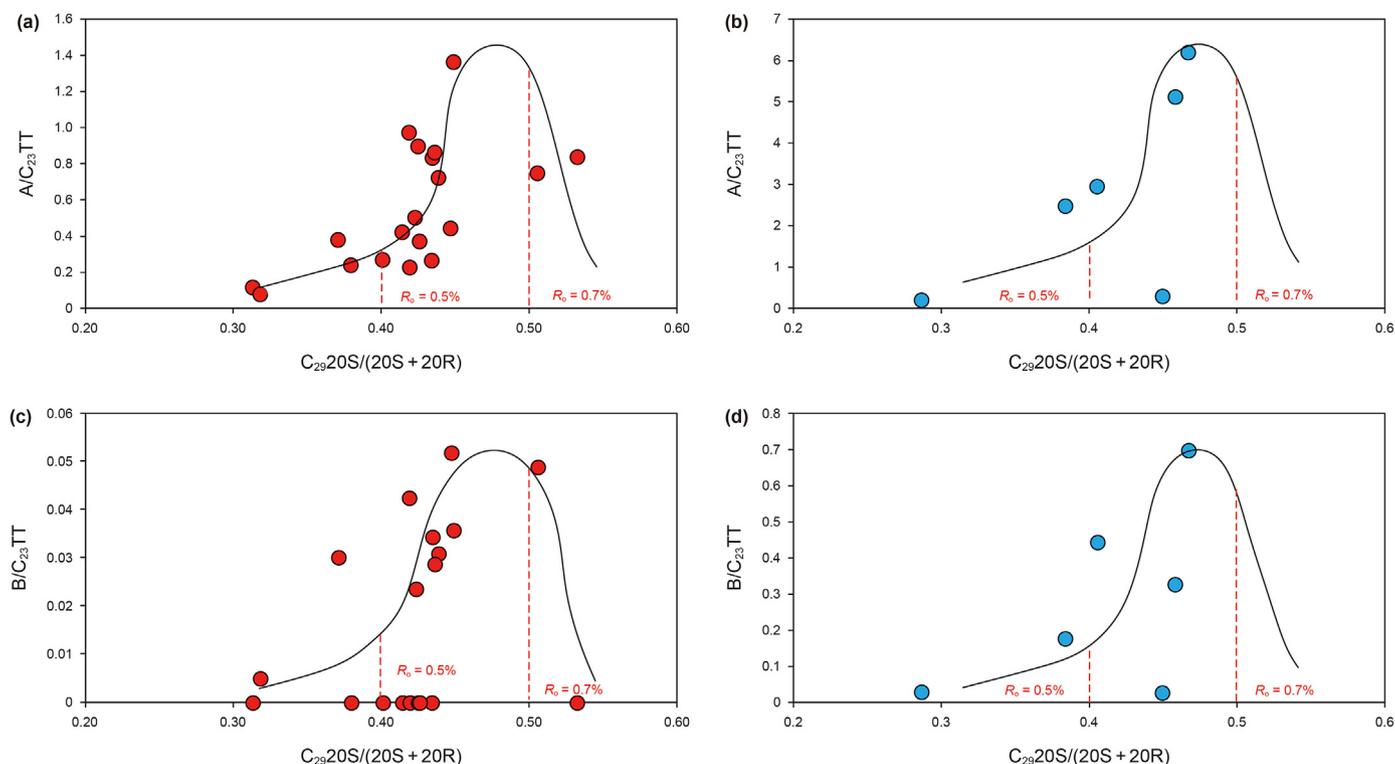


Fig. 7. The crossplot of $C_{29}20S/(20S + 20R)$ versus $A/C_{23}TT$ and $B/C_{23}TT$ of E_{2S1} (b, d) and E_{2S3} (a, c) source rock samples in study area.

contents of these two compounds gradually decreased after R_o was greater than 0.7%.

In addition, the relationship between the contents of compounds A and B and burial depth also supports this view. The contents of compounds A and B in the E_{2S3} source rock samples began to increase at a depth of ~3300 m, reached a maximum value at approximately 3500–3600 m, and then gradually decreased with increasing burial depth (Fig. 8a, c). The concentrations of compounds A and B in the E_{2S1} source rocks also began to increase when the burial depth was approximately 3300 m, but the variation after the burial depth reached more than 3300 m could not be

obtained due to the lack of deeper buried samples (Fig. 8b, d). According to the relationship between the burial depth and R_o of the Shahejie Formation in the Bozhong sag, the R_o values of source rocks buried at ~3300 m and ~3600 m are approximately 0.5% and 0.7%, respectively (Yu et al., 2021).

Based on the data analysis in this study, the distribution and concentration of compounds A and B are affected by the thermal maturity and biological source, while the sedimentary environment has a limited influence. The degree of thermal maturity controls the chemical bond rupture of the precursors of compounds A and B, and finally leads to the enrichment or deficiency of the two

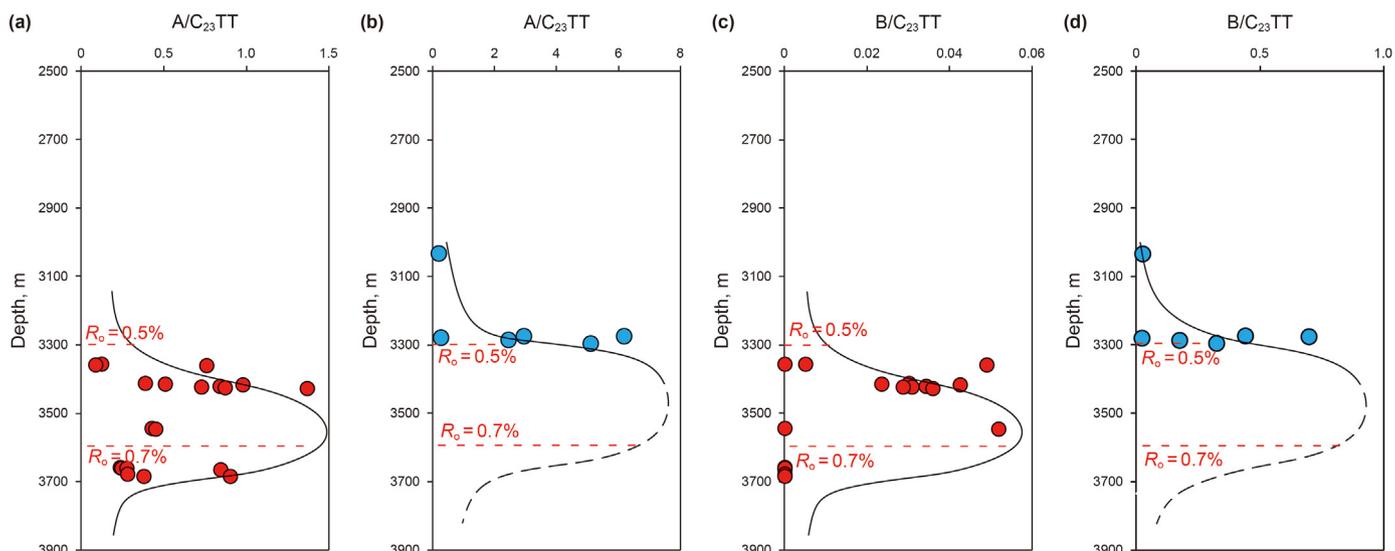


Fig. 8. The relationship between the $A/C_{23}TT$ and $B/C_{23}TT$ ratios and burial depth of E_{2S1} (b, d) and E_{2S3} (a, c) source rock samples in study area.

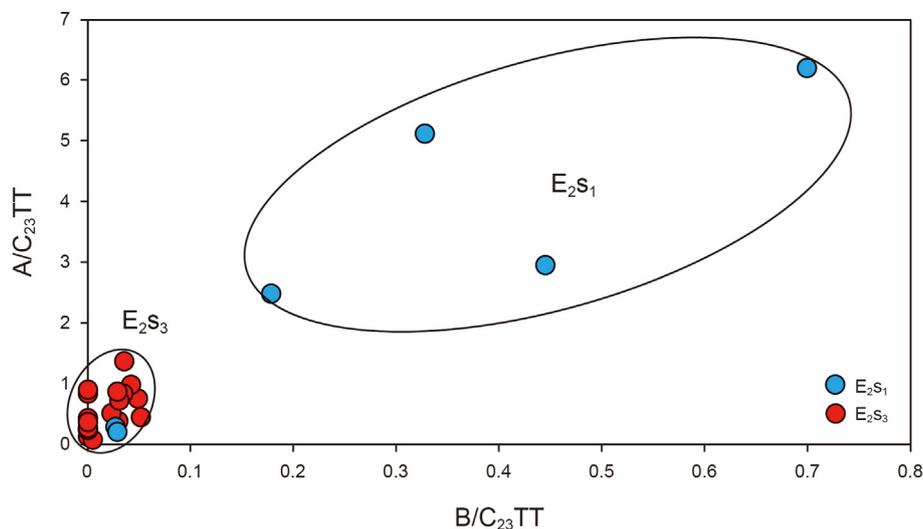


Fig. 9. Crossplot of $A/C_{23}TT$ versus $B/C_{23}TT$ of E_2S_1 and E_2S_3 source rock samples in study area.

compounds in the source rocks. Generally, in the low maturity stage ($0.5\% < R_o < 0.7\%$), the concentrations of compounds A and B in source rocks are high, and their contents decrease with the increasing maturity. However, it should be noted that the biological source of organic matter also plays an important role in controlling the concentrations of these two compounds in the source rocks, which is why the concentrations of compounds A and B in the E_2S_1 source rocks are significantly higher than those in the E_2S_3 source rocks with the same thermal maturity degree. In this study, compound C has no obvious correlation with the sedimentary environment and thermal maturity, and its controlling factors need to be further studied.

4.5. Application of unusual C_{24} tetracyclic terpanes

Compounds A and B are closely related to the biological source and thermal maturity degree and thus are helpful for distinguishing the source rocks and crude oil samples. In this study, the high contents of compounds A and B in the E_2S_1 source rock samples are significantly different from those in the E_2S_3 samples, suggesting a large amount of terrestrial angiosperm input and lower thermal maturity. This finding is consistent with the basic geological information on the E_2S_1 and E_2S_3 source rock samples, which provides indirect evidence for the validity of these new parameters. The combination of two parameters constructed in this study $A/C_{23}TT$ and $B/C_{23}TT$ can successfully distinguish the E_2S_1 and E_2S_3 source rocks in the study area (Fig. 9). In addition, the $10\beta(H)$ -des-A-oleanane/ C_{24} des-A-hopane ratio has been effectively used for oil-source rock correlation analyses in previous studies. For example, the $10\beta(H)$ -des-A-oleanane/ C_{24} des-A-hopane ratio combined with the oleanane/ C_{30} hopane ratio can adequately distinguish crude oil from the Zhu 1 Depression and Zhu 3 Depression (Zhu et al., 2015). Bao et al. (2018) successfully distinguished lacustrine oils and coaly oils based on a crossplot of the relative content of compounds A and C versus the bicadinane T/C_{30} hopane ratio. All these examples indicate that the parameters constructed by the three unusual compounds are expected to be effective parameters in oil source correlations.

5. Conclusions

Three unusual tetracyclic terpanes, namely, $10\beta(H)$ -des-A-

oleanane, $10\beta(H)$ -des-A-lupane and C_{24} des-A-hopane, are identified in the E_2S_1 and E_2S_3 source rock samples in the Bozhong sub-basin based on diagnostic ion fragments and retention time. $10\beta(H)$ -des-A-oleanane and $10\beta(H)$ -des-A-lupane likely originated from terrestrial angiosperms, and C_{24} des-A-hopane likely originated from prokaryotic organisms. Abundant inputs of terrestrial angiosperms provided the material basis for the formation of compounds A and B. Thermal maturity plays an important role in controlling the formation and enrichment of compounds A and B in geological sediments. The data analysis in this study indicates that compounds A and B are largely generated and enriched in the source rocks in the low maturity stage ($0.5\% < R_o < 0.7\%$). Biological sources and thermal maturity are the main factors controlling the relative contents of compounds A and B in the studied samples. In addition, the $A/C_{23}TT$ and $B/C_{23}TT$ ratios are expected to be effective parameters in oil source correlations in the Bozhong subbasin.

Acknowledgments

This study was supported by open fund of Key Laboratory of Exploration Technologies for Oil and Gas Resources (Yangtze University), Ministry of Education, No. K2021-13, China Postdoctoral Science Foundation (2021M692751) and Tianjin branch of CNOOC (CCL2020TJT0NST1956).

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