Extended series of tricyclic terpanes in the Mesoproterozoic sediments

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ARTICLE INFO

ABSTRACT

Analysis of Mesoproterozoic sediment extracts from the North China Craton by gas chromatography–mass spectrometry metastable reaction monitoring revealed an extended series of C_{18}–C_{33} 13α(*n*-alkyl)-tricyclic terpanes. This discovery extends the previous known series to C_{33} with sixteen homologs. Because of the abundant presence of C_{22} and C_{27} homologs, and no isomeric peaks for the homologs > C_{24}, it was confirmed that the side chain at the C-13 position is a long-chain *n*-alkyl group without a methyl substituent or an asymmetric carbon atom. The distribution of the extended tricyclic terpanes in the Mesoproterozoic sediments is mainly controlled by a primitive biological community, probably from certain specific bacteria and/or cyanobacteria. Their biological precursor was probably inhibited by high-salinity water conditions and not evolved during the deposition of the Gaoyuzhuang Formation.

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1. Introduction

Biomarkers preserved in Precambrian geological samples can be employed to shed light on the origin and evolution of early life on the Earth, and for paleoenvironmental reconstruction (Summons and Powell, 1986; Simoneit et al., 1998; Brocks et al., 1999, 2005, 2016, 2017; Bobrovskiy et al., 2018; Shen et al., 2018; Summons and Douglas, 2018; Jarrett et al., 2019; Zhang et al., 2019). Thus, many researchers have conducted comprehensive analyses on Precambrian biomarkers, dealing with *n*-alkanes, monomethylalkanes, acyclic isoprenoids, hopanes and methylhopanes, gammacerane, C_{26}–C_{29} steranes, and 4-methylsteranes (Summons et al., 1988a, 1998b, 1999; Grantham et al., 1990; Brocks et al., 2003; Dutkiewicz et al., 2003; George et al., 2008, 2009; Grosjean et al., 2009; Blumenberg et al., 2012; Xiao et al., 2021). The 13β(H),14α(H)-tricyclic terpanes (TT), usually known as regular tricyclic terpanes, can be identified up to C_{54} TT (Moldowan et al., 1983; De Grande et al., 1993), and are ubiquitously present in geological samples deposited in various depositional environments from Proterozoic to Phanerozoic age. Regular tricyclic terpanes are considered to originate from tricyclohexaprenol in various prokaryotic microorganisms (Aquino Neto et al., 1982). These have been widely applied in geochemical analyses to determine oil to oil correlations (Xiao et al., 2019a), oil to source correlations (Grosjean et al., 2012; Xiao et al., 2019d), thermal maturity (Farrimond et al.,

1999), depositional environment (De Grande et al., 1993) and organic matter inputs (Ekweozor and Strausz, 1983; Xiao et al., 2019c).

In addition to the regular terpane series, a series of novel tricyclic terpanes was initially detected in the Longtangou bituminous sandstone of the Mesoproterozoic Xiamaling Formation (~1320 Ma) (Li et al., 2009) in the Yanliao Faulted-Depression Zone (Wang, 1989). They have different retention time compared to regular tricyclic terpanes in *m/z* 191 mass chromatogram. This novel series has a known carbon number range from C_{18} to C_{23} with a base peak at *m/z* 123 in their mass spectra (Wang, 1991). The molecular structure of the novel series of tricyclic terpanes was determined by co-injection of the synthetic standards of the C_{18} and C_{20} homologs, and comparison with their mass spectra (Wang, 1990). The series was identified as tricyclic terpanes with 13α(*n*-alkyl)-side chain configuration, namely 13α(*n*-alkyl)-tricyclic terpanes (αNATT) (Wang, 1990, 1991; Wang and Simoneit, 1995). Later, Zhang et al. (2007) detected a distribution of αNATT in black oil shales of the Xiamaling Formation in the Xuanlong Depression, and tentatively proposed a possible contribution from Rhodophyta (Zhang et al., 2007). Huang and Wang (2008) recognized C_{19} αNATT and C_{20} αNATT in saturated hydrocarbons of the Kuangshanliang bitumen in the Sichuan Basin, and used these two diagnostic compounds to determine the hydrocarbon source of the thermally altered bitumen (Huang and Wang, 2008). Recently, Song et al. (2021) analyzed the biomarker compositions of black shales of the Hongshuizhuang and the Xiamaling formations, and further detected C_{18}–C_{30} tricyclic terpenes in these Mesoproterozoic sediments.

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This paper is the first report of the occurrence and identification of an extended series of $13\alpha(n\text{-alkyl})$-tricyclic terpanes up to C_{33} in sediment extracts from the Mesoproterozoic Hongshuizhuang (~1450 Ma) and Xiamaling formations (~1320 Ma). The biological origin of the extended series and the influence of depositional environment and thermal maturity on them are discussed.

2. Geological setting

The Yanliao Faulted-Depression Zone in the North China Craton is the most developed region of Proterozoic sequences in China and the oldest oil-bearing structural unit in China. It can be further divided into five depressions and two uplifts, namely the Xuanlong Depression, Jingxi Depression, Jidong Depression, Jibei Depression, Liaoxi Depression, Shanhaiguan Uplift and Mihuai Uplift (Fig. 1) (Sun and Wang, 2016; Xiao et al., 2021). The Yanliao Faulted-Depression Zone contains a series of extremely thick and stable marine carbonate-clastic rock sequences with a total thickness of more than 8000–9000 m, which were deposited during the Proterozoic. These formations include the Mesoproterozoic Changcheng System (1800–1600 Ma), the Mesoproterozoic Jixian System (1600–1400 Ma), the Mesoproterozoic Jinzhou System (1400–1200 Ma) (Niu and Xin, 2013), the Mesoproterozoic unnamed system (1200–1000 Ma), and the Neoproterozoic Qingbaikou System (1000–780 Ma) (Gao et al., 2010). The Jixian System can be further divided into the Gaoyuzhuang, Yangzhuang, Wumishan, Hongshuizhuang and Tieling formations (Li et al., 2010), while the Jinzhou System currently only contains the Xiamaling Formation (Niu and Xin, 2013).

The Yanliao Faulted-Depression Zone of the North China Craton was a continental rift basin that evolved from an estuarine sedimentary environment to a restricted gulf in the Changcheng Period, then to an epicontinental sea in the Jixian Period, and finally to a gulf and estuary in the Neoproterozoic (Yan and Liu, 1998).

The degree of circulation, salinity, and redox conditions of the water column and the biological communities changed over these different periods of sedimentary environment evolution (Li et al., 2003). There are three sets of potential source rocks in the study area, including the black argillaceous dolomite of the Gaoyuzhuang Formation, and the black shales of the Hongshuizhuang and Xiamaling formations. These have high organic matter abundance, favorable organic matter type, and moderate to high thermal maturity (Wang et al., 2016; Zhao et al., 2019).

3. Samples and experiments

3.1. Samples

Four black oil shales of the Xiamaling Formation were collected from the XHY section in the Xuanlong Depression (Fig. 1). Their Tmax value is in the range of 434–442 °C with high TOC values in the range of 6.4–12.6% (Table 1). Three black shales of the Hongshuizhuang Formation were taken from the JQ-1 well in the Jibei Depression, which also contains moderate to high organic matter abundance (TOC average is 2.4%) and are in the main peak of oil generation window (Tmax average is 451 °C) (Table 1). Two black argillaceous dolomites of the Gaoyuzhuang Formation in the JQ-3 well were also analyzed, which have relatively higher maturity and lower TOC than the other samples (Table 1).

3.2. Experimental preparation

3.2.1. Laboratory glassware cleaning

All glassware, such as round-bottomed flasks, funnels, chromatography columns, weighing bottles, etc., were successively washed with detergent and deionized water. Then, potassium dichromate in concentrated sulfuric acid was used to deeply clean
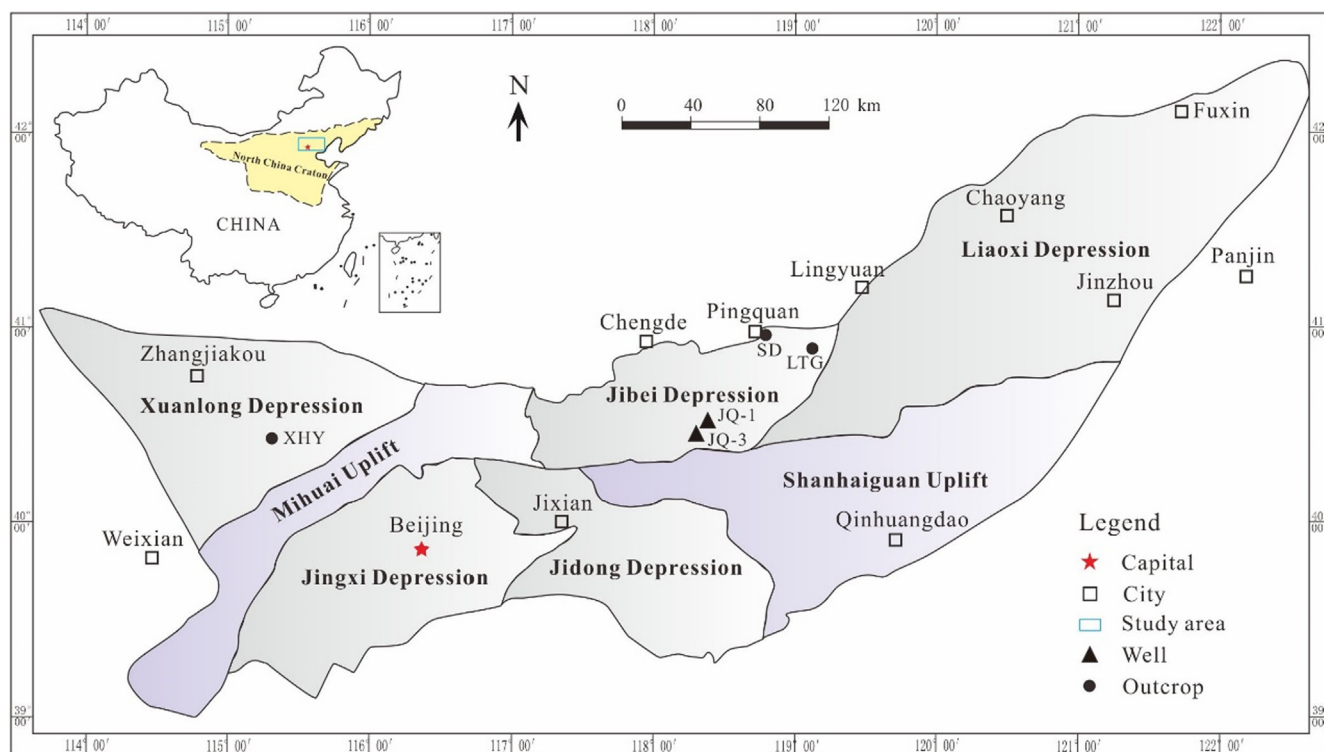

Fig. 1. Map of the geographic location and tectonic units of the Yanliao Faulted-Depression Zone, and locations of the sampled wells and field sections (modified from Xiao et al., 2021).

Table 1
Analytical data (TOC and Rock-Eval) for the Mesoproterozoic sediments.

No.	Wells/sections	Formation	TOC(%)	$S_1 + S_2$(mg/g)	Tmax(°C)
1	XHY	Xiamaling	6.4	25.7	434
2	XHY	Xiamaling	12.1	66.0	438
3	XHY	Xiamaling	7.4	36.2	442
4	XHY	Xiamaling	12.6	56.8	436
5	JQ-1	Hongshuizhuang	4.4	13.8	450
6	JQ-1	Hongshuizhuang	1.1	3.3	451
7	JQ-1	Hongshuizhuang	1.6	3.2	451
8	JQ-3	Gaoyuzhuang	0.4	0.2	509
9	JQ-3	Gaoyuzhuang	0.5	0.3	501

Note: TOC: total organic carbon; $S_1 + S_2$: genetic potential; Tmax: temperature at maximum generation.
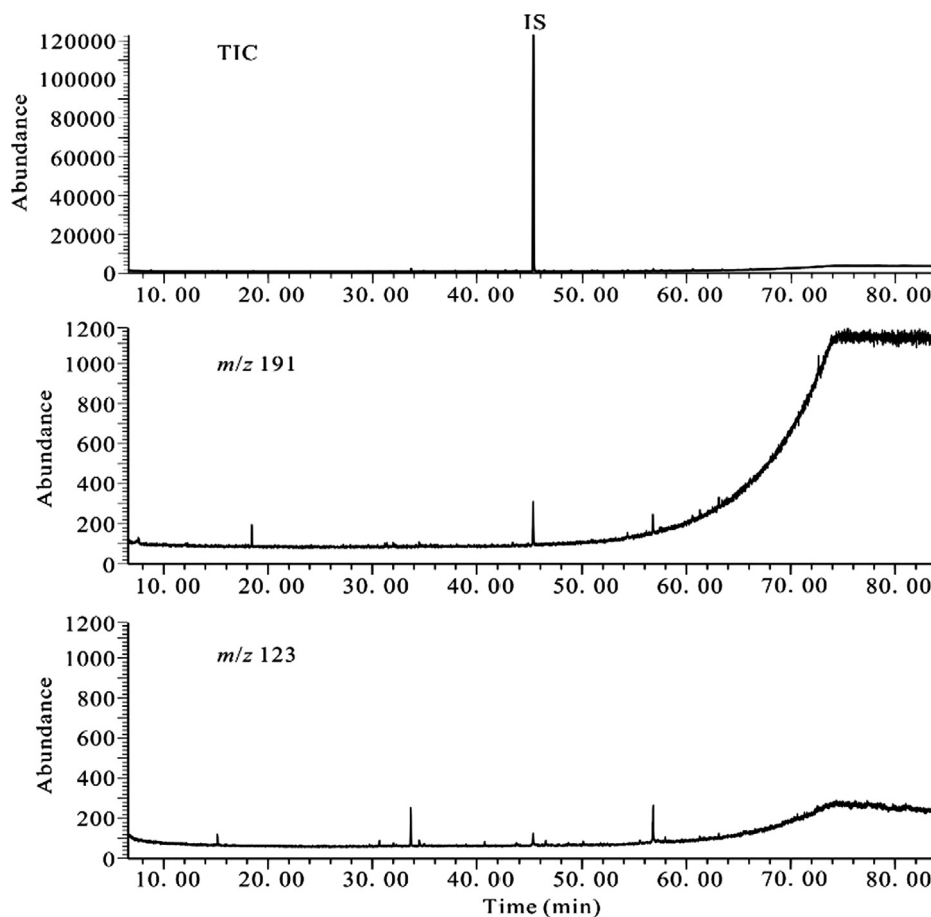

Fig. 2. TIC, *m/z* 191 and *m/z* 123 partial mass chromatograms of the blank. Note: IS = internal standard ($C_{24}D_{50}$).

the glassware, then rinsed with deionized water and dried. After drying, the glassware was heated in an oven at 450–500 °C for 4 h.

3.2.2. Reagent purification and laboratory materials

All solvents, such as dichloromethane, petroleum ether, *n*-hexane and methanol were redistilled. The filter papers, silica gel, alumina, and copper turnings were extracted with dichloromethane for 48–72 h using a Soxhlet.

3.2.3. Decontamination of core samples

The rock samples were initially cleaned with distilled water and then dried in oven at 40 °C. Then a minor portion of the rock surface was removed with abrasive paper before crushing, and the remaining portion was further soaked and washed with dichloromethane to remove potential organic pollutants.

3.2.4. Pulverization and extraction of samples

After crushing the previous sample, approximately 100 g of silica gel was put into the iron crushing bowl and crushed so as to attempt to remove the residue of the last sample. Then, the inner wall of the iron bowl was deeply cleaned with defatted cotton soaked with dichloromethane for 3–5 times. After completing the above process, the next sample was crushed to 80 mesh. More than 150 g of powdered sample was weighed and extracted for 72 h with dichloromethane and methanol (93:7, v/v) using a Soxhlet apparatus. The asphaltenes in the extracts were precipitated using *n*-hexane for 24 h and then filtered using a funnel with filter paper, and then the residual solution was fractionated into three components: saturated hydrocarbons, aromatic hydrocarbons, and resin fractions by liquid chromatography (Xiao et al., 2019c).

3.3. Gas chromatography–mass spectrometry analysis

The GC–MS analyses of the saturated hydrocarbons were performed on an Agilent 6890 gas chromatograph coupled with an Agilent model 5975i mass selective detector equipped with an HP-5 MS fused silica capillary column (60 m × 0.25 mm inner diameter with a 0.25 μm film coating). The initial temperature of the GC oven was 50 °C (hold 1 min), and then increased to 120 °C at a rate of 20 °C/min, then finally raised to 310 °C at 3 °C/min (hold 25 min). The mass spectrometer was operated in electron impact ionization at 70 eV, in full-scan mode with a scan range of 50–600 Da.

3.4. Gas chromatography–mass spectrometry-mass spectrometry analysis

The metastable reaction monitoring (MRM) technique was used to identify the extended series of tricyclic terpanes. GC–MS–MS analyses were conducted on an Agilent 6890 Series gas chromatograph interfaced to a Quatro II mass spectrometer. An HP-5MS column (60 m × 0.25 mm × 0.25 mm) was used. The initial temperature of the GC oven was 50 °C (hold 1 min), and then increased to 120 °C at a rate of 20 °C/min, and then raised to 250 °C at 4 °C/min and 310 °C at 3 °C/min (hold 30 min). The carrier gas was He at a constant flow of 1 ml/min. The ionization energy was 70 eV, and Ar was used as collision gas at 2×10^{-4} mbar with a collision energy of 20 eV. The mass spectrometer was operated in the MRM mode using $M^+ \rightarrow m/z$ 123, where M^+ was m/z 248 + 14n ($0 \leq n \leq 15$).

4. Results and discussion

4.1. Blank experiment analysis

In order to exclude potential contamination in laboratory instruments, a blank experiment analysis was conducted under the same conditions. Fig. 2 shows the total ion current, m/z 191 and m/z 123 of the blank analysis by GC–MS. Except for the peak due to the internal standard, the other compounds are below the detection limit (Fig. 2).

4.2. Occurrence and identification

Aquino Neto et al. (1982) determined the molecular structure of regular tricyclic terpanes (TT) by comparison with an artificially synthesized standard. In our study, in addition to the regular tricyclic terpanes and pentacyclic triterpanes in m/z 191 mass chromatograms, an unusual series of terpanes (solid inverted triangles in Fig. 3a) can also be recognized in the Mesoproterozoic sediments (Fig. 3a). Consistent with a previous study (Wang and Simoneit, 1995), the unusual series is identified as 13α(n-alkyl)-tricyclic terpanes (αNATT), which has a clearer and more complete distribution in m/z 123 mass chromatograms with the carbon number range of C_{18}–C_{23} (Fig. 3b). The low-molecular weight 13α(n-alkyl)-tricyclic terpanes (C_{19}–C_{21} αNATT) have earlier retention times than that of the corresponding C_{19}–C_{21} TT, but with increase of carbon number (C_{22}–C_{23}), the retention times of the C_{22}–C_{23} αNATT are later that of the regular tricyclic terpanes (Fig. 3).
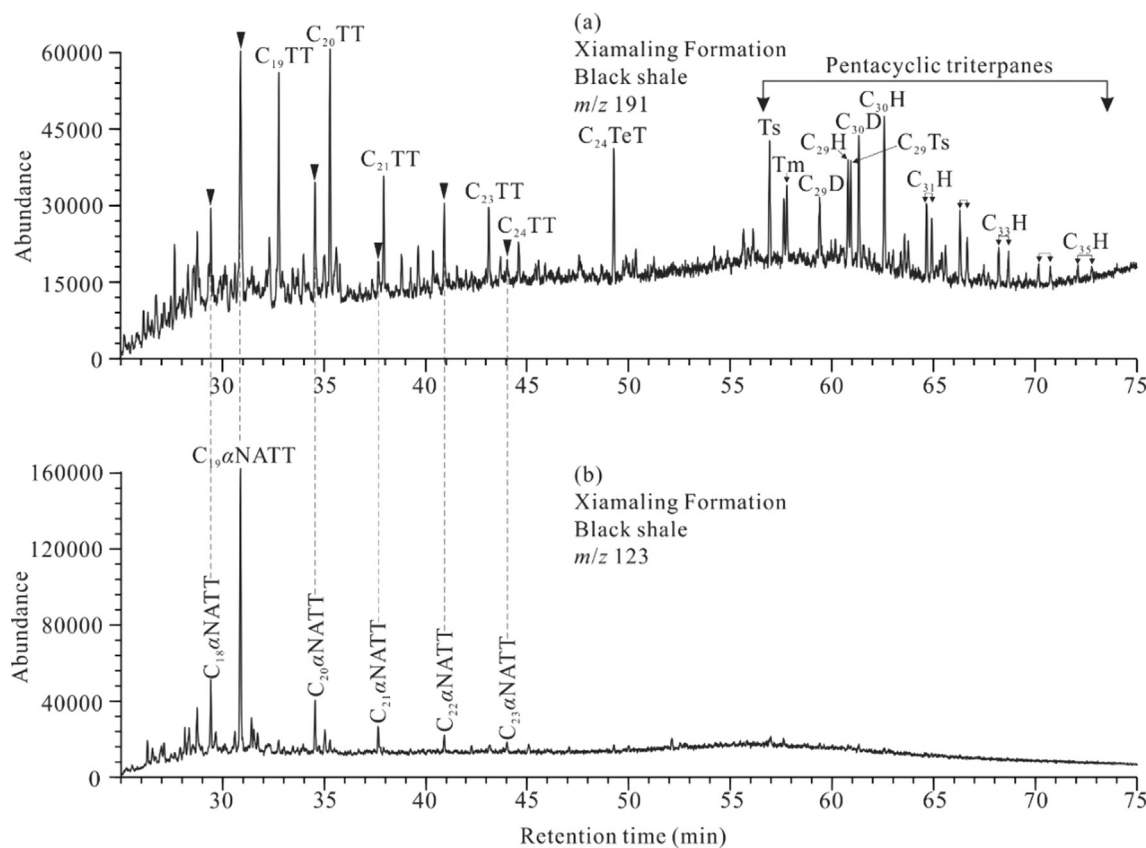

Fig. 3. Partial mass chromatograms showing two series of tricyclic terpanes in the Xiamaling Formation: (a) m/z 191 for the 13β(H),14α(H)-tricyclic terpanes (regular series); (b) m/z 123 for the 13α(n-alkyl)-tricyclic terpanes. Notes: TT = tricyclic terpane; TeT = tetracyclic terpane; H = regular hopane; Ts = 18α(H)-neohopane terpane; D = 17α(H)-diahopane (Xiao et al., 2019b); αNATT = 13α(n-alkyl)-tricyclic alkane.
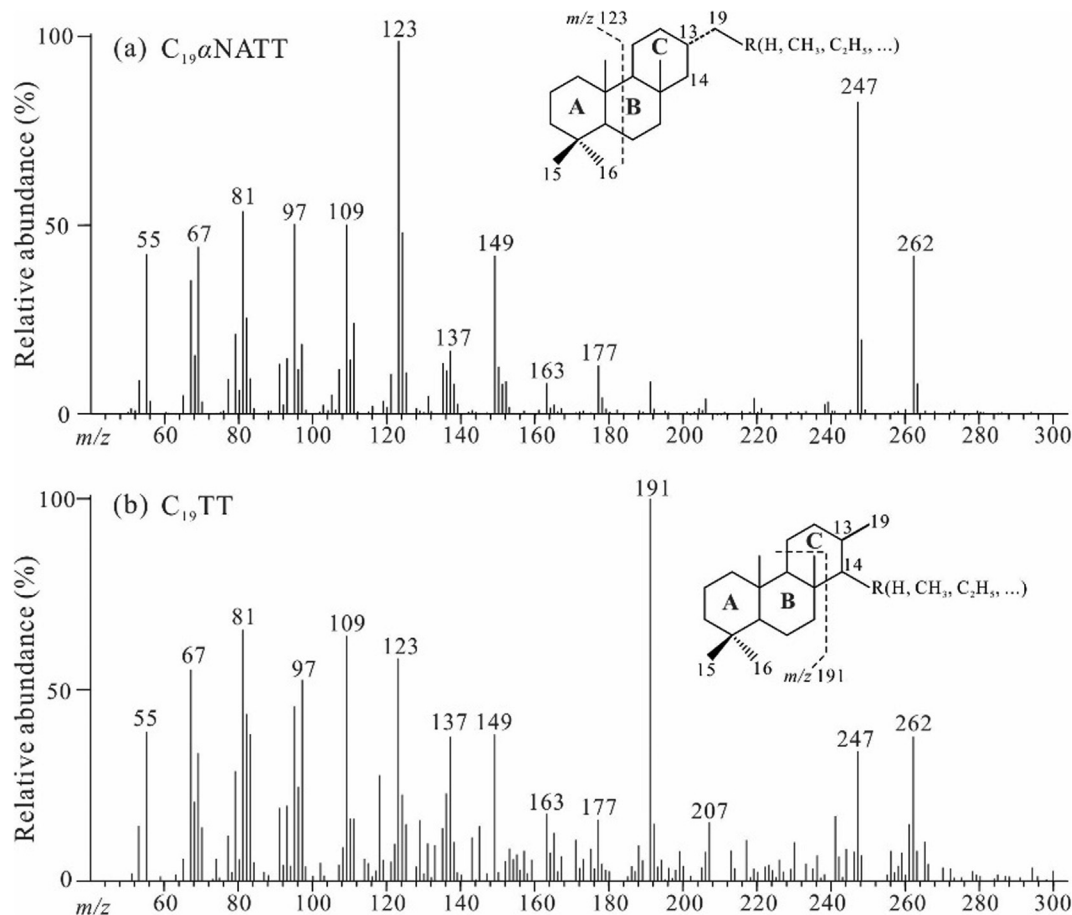
Fig. 4. Mass spectra of C$_{19}$ regular tricyclic terpane and C$_{19}$ 13α(n-alkyl)-tricyclic terpane in the Xiamaling Formation.

To be better understand the difference between two series of tricyclic terpanes, it is necessary to compare their mass spectra. Background subtracted mass spectra of C$_{19}$ αNATT and C$_{19}$ TT are shown in Fig. 4. C$_{19}$ αNATT has a molecular ion peak of M+ 262 with a base peak of m/z 123, and contains several diagnostic ion fragments at m/z 247, 149, 177, 109, etc. (Fig. 4a). The base peak at m/z 123 of 13α(n-alkyl)-tricyclic terpanes is indicative of the A-ring fragment formed by the cleavage of the B-ring, whereas the regular tricyclic terpanes gives a base peak at m/z 191 which is a fragment of the A and B-rings remaining after cleavage of the C-ring. Except for the different base peaks, C$_{19}$ αNATT has the same molecular ion peak of M$^+$ 262 and similar diagnostic fragments as C$_{19}$ TT (Fig. 4b). One other difference is that C$_{19}$ αNATT gives a stronger ion fragment at m/z 247 than that of C$_{19}$ TT (Fig. 4).

In terms of their molecular structures, the series of regular tricyclic terpanes has a methyl group at the C-13 position and an acyclic isoprenoid side chain at the C-14 position (Fig. 4b) (Aquino Neto et al., 1982). The 13α(n-alkyl)-tricyclic terpane series only contains one substituent at the C-13 position (Fig. 4a), which is most likely an n-alkyl group because of the distinct presence of the C$_{22}$ homolog (Fig. 3b) (Wang, 1990).

4.3. Distribution characteristics

As shown in Fig. 5a, the lithology of the Hongshuizhuang and Xiamaling formations is dominated by clastic rocks in the Yanliao Fault-Depression Zone, while the other strata are mainly composed of carbonate rocks (Fig. 5a). It is known that the black argillaceous dolomites from the third to sixth members of the Gaoyuzhuang

Formation, the black shale of the Hongshuizhuang Formation, and the black shale or oil shale of the third member of the Xiamaling Formation in the study area contain high organic matter abundance and are considered to be three sets of potential source rocks (Sun and Wang, 2016; Zhao et al., 2019).

However, there is a striking difference in the biomarker compositions of the three sets of source rock extracts. The C$_{18}$–C$_{23}$ αNATT are completely and abundantly present in the sediments of the Mesoproterozoic Hongshuizhuang (Fig. 5c) and Xiamaling formations (Fig. 5b), but are absent or below detection limit in the sediments of the Gaoyuzhuang Formation (Fig. 5d). 13α(n-alkyl)-tricyclic terpanes have never been reported in Phanerozoic sediments (Wang et al., 2016). All samples from the Hongshuizhuang and Xiamaling Formations show an identical distribution pattern of C$_{18}$–C$_{23}$ 13α(n-alkyl)-tricyclic terpanes with C$_{19}$ αNATT as the dominant homolog. The relative concentration of the 13α(n-alkyl)-tricyclic terpanes is 2–6 times greater than of the regular tricyclic terpanes, based on the comparison of the m/z 123 and 191 mass chromatograms.

4.4. Extended tricyclic terpanes

4.4.1. C$_{18}$–C$_{33}$ 13α(n-alkyl)-tricyclic terpanes

In order to determine the composition and carbon number distribution of 13α(n-alkyl)-tricyclic terpanes, selected saturated hydrocarbon fractions of the sediment extracts from the Xiamaling Formation were analyzed by GC–MS-MS. C$_{18}$–C$_{23}$ and C$_{18}$–C$_{30}$ 13α (n-alkyl)-tricyclic terpanes have previously been detected in the Mesoproterozoic bituminous sandstones by Wang (1989) and in
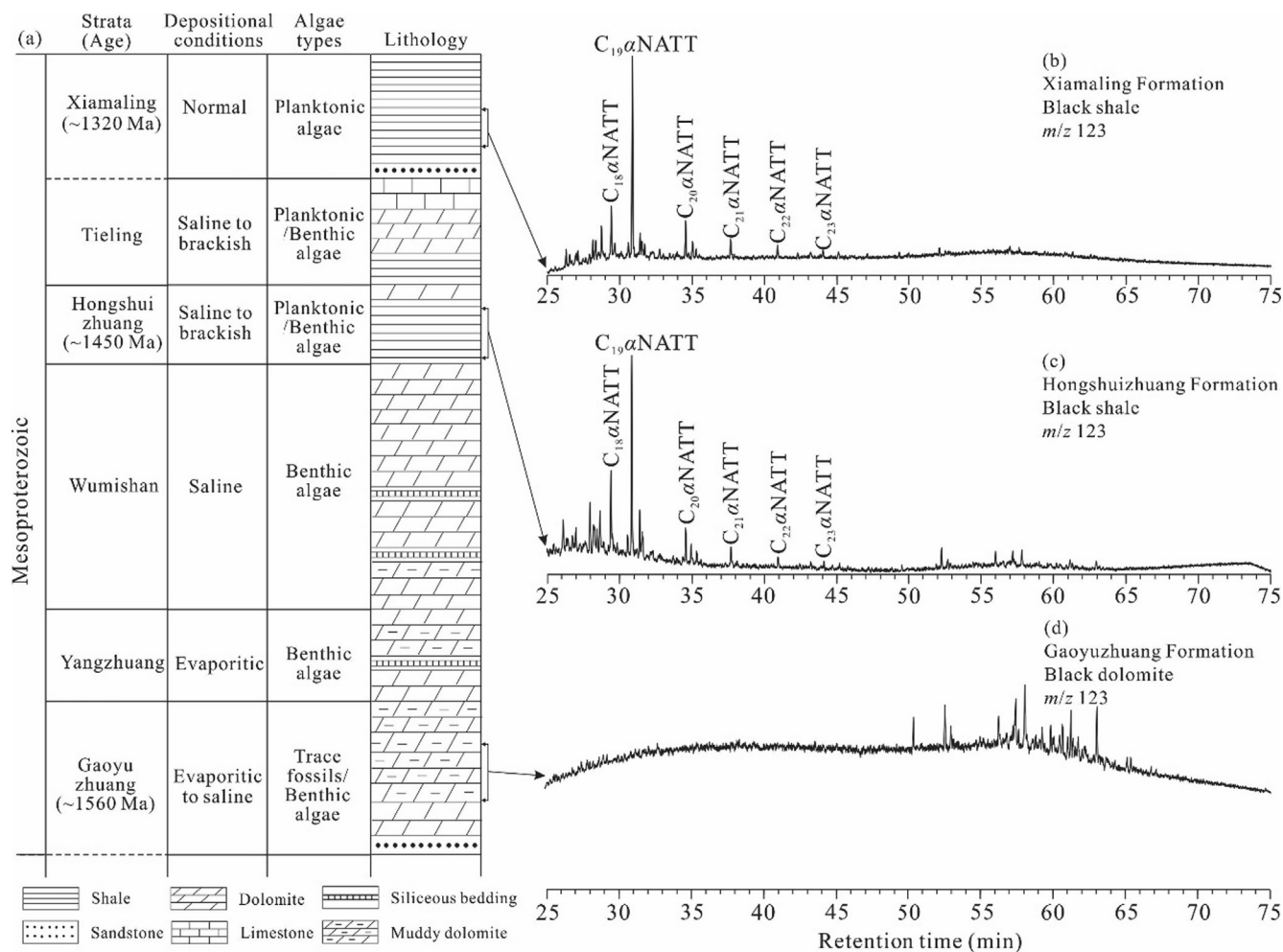
Fig. 5. (a): Simplified lithologic column, inferred depositional conditions and biological community of the Mesoproterozoic Gaoyuzhuang Formation (1560 Ma) to Xiamaling Formation (1320 Ma) in the study area (modified from Yan and Liu, 1998), and (b–d): m/z 123 partial mass chromatograms showing the distribution of C_{18}–C_{23} 13α(n-alkyl)-tricyclic terpanes in Mesoproterozoic sediments.
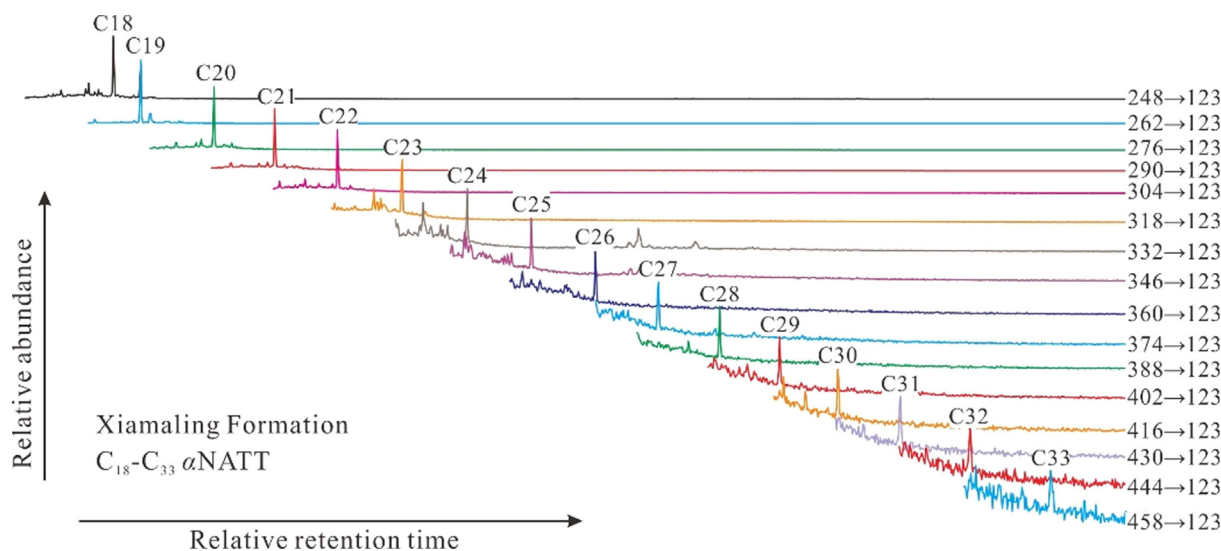
Fig. 6. Metastable reaction monitoring (MRM) chromatograms showing C_{18}–C_{33} 13α(n-alkyl)-tricyclic terpanes in the saturate fraction of the Xiamaling Formation.

the Mesoproterozoic source rocks by Song et al. (2021), respectively. In our study, not only C_{18}–C_{30} 13α(n-alkyl)-tricyclic terpanes but also C_{31}–C_{33} 13α(n-alkyl)-tricyclic terpanes were detected and identified in the sediments of the Mesoproterozoic Xiamaling Formation (Fig. 6). Therefore, the number of homologs in the unusual series of 13α(n-alkyl)-tricyclic terpanes increases
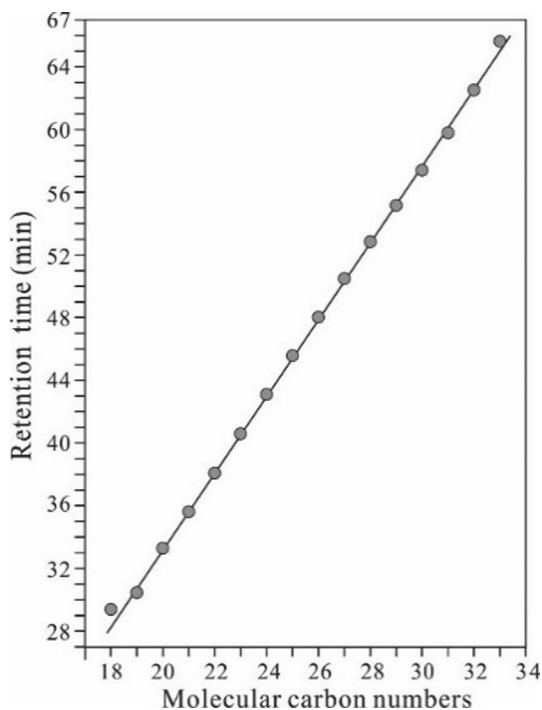
Fig. 7. Correlation between the retention times and carbon numbers for C_{18}–C_{33} 13α(*n*-alkyl)-tricyclic terpanes.

from thirteen (C_{18}–C_{30}) to sixteen (C_{18}–C_{33}), adding three homologs to the series.

Correlation between the retention times of C_{18}–C_{33} 13α(*n*-alkyl)-tricyclic terpanes versus their carbon numbers is shown in Fig. 7. The good linearity further confirms that these compounds belong to the same series. The carbon number range of the 13α(*n*-alkyl)-tricyclic terpanes could be consistent with that of the regular tricyclic terpane series, which means that they may extend to C_{54} (De Grande et al., 1993). However, the homologs with high carbon number (>C_{33}) were not detected in these samples, most likely because of their extremely low abundance even in GC–MS–MS. In addition, the C_{18} αNATT slightly plots away from the line in Fig. 7, which may be attributed to the structural difference. C_{19}–C_{33}

homologs all have an alkyl substituent at C-13, but this is absent from the C_{18} homolog.

4.4.2. Molecular structure characteristics

The relative contents of the C_{18}–C_{33} 13α(*n*-alkyl)-tricyclic terpanes in three rock samples are shown in Fig. 8a. The C_{19} αNATT has a significantly greater abundance than the other homologs. As the carbon number increases, the relative content of C_{19}–C_{33} αNATT gradually decreases without significant fluctuations. Unlike regular tricyclic terpanes, there is no absence or extremely low abundance of C_{22} and C_{27} homologs (Fig. 8a–b), which means that there is no methyl group at the C-22 or C-27 positions.

Importantly, if there was a methyl group at the C-22 position, the homologs above C_{24} αNATT would appear in isomeric pairs, as is the case for regular tricyclic terpanes. However, the highest carbon number homolog revealed by previous studies is only up to C_{23} αNATT, so previously it was not clear whether high-carbon number compounds exist as pairs. Fortunately, the homologs above C_{24} αNATT were detected in this study, but all of them only exhibit a single peak rather than a pair of isomeric peaks (Fig. 6) indicating that there is no asymmetric carbon atom on the substituent of the 13α(*n*-alkyl)-tricyclic terpanes. Based on the above evidence, we can confirm that the extended tricyclic terpanes have a long-chain *n*-alkyl group at the C-13 position and no methyl or extended alkyl substituent at the C-14 position (Fig. 8c).

4.5. Potential biological origins

4.5.1. Primary producers

In the Mesoproterozoic, primary producers in the ancient ocean were predominantly prokaryotes, mainly consisting of cyanobacteria, bacteria, heterotrophic archaea and primitive planktonic algae. Several previous studies reported the presence of steranes in Archean (Brocks et al., 1999) and Mesoproterozoic sediments (Li et al., 2001, 2003), representing the existence and contribution of eukaryotes. After more rigorous laboratory procedures including slice experiments and in-situ carbon isotope measurement on the previous samples, the biomarkers previously detected in Archean samples have been confirmed to be caused by later hydrocarbon migration into the rocks or anthropogenic and experimental contamination (Rasmussen et al., 2008; French et al., 2015; Nguyen et al., 2019; Ai et al., 2020). Recently, the fossils of
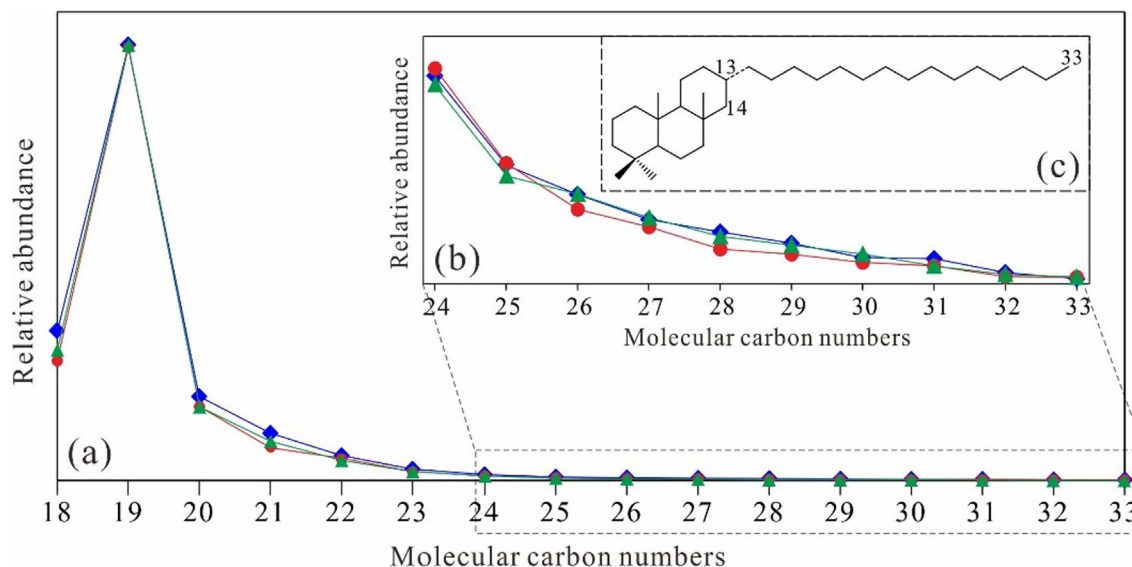

Fig. 8. Relative abundance of C_{18}–C_{33} 13α(*n*-alkyl)-tricyclic terpanes in three samples of the Xiamaling Formation.
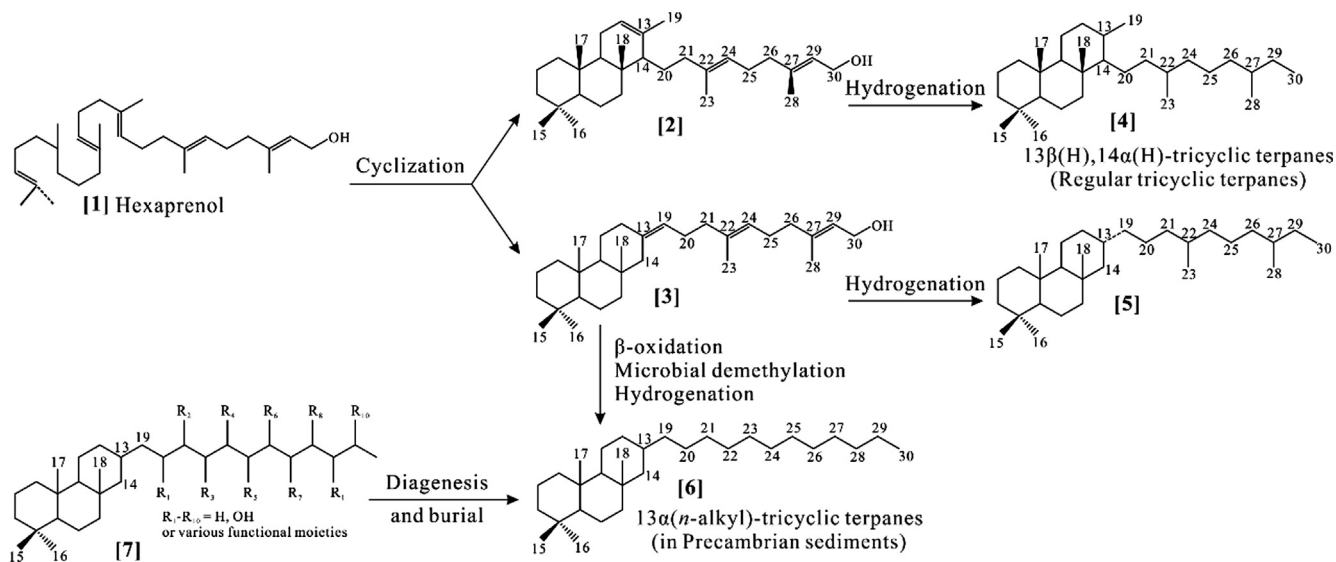
Fig. 9. Proposed biosynthetic reaction schemes for the formation of two series of tricyclic terpanes (modified from Aquino Neto et al., 1983; Wang and Simoneit, 1995).
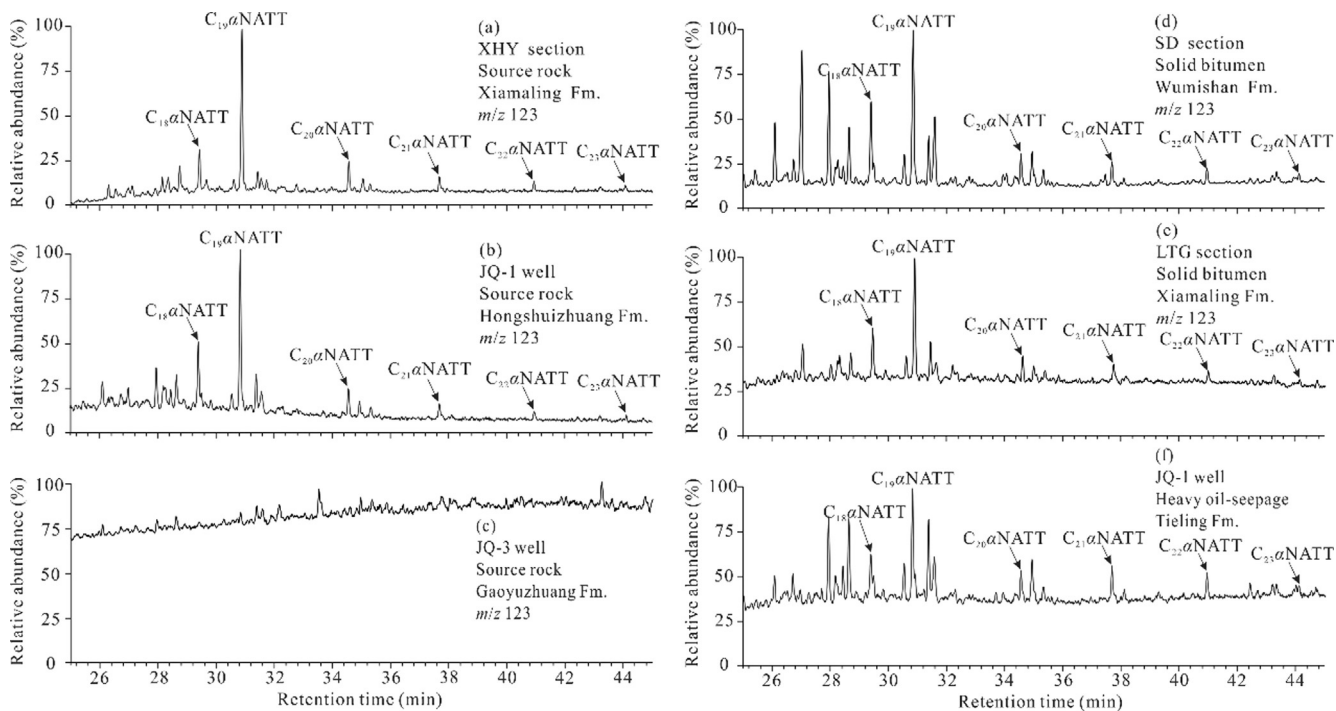

Fig. 10. Representative partial m/z 123 mass chromatograms showing the distribution of C$_{18}$–C$_{23}$ 13α(n-alkyl)-tricyclic terpanes in Mesoproterozoic sediments and oil seepages.

decimeter-scale multicellular macroscopic eukaryotes (Zhu et al., 2016) as well as steranes (Sun and Wang, 2016) were observed in the sediments of the Gaoyuzhuang Formation (1.56 Ga) in the North China Craton. This provides strong evidence that eukaryotic algae, especially benthic algae, flourished in the marine biosphere, which may have become a significant component of primitive biological organic matter during deposition of the Gaoyuzhuang Formation (Fig. 5a). In contrast, the absence or low detection level of steranes in sediments of the Hongshuizhuang and Xiamaling formations directly reveals a minor or limited contribution of benthic eukaryotic algae (Luo et al., 2016). Thus, their soluble hydrocarbons are mainly derived from bacteria, cyanobacteria and possibly some primitive planktonic algae (Fig. 5a). Based on the distribution

of microbial fossils and biomarkers in the sediments of Gaoyuzhuang, Hongshuizhuang and Xiamaling formations, the biological source of the 13α(n-alkyl)-tricyclic terpanes cannot be derived from benthic eukaryotic algae, but most likely was from prokaryotic organisms, such as specific bacteria and/or cyanobacteria.

4.5.2. Biosynthetic reactions

Fig. 9 shows proposed biosynthetic reaction schemes for the formation of two series of tricyclic terpanes. The ubiquitous occurrence of regular tricyclic terpanes are widely accepted (but not proven) to be derived from the tricyclohexaprenol in members of prokaryotic microorganisms (Aquino Neto et al., 1982). As reported previously, because of the similar molecular structures of the two

series of tricyclic terpanes, the unusual series of 13α(n-alkyl)-tricyclic terpanes is also considered to originate from similar biological precursors to regular tricyclic terpanes, but with different cyclization reaction of regular hexaprenols (Fig. 9) (Wang and Simoneit, 1995). However, the biological source of 13α(n-alkyl)-tricyclic terpanes remains to be further studied. If 13α(n-alkyl)-tricyclic terpanes had similar biological sources to the regular tricyclic terpanes, it is hard to explain why the regular tricyclic terpanes are ubiquitously distributed in sediments deposited in various depositional environment from the Proterozoic to Cenozoic, while the 13α(n-alkyl)-tricyclic terpanes have a very limited distribution, only occurring in the sediments of the Mesoproterozoic Hongshuizhuang and Xiamaling Formations in the North China Craton.

According to the proposed biosynthetic reaction schemes for the formation of the two series of tricyclic terpanes (Fig. 9), hexaprenol (**1**) can produce the regular tricyclic terpene (**2**) by first a cyclization reaction, and then the terpene is directly converted into the corresponding saturated compound (regular tricyclic terpane, **4**) by hydrogenation reactions (Fig. 9) (Aquino Neto et al., 1983). On the other hand, previous studies have proposed a relatively complex and speculative biosynthetic scheme for 13α(n-alkyl)-tricyclic terpanes (Fig. 9) (Aquino Neto et al., 1983; Wang and Simoneit, 1995). In detail, the hexaprenol (**1**) may also generate another unusual tricyclic terpene (**3**) by a cyclization reaction, and then the methyl groups of the isoprenoids in compound (**3**) are removed by β-oxidation reaction by certain bacteria, leaving a normal alkyl substituent (Cantwell et al., 1978; Förster-Fromme et al., 2006). Eventually, the terpanes are naturally converted into 13α(n-alkyl)-tricyclic terpanes (**6**) by hydrogenation reactions (Fig. 9) (Wang and Simoneit, 1995). However, if the hexaprenol (**1**) can be cyclized to compound (**3**) in geological conditions, according to the formation process of regular tricyclic terpanes (**4**), compound (**3**) as an intermediate product should be easier to convert into compound (**5**) rather than preferentially form compound (**6**) by a complicated reaction process (Fig. 9). Most importantly, the removal of those monomethyl groups from the side chain substituents one by one in the natural geological conditions (i.e., diagenetic processes) is difficult to accept. Moreover, compound (**5**) or its biodegradation products have not been reported in sediments. Therefore, the 13α(n-alkyl)-tricyclic terpanes are likely not derived from hexaprenol (**1**), but from other biological precursors which may also contain a long side chain with multiple hydroxyl substituents or other functional group substituents such as the skeleton of compound (**7**). 13α(n-alkyl)-tricyclic terpane products can be naturally formed on diagenesis and burial in sediments from compound (**7**), which has a similar process to formation of regular hopanes from bacteriohopanepolyols (Ourisson et al., 1984; Summons et al., 1999).

In summary, the series of 13α(n-alkyl)-tricyclic terpanes in the sediments of the Mesoproterozoic Hongshuizhuang and Xiamaling Formations are orphan biomarkers that occur only in a quite narrow geological time range and disappear in the Phanerozoic. Its specific biological source is still unclear, but it is most likely derived from certain prokaryotic microbes.

4.6. Influence of depositional conditions and thermal maturity

Generally, the abundant acyclic isoprenoids (>C_{20}) (Li et al., 2003), aryl isoprenoid hydrocarbons (Wang, 2009) and gammacerane (Cui, 2011) are distributed in the sediments of the Gaoyuzhuang Formation, which is indicative of high-salinity stratified ocean conditions during the early Mesoproterozoic in the North China Craton. However, only trace amount of these molecular markers were present in the sediments of Mesoproterozoic Hongshuizhuang and Xiamaling Formations, which indicates a moderate

salinity condition (Fig. 5a) (Yan and Liu, 1998). According to the sedimentological difference of the Mesoproterozoic successions, the absence of the series of 13α(n-alkyl)-tricyclic terpanes in the sediments of Mesoproterozoic Gaoyuzhuang Formation could imply that its biological precursor was probably inhibited by high-salinity water condition or had not yet evolved.

Moreover, the black shale of the third member of the Xiamaling Formation from XHY section has characteristics of high abundance of organic matter (TOC is ~ 9.6%) and low thermal maturity (Tmax is ~ 438 °C). In addition, because these two series of tricyclic terpanes have similar molecular structures, especially the low carbon number homologs (e.g., C_{19}), their thermal stability should be also similar. Therefore, a thermogenic origin for the abundant 13α(n-alkyl)-tricyclic terpanes in the sediments of the Xiamaling Formation can be ruled out.

4.7. Application in oil to source correlation

C_{18}–C_{23} 13α(n-alkyl)-tricyclic terpanes are prevalently distributed in the solid bitumen from the Wumishan Formation in the Shuangdong section and the Xiamaling Formation in the Longtangou section, as well as in oil-seepages from the Tieling Formation in the JQ-1 well (Fig. 10d–f). Both our study (Fig. 5) and previous work (Sun and Wang, 2016) have shown that 13α(n-alkyl)-tricyclic terpanes are commonly present in the source rocks of the Hongshuizhuang and the Xiamaling Formations in the North China Craton, but are absent from the Gaoyuzhuang Formation. Based on oil to source correlation, it can be preliminarily judged that the discovered solid bitumen and oil-seepages in the Wumishan, Xiamaling and Tieling formations were derived from the source rocks of the Hongshuizhuang and/or Xiamaling formations (Fig. 10). Therefore, the series of 13α(n-alkyl)-tricyclic terpanes can be used as a potential molecular fossil for oil to source correlation of Precambrian sediments in the North China Craton.

5. Conclusions

An extended series of C_{18}–C_{33} 13α(n-alkyl)-tricyclic terpanes was detected in Mesoproterozoic sediments from the North China Craton. The number of homologs in the unusual series increases from thirteen (C_{18}–C_{30}) to sixteen (C_{18}–C_{33}), with three homologs added to the series based on this work. Based on the abundant distribution of C_{22} and C_{27} homologs, and only a single peak for the homologs above C_{24} αNATT, the molecular structure was further confirmed to have a long-chain n-alkyl group at the C-13 position, and no methyl or extended alkyl substituent at the C-14 position.

The series of 13α(n-alkyl)-tricyclic terpanes is ubiquitously distributed in the sediments of the Mesoproterozoic Hongshuizhuang (~1450 Ma) and Xiamaling formations (~1320 Ma) and are probably derived from certain specific bacteria and/or cyanobacteria. However, this series is absent in the sediments of Mesoproterozoic Gaoyuzhuang Formation (~1560 Ma), indicating that the biological precursor was not present during deposition of the Gaoyuzhuang Formation. Moreover, the series of 13α(n-alkyl)-tricyclic terpanes does not have a thermogenic origin, so it may be a potential molecular fossil for oil-source correlation of Precambrian sediments in the North China Craton.

Declaration of Competing Interest

Acknowledgements

Associate Editor–Cliff Walters

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