



Original Paper

Petrology and organic geochemistry of the Baishaping and Damaidi Devonian cutinitic liptobioliths, west of the Kangdian Uplift, China

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ABSTRACT

Devonian cutinitic liptobiolith is a special type of coal formed during the early evolutionary stage of land plants. The Baishaping and Damaidi Devonian coals are notable for their distinct papery, sheet-like texture, and unusually high cutinite content (>50%), belonging to typical cutinitic liptobiolith. They are bituminous coals and have a suppressed vitrinite reflectance. Compared with typical type III kerogen, these liptobioliths are characterized by extremely high yields of volatile matter and high hydrogen contents owing to their enhanced cutinite contents. As indicated by pyrolysis and elemental analysis results, the Devonian cutinitic liptobioliths are dominated by type I-II kerogens and have an excellent potential to generate liquid hydrocarbons. The Baishaping cutinitic liptobioliths are mainly composed of ribbon-like thick-walled cutinites, with small amounts of thin-walled type. Vitrinite is only present in trace amounts and is dominated by telinite. Meanwhile, the Damaidi Devonian coals are primarily composed of ribbon-like thin-walled cutinites, followed by collotelinites which are usually sandwiched by cutinites. The different petrological characteristics of the Baishaping and Damaidi liptobioliths might indicate a structural variation in the coal-forming plant cuticles and two distinct coal-forming conditions. The molecular biomarkers in the Devonian coals are mainly composed of C₁₈–C₂₀ tetracyclic diterpenoids, which are assumed to be the dominant soluble constituent of the Devonian land-plant cuticles and might have played an important role in early land plant radiation. Other molecules include aromatic tetracyclic diterpenoids, 3–5 ring polycyclic aromatic hydrocarbons and their methylated counterparts, and C₁₆- and C₁₈-monocarboxylic acids. *n*-Alkanes are present only in small amounts. The molecular composition of the cutinite-rich coals is unexpected, because cuticular waxes are one of the most important sources of *n*-alkanes. In general, the petrology and geochemistry of the Devonian cutinitic liptobiolith indicate a distinct structure and composition for the early land-plant cuticles, which is significantly different from that of the plant cuticles since Carboniferous.

Devonian cutinitic liptobioliths are of great interest because of their unique petrography, geochemistry, coal-forming plants, and oil-prone potential. Studies on this unique coal type provide a better understanding of coal-forming plants, paleoenvironment, paleoclimate, and early land-plant evolution in the Devonian.

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1. Introduction

Different geological ages developed distinct types of coal due to the evolution of coal-forming plants and changes in coal-forming conditions, such as the cutinitic liptobiolith of the Devonian, the humic bituminous coal of the Carboniferous, the bark liptobiolith of the Late Permian, and the resinite liptobiolith of the Cretaceous and

Paleogene (Han et al., 1996; Yang, 1996; Tang et al., 2011; Wang et al., 2016; Du et al., 2021; Song et al., 2021). The Devonian is a particularly important period in the history of coal accumulation, because it marks the beginning of the entire geological time period of coal formation (Han et al., 1996; Fowler et al., 1991; Stein et al., 2012; Giesen and Berry, 2013). Cutinitic liptobiolith, a special cuticle-rich coal with more than 50% cutinite (on a mineral free basis; Han et al., 1996), was formed by early land plants during the Middle Devonian. Its formation marks a new stage of geological development and early land plant evolution. While the appearance

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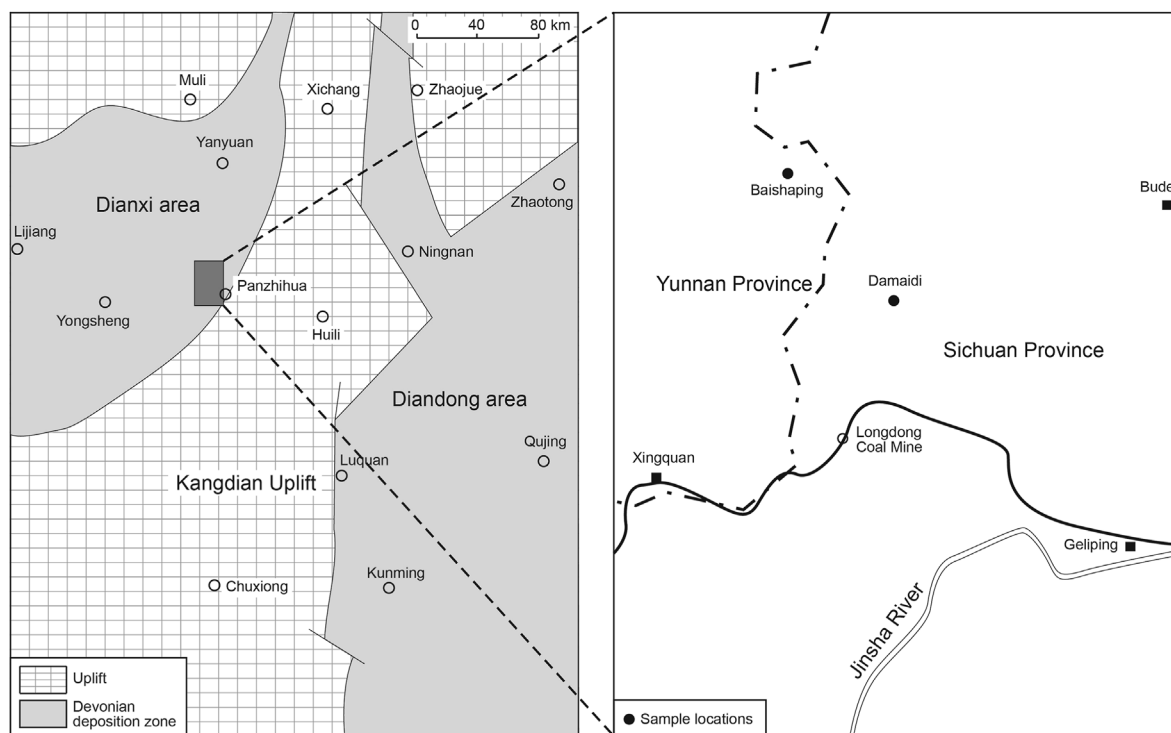


Fig. 1. General location map of the studied area.

of vascular plants can date back to the Ordovician, the onset of advanced terrestrial vegetation systems occurred in the Middle Devonian (Edwards et al., 1983; Berry and Fairon-Demaret, 2001; Stein et al., 2007; Meyer-Berthaud and Decombeix, 2009). Until the Middle Devonian (Givetian), the first true vegetation forests formed by vascular land plants appeared at low latitudes, which provided the material basis for the formation of humic coal (Han et al., 1996; Stein et al., 2007; Giesen and Berry, 2013; Berry and Marshall, 2015). During that time, early land plants, such as *psilophyte* and *lycopsid*, had well-developed cuticles to adapt to the terrestrial environment. Under favorable conditions, these cuticles massively accumulated as cutinite to form cutinitic liptobiolith.

Devonian cutinitic liptobioliths are rare and are only known from a few localities worldwide. (Ammosov II, 1964; Han, 1964; Sheng et al., 1991; Volkova, 1994; Cheng et al., 1995; Goodarzi and Gentzis, 2018). In China, this type of coal has been reported in northwestern Xinjiang and in the regions near the Kangdian Uplift (Han, 1964; Han et al., 1996; Song et al., 2017, 2021), including the Luquan and Baishaping areas of the Yunnan Province and the Damaidi area of the Sichuan Province. The Luquan cutinitic liptobiolith, located on the east side of the Kangdian Uplift, is internationally renowned and has been the most widely studied. Han et al. (1993, 1996) and Cheng et al. (1995) detailedly summarized their quality and petrographic characteristics, and suggested that the cutinite content in the coals can be up to 85%. Meanwhile, Sheng et al. (1991, 1992) and Cheng et al. (1997) reported the organic geochemical compositions of these special coals, especially their biomarkers. Based on elemental concentration and palynology study results, Quan and Han (1997, 1998) and Dai et al. (2006) attributed the *Psilopsid* and *Lycopsida* to be the dominant coal-forming plants for the Luquan cutinitic liptobiolith, and suggested a seawater influence during peat accumulation. Recently, this type of coal was also reported in northwestern Xinjiang. Their quality, petrology and organic geochemistry were well documented by Song et al. (2017, 2021). By contrast, there is very little research on

the cutinitic liptobioliths from the Baishaping and Damaidi areas, on the west side of the Kangdian Uplift. Therefore, in this study, the petrological and organic geochemical characteristics of the Baishaping and Damaidi cutinitic liptobioliths are discussed in detail, as well as their coal-forming conditions. As cutinitic liptobiolith is a special type of coal formed by unique early land plants in a distinct ecological environment, understanding its petrology and organic geochemistry will provide valuable information regarding early land-plant evolution and coal-forming conditions.

2. Geological setting

The Baishaping and Damaidi areas are located in the western part of Panzhihua City and are situated near the bank of the Jinsha River. Baishaping is only approximately 20 km northwest of the Damaidi area. In geology, they are situated on the west side of the Kangdian Uplift and next to the Dianxi Trough (Fig. 1). The Baishaping-Damaidi region began to receive deposit from the Middle Devonian as a result of a transgression. The deposited Middle Devonian strata were named the Lagude Formation, which was subdivided into the Damaidi and Suoshapo units (Fig. 2; Wang et al., 1997; Fang, 2000). The Damaidi Unit is mainly comprised of clastic rocks interbedded with muddy-limestones and limestones. Its geological age is regarded as late Middle Devonian (Givetian), which is equivalent to the age of the Haikou Formation in the Diandong area. The upper Suoshapo Unit is composed of limestones and little dolomite, which is equivalent to the Qujing Formation in the Diandong area. Cutinitic liptobioliths are present in the Damaidi Unit of both the Baishaping and Damaidi areas, and have the same geological age as the Luquan cutinitic liptobiolith, which occurred in the Haikou Formation of the Diandong area.

Rock assemblages indicate that the Damaidi Unit was deposited in shallow marine and lagoonal tidal-flat environments (Wang et al., 1997). However, the sedimentary conditions in the Baishaping-Damaidi region changed radically during the Middle

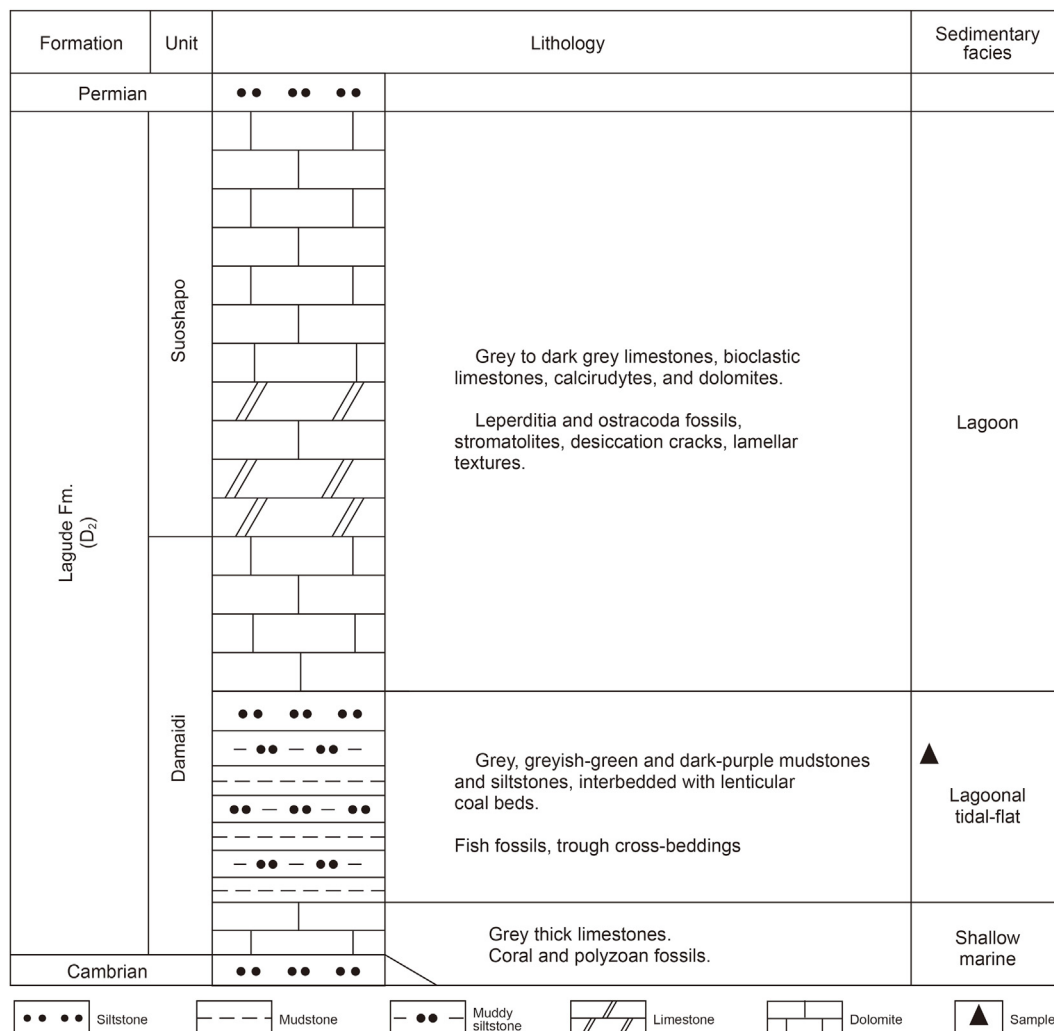


Fig. 2. Generalized lithology and sedimentary environment of the Lagude Formation in the Dianxi area (modified after Wang et al., 1997).

Devonian because the location adjacent to terrigenous provenance and the complex paleo-terrain. According to previous research, the Baishaping area was closer to the ancient land and at a relatively higher elevation, whereas the Damaidi area was located in deeper waters (Wang et al., 1997; Wang and Han, 1998).

3. Samples and methods

Fourteen cutinitic liptobiolith samples were collected from the outcrops in the Baishaping and Damaidi areas. To avoid the effects of weathering, a trench perpendicular to the strike of the liptobiolith streak was dug. Representative bulk samples of the cutinitic liptobiolith were taken from the trench. In the lab, the outer surfaces were removed to avoid contamination, and then the bulk samples were crushed into small pieces and those deemed to be the freshest were handpicked for subsequent analysis.

The coal blocks for microscopic examination (perpendicular to bedding) were polished on a Buehler automatic grinding and polishing machine (EcoMet 250 with AutoMet 250) to give a smooth surface. Then, the maceral characteristics and compositions were analyzed on a Leica DMRXP microscope under reflected and fluorescent lights. The maceral classification and terminology applied in the current study are based on the ICCP System1994 (International Committee for Coal and Organic Petrology, 2001).

Vitrinite reflectance was measured following ASTM Standard D2798-11a (2019) using a Leica DM4500P microscope with a CRAIC microscope photometer, after calibration with standards of known reflectance (Saphir, $R_0 = 0.589\%$).

Proximate analysis, including moisture, volatile matter, and ash yield, were performed in accordance with ASTM Standards D3173-11 (2011), D3174-11 (2011), and D3175-11 (2011), respectively. The total sulfur values were determined following the ASTM Standard D3177-02 (2011). Ultimate analysis (C, H, O, and N contents) was performed using a Vario Macro Elemental Analyzer. Total organic carbon (TOC) content was measured using a Leco CS-230 analyzer. Before the measurement, 12.5% HCl was added into the ground sample to remove carbonates, and then the sample was washed with distilled water for three days. Rock pyrolysis measurement was analyzed using a Rock-Eval 6 instrument. The pyrolysis temperature was programmed from an initial temperature of 300 °C (held for 3 min) to a final temperature of 600 °C at 50 °C/min. The free hydrocarbon (S_1) can be achieved during thermal heating at 300 °C, whereas the hydrocarbons generated from pyrolysis from 300 °C to 600 °C were defined as the residual hydrocarbon (S_2).

The fresh samples were powdered and Soxhlet extracted for 24 h with a dichloromethane/methanol mixture (97:3). The extracts were deasphalted using *n*-hexane, and separated using column chromatography (silica gel over alumina, 3:1) into saturate,

Table 1
Results of proximate and ultimate analyses, total sulfur content, caloric value, TOC and Rock-Eval pyrolysis, as well as random vitrinite reflectance data.

Sample no.	Location	Proximate analysis			Ultimate analysis			TOC and pyrolysis analysis							R _{ovitr} -%						
		M _{ad} -%	A _d -%	V _d -%	FC _d -%	S _t -%	Q _{gr,daf} MJ/kg	C _{daf} -%	H _{daf} -%	O _{daf} -%	N _{daf} -%	H/C	O/C	TOC-%	S ₁ -mg/g	S ₂ -mg/g	S ₃ -mg/g	HI-mg/g.TOC	PI	T _{max} -°C	R _{ovitr} -%
BSP-1	Baishaping	2.42	26.64	81.94	18.06	0.86	32.34	65.67	7.18	11.77	0.06	1.31	0.13	60.36	12.01	355.06	5.76	588.24	0.03	435	0.44
BSP-2		2.50	26.70	81.38	18.62	0.86	31.87	70.41	7.88	14.29	0.08	1.34	0.15	58.14	15.83	362.96	5.74	624.29	0.04	436	0.46
BSP-3		3.28	29.56	80.99	19.01	0.48	29.40	71.45	7.53	13.73	0.05	1.26	0.14	52.28	16.94	311.68	5.05	596.17	0.05	434	0.44
BSP-4		2.26	26.68	82.13	17.87	0.54	32.28	71.52	7.85	12.58	0.08	1.32	0.13	52.41	10.95	283.34	4.86	483.38	0.04	440	0.48
BSP-5		4.70	28.76	82.53	17.47	0.49	31.64	70.33	7.99	13.18	0.06	1.36	0.14	53.94	13.93	308.00	5.14	515.39	0.04	441	0.50
BSP-6	1.96	31.58	78.85	21.15	0.48	29.05	69.34	7.67	13.54	0.06	1.33	0.15	51.67	14.84	316.74	5.16	554.94	0.04	441	0.48	
BSP-7	2.68	28.40	83.25	16.75	0.47	31.24	69.75	8.12	14.04	0.03	1.40	0.15	56.10	11.18	331.04	5.22	536.61	0.03	438	0.47	
BSP-8	2.60	27.00	83.38	16.62	0.48	32.13	67.82	7.71	13.72	0.04	1.36	0.15	57.67	13.96	349.60	5.75	554.18	0.04	440	0.48	
DMD-1	Damaidi	5.42	38.51	49.52	50.48	3.10	28.17	71.89	5.54	12.40	0.47	0.92	0.13	42.15	5.24	136.42	5.26	323.65	0.04	442	0.62
DMD-2		5.38	38.91	49.93	50.07	3.02	29.91	67.54	5.32	15.15	0.48	0.95	0.17	41.49	4.13	146.83	5.29	353.89	0.03	441	0.69
DMD-3		5.39	39.09	50.04	49.96	3.00	29.52	70.17	5.19	14.60	0.48	0.89	0.16	40.54	3.83	135.44	5.42	334.09	0.03	442	0.65
DMD-4		6.16	41.66	51.68	48.32	3.28	27.77	72.31	5.53	14.85	0.47	0.92	0.15	41.14	5.40	144.01	5.48	350.06	0.04	442	0.68
DMD-5		5.22	38.37	49.50	50.50	3.77	29.52	71.44	5.62	14.84	0.50	0.94	0.16	42.29	5.73	146.03	4.96	345.31	0.04	440	0.67
DMD-6		4.80	40.42	51.49	48.51	3.42	28.87	72.56	5.43	14.81	0.47	0.90	0.15	41.92	6.27	154.17	4.42	367.77	0.04	442	0.69

M, moisture; A, ash yield; V, volatile matter; FC, fixed carbon; S_t, total sulfur; Q_{gr}, gross calorific value; C, carbon; H, hydrogen; O, oxygen; N, nitrogen; ad, as-received basis; d, dry basis; daf, dry and ash-free basis; TOC, total organic carbon content; HI, hydrogen index; PI, production index.

aromatic, and NSO fractions by sequential elution with *n*-hexane, toluene, and chloroform. Prior to the gas chromatography analysis, the silylation of the NSO fraction was accomplished using BSTFA + TMCS (99/1). Gas chromatography–mass spectrometry (GC–MS) analyses of the saturated, aromatic, and NSO fractions were conducted using an Agilent Model 6890 gas chromatograph coupled to an Agilent Model 5975i mass selective detector, and fitted with a HP-5MS capillary column (60 m, 0.25 mm i.d., 0.25 μm film thickness). The GC operating conditions for the saturated and NSO fractions were: 50 °C (1 min) to 120 °C at 20 °C/min, and then to 260 °C at 2 °C/min (hold for 25 min); for the aromatic fraction were: 80 °C (1 min) to 310 °C at 3 °C/min (hold for 25 min). The MS transfer line temperature was held at 280 °C and the ion source temperature was 250 °C. The sample was injected in a splitless mode, with an injector temperature at 300 °C. The ion source was operated in the electron impact (EI) ionization mode at 70 eV. Helium was used as the carrier gas (flow rate 1.0 mL/min).

Reference standards of phyllocladanes and kauranes were obtained by catalytic hydrogenation of the natural products phyllocladene and kaurene. Reduction of phyllocladene yielded 16α(H)- and 16β(H)- phyllocladane in a ratio of 4:1 and similarly for kaurene, with the GC elution order of β before α for both sets of standards, as previously reported (Noble et al., 1985, 1986). The yielded phyllocladanes and kauranes were analyzed by GC–MS as external standards. Identification of individual diterpene in the coal samples was based on a comparison of the mass spectra and the relative GC retention times with the external standards and those previously reported. Quantitative results of diterpanes and *n*-alkanes were achieved by peak area integration using phyllocladene and *n*-C₂₄D₅₀ as internal standards, respectively.

4. Results

4.1. Coal chemistry and vitrinite reflectance

Table 1 summarizes the results of the proximate and ultimate analyses, total sulfur content, calorific value, and random vitrinite reflectance data, as well as the pyrolysis results. The fixed carbon, volatile matter, and gross calorific values of the Baishaping and Damaidi liptobioliths indicate a high volatile bituminous rank according to the ASTM standard D388-18 (2018). However, the volatile matter yield in the analyzed samples (49.50%–83.38%, daf: dry and ash-free basis) was much higher than expected for a common bituminous coal, which is attributable to the elevated cutinite content. Similarly, special high volatile matter yield was also observed in the Devonian cutinitic liptobioliths from the Luquan area of the Yunnan Province, China (69%–89% daf; Cheng et al., 1995; Han et al., 1996; Dai et al., 2006) and in the Barzas Basin of Siberia (78.2%–87.7%, daf; Ergolskaya, 1936; Han, 1964; Volkova, 1994). Compared to the Baishaping liptobioliths, the Damaidi coals have a relatively higher ash yield (38.37%–41.66%, daf) and a lower TOC content (40.54%–42.29%), which suggest an elevated inorganic mineral contribution. Owing to the accumulation of cutinites, the hydrogen contents (5.19%–8.12%, daf) and pyrolysis HI values (323.65–624.29 mg/g.TOC) in the analyzed samples are much higher than that of a typical type-III kerogen. The H/C and O/C ratios of the Baishaping (1.26–1.40 and 0.13–0.15, respectively) and Damaidi liptobioliths (0.89–0.95 and 0.13–0.17, respectively) indicate a type-II kerogen (Fig. 3a, Tissot et al., 1974). The average HI values of the Baishaping and Damaidi coals are 557 mg/g.TOC and 346 mg/g.TOC, respectively. In the cross-plot of HI versus T_{max} values (Fig. 3b), the Baishaping coals are plotted in the zone of Type I-II kerogens, whereas the Damaidi liptobioliths are dominated by Type II kerogen. Generally, the very high pyrolysis S₁, S₂, and HI values indicate a great oil generation potential for these cutinitic

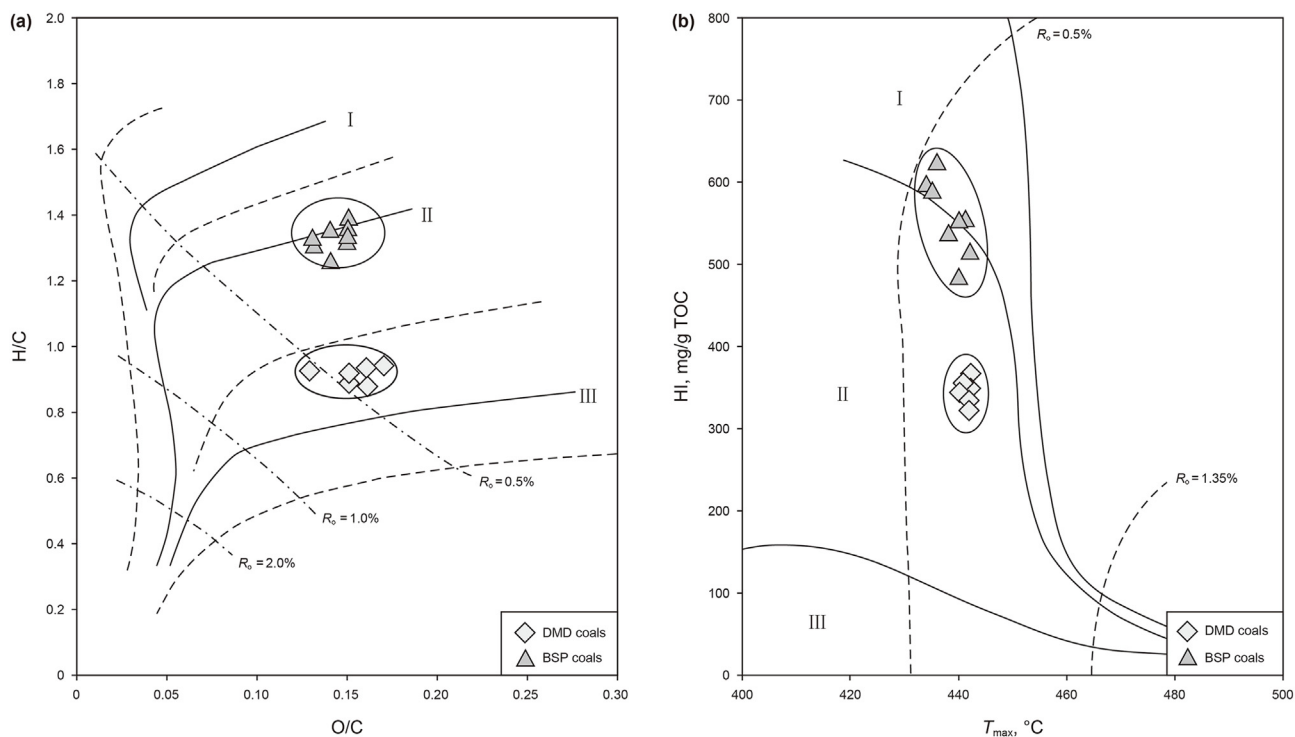


Fig. 3. Plots of T_{max} vs. HI (a, based from Mukhopadhyay et al., 1991) and O/C vs. H/C (b, based from Van Krevelen, 1961) indicating the kerogen types of the Baishaping and Damaidi liptobioliths.

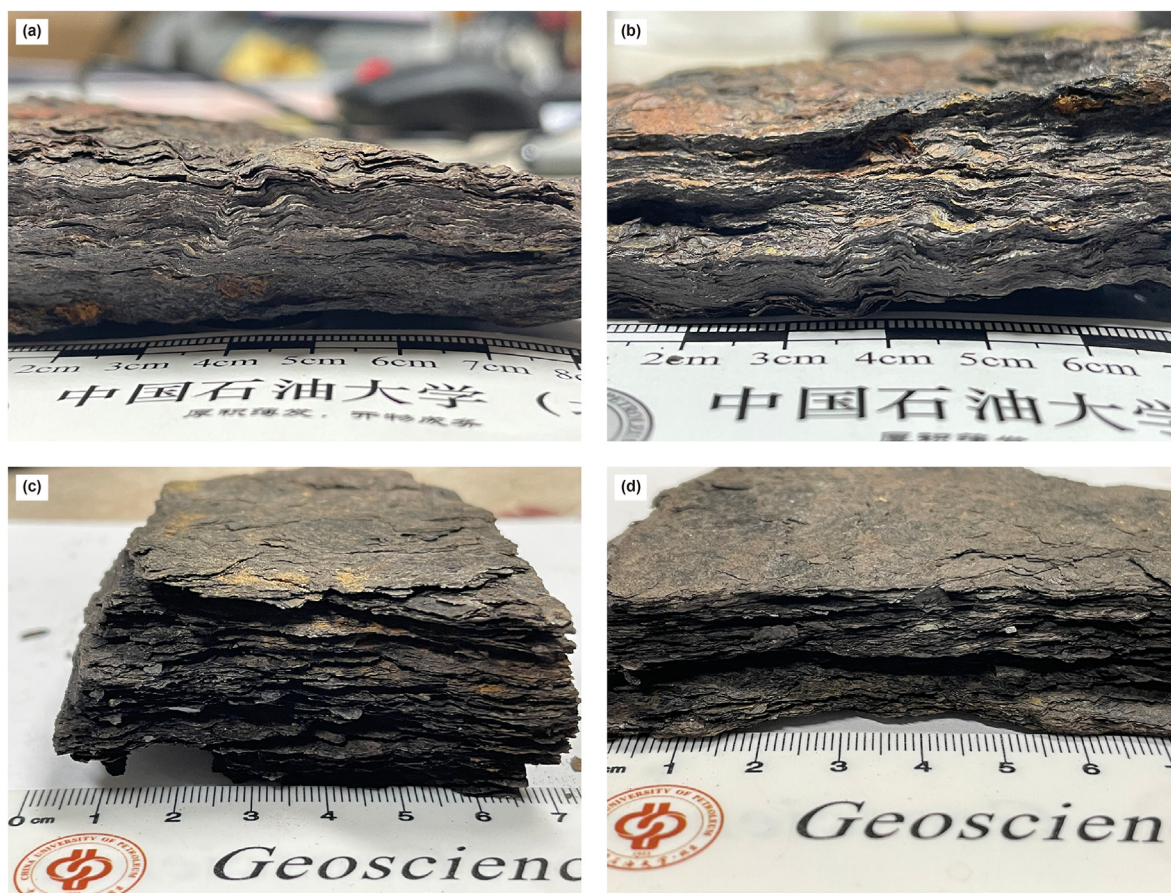


Fig. 4. Macroscopic characteristics of the Devonian cutinitic liptobioliths from the Baishaping (a, b) and Damaidi areas (c, d).

Table 2
Maceral compositions of the Baishaping and Damaidi cutinitic liptobioliths.

Sample no.	Location	Maceral composition (vol%; on mineral-free basis)										
		Cut (thick-walled)	Cut (thin-walled)	LD	SP	EX	TE	CT	VD	F	Mac	ID
BSP-1	Baishaping	79.7	7.5	1.0	1.2	0.6	4.3	1.1	1.6	1.7	0.5	0.8
BSP-2		74.9	10.7	0.6	1.1	0.8	5.4	0.8	1.2	0.8	3.1	0.6
BSP-3		81.9	7.8	0.6	0.8	0.8	3.5	0.4	1.0	1.3	1.1	0.8
BSP-4		78.4	5.7	0.4	0.5	0.7	8.6	0.9	1.1	0.8	2.3	0.6
BSP-5		82.0	6.8	0.7	0.6	1.0	5.3	0.6	0.8	0.6	1.1	0.5
BSP-6		78.6	5.7	0.8	0.6	0.8	8.1	1.0	1.3	1.1	1.3	0.7
BSP-7		76.3	7.1	0.6	1.1	0.8	8.1	1.1	1.1	1.3	1.8	0.7
BSP-8		77.9	6.8	0.6	0.9	0.9	7.9	1.0	1.0	1.1	1.4	0.7
DMD-1	Damaidi	0.5	66.5	2.3	0.8	–	–	27.3	1.1	0.4	0.8	0.3
DMD-2		–	70.2	2.5	0.6	–	–	24.1	1.6	0.2	0.6	0.2
DMD-3		–	60.4	4.4	0.9	–	–	29.3	4.0	0.2	0.3	0.5
DMD-4		–	56.3	2.1	1.2	0.2	–	34.4	3.6	0.7	0.9	0.6
DMD-5		0.2	57.7	3.1	1.1	–	–	32.6	3.3	0.4	1.0	0.6
DMD-6		–	56.3	3.3	1.1	0.2	–	31.7	2.8	2.6	1.2	0.8

Cut, cutinite; LD, liptodetrinite; Sp, sporinite; Ex, exsudatinitite; TE, telinite; CT, collotelinite; VD, vitrodetrinite; F, fusinite; Mac, macrinite; ID, inertodetrinite. Cutinite can be subdivided into thick-walled (with a width >50 μm) and thin-walled types (with a width <50 μm) according to Han et al. (1996).

liptobioliths. Compared with the Baishaping coals, the Damaidi liptobioliths have relatively lower H/C ratios, S_1 , S_2 and HI values, and higher O/C ratios. These differences may result from their different maturities, maceral compositions and secondary alteration.

The measured random values of vitrinite reflectance for the Baishaping cutinitic liptobioliths range from 0.44% to 0.50%, corresponding to a sub-bituminous rank (ISO 11760, 2005). The values of the Damaidi liptobioliths are higher, ranging from 0.62% to 0.69%, suggesting a bituminous rank. The T_{max} values, a commonly used maturation index of organic matter (Tissot and Welte 1984; Peters and Moldowan, 1993), range from 434 °C to 441 °C for the Baishaping coals and from 440 °C to 442 °C for the Damaidi liptobioliths. The corresponding R_c values, calculated based on the T_{max} values ($R_c = 0.018 \times T_{\text{max}} - 7.16$; Jarvie et al., 2001), range from 0.65% to 0.78% for the Baishaping coals and from 0.76% to 0.80% for the Damaidi liptobioliths. These R_c values are much higher than their measured R_o values, which indicates a suppression of vitrinite reflectance in the cutinitic liptobioliths. In fact, it has been confirmed that the reflectance of the vitrinite which is surrounded by cutinite is prefer to be suppressed (Hutton and Cook, 1980; Price and Baker, 1985). Therefore, the liptobioliths from both the Baishaping and Damaidi areas should be of bituminous rank. Compared with the Damaidi coals, the suppression degree of vitrinite reflectance in the Baishaping cutinitic liptobioliths is stronger, which is probably attributed to their higher contents of cutinite and hydrogen.

The sulfur contents in the Baishaping and Damaidi liptobioliths were significantly different. The Baishaping liptobioliths are characterized by low sulfur contents (0.47%–0.86%) and, thus, are classified as a low-sulfur coal (Chou, 2012). However, the Damaidi liptobioliths have a much higher sulfur content (3.00%–3.77%), belonging to a high-sulfur coal. The sulfur content in coal is closely related to the depositional environment of coal seams, wherein coal abundant in sulfur is commonly controlled by the seawater influence during peat accumulation (Diessel, 1992; Ren et al., 2006; Zhao and Shu, 2006; Chou, 2012). As discussed in geological setting, the Damaidi area was closer to the sea relative to the Baishaping area, during Middle Devonian. Therefore, the high sulfur content of the Damaidi coals may be explained by seawater influences during coal formation.

4.2. Coal petrology

4.2.1. Macroscopic characteristics

Devonian cutinitic liptobiolith seams occur as lenticular bodies

in the Baishaping and Damaidi areas, extending for approximately 500–700 m in the horizon direction. These disconnected coal seams are 0.3–0.7 m thick, reaching a maximum of 1.2 m thick in the Damaidi area. These cutinitic liptobioliths have a dark gray or black color on their fresh surfaces, whereas weathered surfaces are usually yellowish-brown. They are dull coals with a dull or resinous luster. The coal is notable for its distinct papery, sheet-like texture resembling a pile of paper sheets in appearance, which is famous as the so-called paper coal (Fig. 4; Han, 1989). The liptobiolith can easily split into laminae (with weak elastic properties), which segregate during weathering.

4.2.2. Maceral compositions

The macerals in the Baishaping and Damaidi cutinitic liptobioliths are dominated by ribbon-like cutinites. However, the coals from different areas vary in distinct cutinite types, microstructures and maceral compositions (Table 2). Differences in petrological characteristics might result from structural variations in the coal-forming plant cuticles and different coal-forming conditions.

The macerals in the Baishaping cutinitic liptobioliths are dominated by thick-walled cutinites (50–400 μm thick, Fig. 5), with small amounts of thin-walled types (<50 μm thick; Han et al., 1996). The content of thick-walled cutinites is of 74.9%–82.0%, with an average of 78.7%. These thick-walled cutinites are ribbon-like and superposed in parallel. They are characterized by slightly serrated outer and inner edges and exhibit brilliant yellow fluorescence. The content of thin-walled cutinites is much lower, ranging from 5.7% to 10.7%. In general, they are sparse or agminated distribution in the mineral layers between the thick-walled cutinites, exhibiting a parallelly superposed shape or an enterolithic shape (Fig. 5a, b, d). The thin-walled cutinites have a smooth outer edge and also show brilliant yellow fluorescence. The cutinites in the Devonian cutinitic liptobioliths can reach a length up to a dozen centimeters, which is distinct from the cutinites in typical humic coal. The vitrinite in the Baishaping liptobioliths is mainly composed of telinite (3.5%–8.6%), with trace amounts of collotelinite and vitrodetrinite. Telinites are usually distributed in the mineral layers as lenticular or elliptical shapes and are commonly surrounded by thin-walled cutinites (Fig. 5c and d). Trace exsudatinitite is usually distributed in the cell cavities of telinite, or along cracks in the mineral layers (Fig. 5f). Other trace amounts of macerals include liptodetrinite, sporinite, fusinite, inertodetrinite and macrinite, which are mainly dispersed in the mineral layers (Fig. 5e and f).

The cutinites in the Damaidi liptobioliths are almost entirely thin-walled type (56.3%–70.2%), with widths of 2–5 μm (Fig. 6).

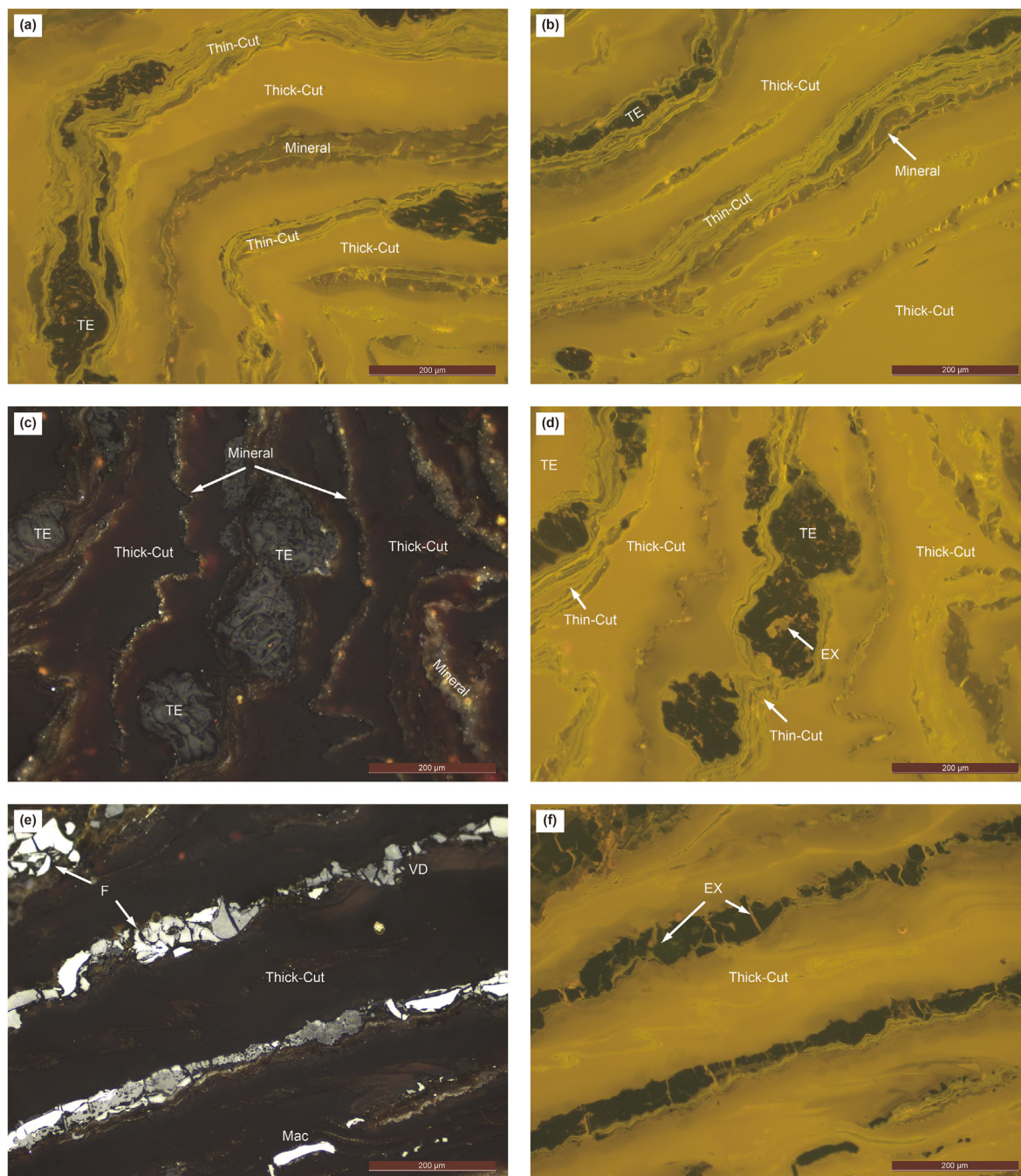


Fig. 5. Microscopic characteristics of the Baishaping Devonian cutinitic liptobioliths (c, e-in reflected light and oil immersion; a, b, d, f-in fluorescent light). Thick-Cut, thick-walled cutinite; Thin-Cut, thin-walled cutinite; TE, telinite; EX, exsudatinite; F, fusinite; Mac, macrinite; VD, vitrodetrinite.

These thin-walled cutinites are present in various forms, including enterolithic, parallelly superposed together, bordered around collotelinite or mixed in mineral layers. The cutinites have a slightly serrated or smooth edge and show a yellowish-brown color in fluorescent light. However, their fluorescence is much weaker than that of the cutinites in the Baishaping liptobioliths, which probably resulted from their high maturity and intense weathering. The vitrinite in the Damaidi liptobioliths is dominated by ribbon-like collotelinite, which has a width of <math><400\ \mu\text{m}</math> and a content of 24.1%–34.4%. The most notable feature of the collotelinites is that they were bordered with thin-walled cutinites (Fig. 6c and d). This collotelinite bordered by cutinite commonly originate from plant

leaves or small stems, which are usually called “leaf vitrinite” (Han et al., 1996). Leaf vitrinites, as well as those surrounded by hydrogen-rich macerals, usually have a suppressed reflectance and strong fluorescence (Fig. 6d). Other trace macerals, including lipodetrinite, sporinite, vitrodetrinite, fusinite, inertodetrinite and macrinite, are mainly distributed in the mineral matrix. In general, the Damaidi cutinitic liptobioliths exhibit two microscopic structures. The first is the ribbon-like collotelinites are bordered by thin-walled cutinites, that are superposed in parallel (Fig. 6c and d). In this situation, the collotelinites are usually intact and can extend over a long distance. The second microscopic structure is the thin-walled cutinites, collotelinites, and other macerals randomly

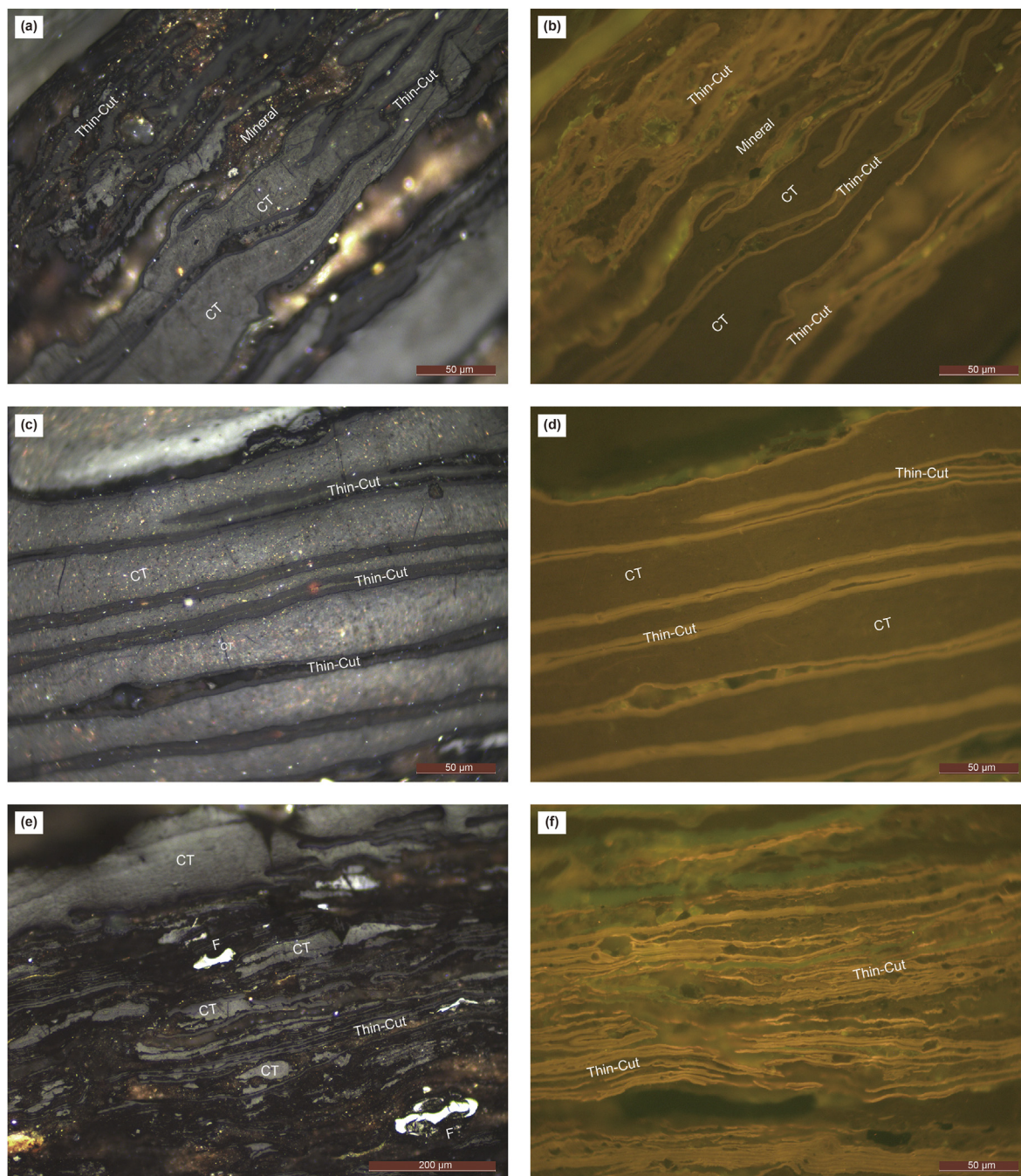


Fig. 6. Microscopic characteristics of the Damaimi Devonian cutinitic liptobioliths (a, b, c-in reflected light and oil immersion; b, d, f-in fluorescent light). Thin-Cut, thin-walled cutinite; CT, collotelinite; F, fusinite.

distributed in the mineral matrix (Fig. 6e and f). In this structure, the cutinites usually present in enterolithic shapes and the collotelinite are commonly fragments.

4.3. Molecular compositions

C_{18} – C_{22} tetracyclic diterpanes are predominant in the saturated fraction of the Devonian cutinitic liptobioliths (Fig. 7). Their concentration in the saturated fraction is 373.97–411.80 $\mu\text{g}/\text{mg}$, while in the liquid extracts, it is 85.85–143.56 $\mu\text{g}/\text{mg}$. These compounds eluted between nC_{18} and nC_{24} and have a same general formula of

C_nH_{2n-6} . Most of them have a key ion or base peak at m/z 123, which has been shown to be a significant fragment for diterpanes (Philp et al., 1981; Richardson and Miller, 1982; Snowdon and Powell, 1982; Noble et al., 1985, 1986). Currently, such compounds mainly include beyeranes, kauranes, phyllocladanes and atisanes. However, in the analyzed samples herein, only the C_{20} tetracyclic diterpanes (molecular weight, 274) have a dozen isomers and their homologues are up to dozens or hundreds, which is far beyond that previous reported (Fig. 8). Six tetracyclic diterpanes (labelled 1 to 6 in Fig. 8) with relatively high abundances were carefully identified by a comparison of their GC retention times and mass spectra

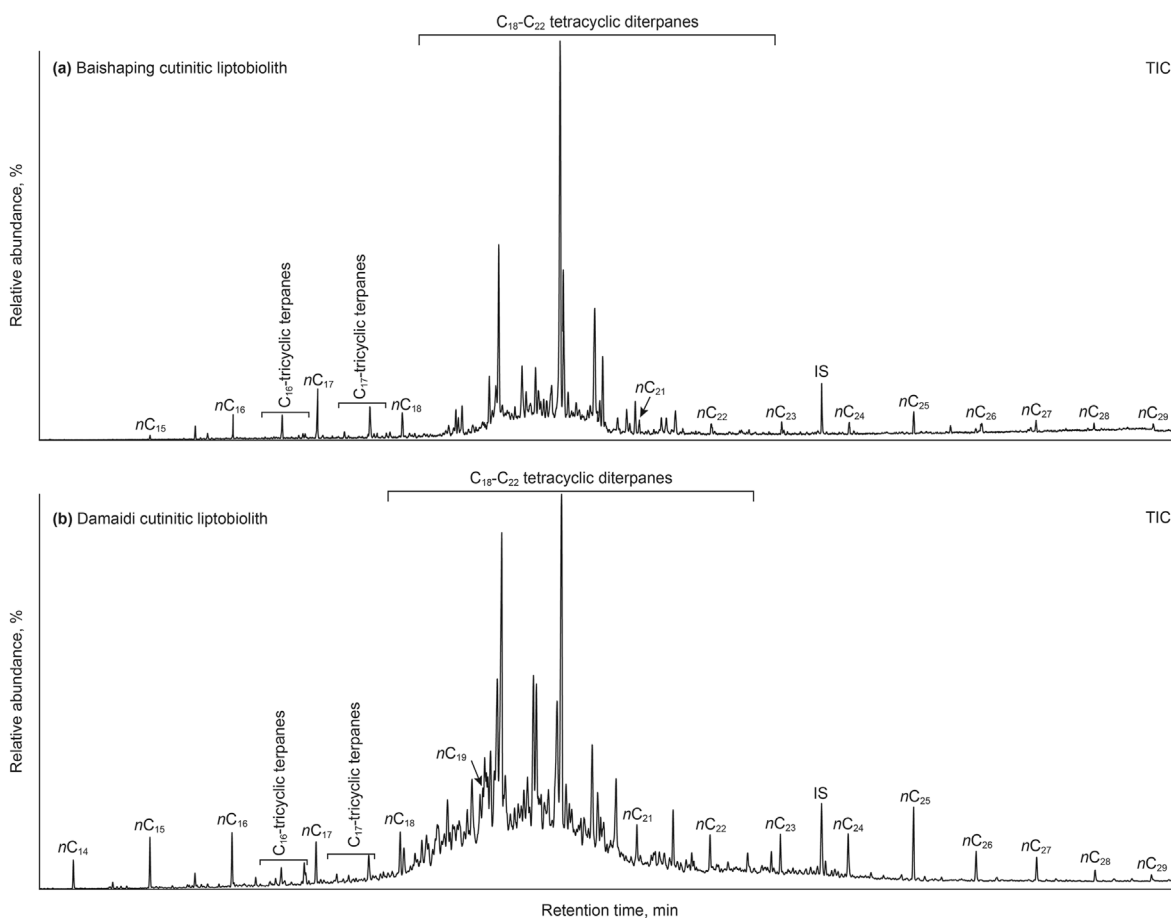


Fig. 7. Representative saturate fraction gas chromatograms of the Baishaping and Damaidi cutinitic liptobioliths. *n*, normal alkanes; *C_i*, carbon number; IS, internal standard.

(Fig. 9) with the external standards and those in previous reports. Of the six identified diterpanes, diterpane 2 are C_{19} demethylated tetracyclic diterpanes with a molecular ion at m/z 260, and the others are C_{20} tetracyclic diterpanes. Diterpane 1 has a base peak at m/z 123, and a remarkable key ion at m/z 245, which was identified as beyerene (Fig. 9). Diterpanes 3 and 6 were identified as $16\beta(H)$ - and $16\alpha(H)$ -kaurane based on their GC retention times and mass spectra, which are characterized by a base peak at m/z 123 and key ions at m/z 231 and 259. The ratio of m/z 231/259 is a diagnostic indicator to distinguish between kauranes and phyllocladanes. The ratio values for diterpanes 3 and 6 are <0.3 , which is a typical feature of kauranes (Noble et al., 1985; Mei et al., 1989). However, it is notable that $16\beta(H)$ -atisane usually co-elutes with $16\beta(H)$ -kaurane under typical GC-MS conditions (Peters et al., 2005). Diterpane 5 has a base peak of m/z 123 and key ions at m/z 189 and 259 (Fig. 9). It was identified as $16\alpha(H)$ -atisane based on its retention time and mass spectra. In general, tetracyclic diterpanes of the $16\beta(H)$ series are more abundant relative to their $16\alpha(H)$ isomers in sedimentary organic matter, because of their stability during catagenesis. In the low-matured Baishaping coals, high abundance of $16\alpha(H)$ -atisane implies a higher abundance of $16\beta(H)$ -atisane present in the samples. Therefore, the diterpane 3 is likely primarily $16\beta(H)$ -atisane, co-eluting with a small proportion of $16\beta(H)$ -kaurane. Considering the high abundance and stability of atisane, the mass spectra of most unknown compounds were interpreted as being based on the atisane skeleton. Diterpane 2 was present in abundance in the analyzed samples, especially in the more mature Damaidi coals. It has a molecular ion at m/z 260, a base peak at m/z

123, and key ions at m/z 175 and 245. It is mostly like to be 17-noratisane. Diterpane 4 has a molecular ion at m/z 274, but its exact structure is speculative because it does not conform to the spectra of other known tetracyclic diterpanes. It has major ions at m/z 109, 161 and 189, which possibly indicate 20-normethylatisane. While all the samples have abundant tetracyclic diterpanes, the liptobioliths from different areas were characterized by different tetracyclic diterpane compositions. The Baishaping coals are mainly composed of C_{20} tetracyclic diterpanes, whereas the Damaidi liptobioliths are dominated by C_{18} – C_{19} nor-homologues. Relative to their C_{20} counterparts, C_{18} – C_{19} nor tetracyclic diterpanes which have fewer side-chains should be more mature stable and resistant to biodegradation.

n-Alkanes, which are usually the predominant constituents of source rock extracts, are present only at a relatively low abundance (Fig. 7). The concentrations of *n*-alkanes in the saturated fraction and liquid extracts are 32.33–81.43 $\mu\text{g}/\text{mg}$ and 6.72–23.86 $\mu\text{g}/\text{mg}$, respectively, both of which are less than one-fifth of the tetracyclic diterpane concentration. The distribution of long-chain *n*-alkanes is characterized by a predominance of C_{25} . Pristane (Pr) and phytane (Ph) are only present in trace amounts. Common steranes and hopanes are below the detection limit. Phenanthrene, chrysene, perylene and their methylated counterparts are detected in all analyzed samples. In addition to these common aromatic compounds, abundant monoaromatic and diaromatic tetracyclic diterpenoids are detected in the aromatic fraction of the Devonian cutinitic liptobiolith. Their carbon numbers are in the range of C_{18} – C_{22} . Especially in the Damaidi liptobioliths, the aromatic

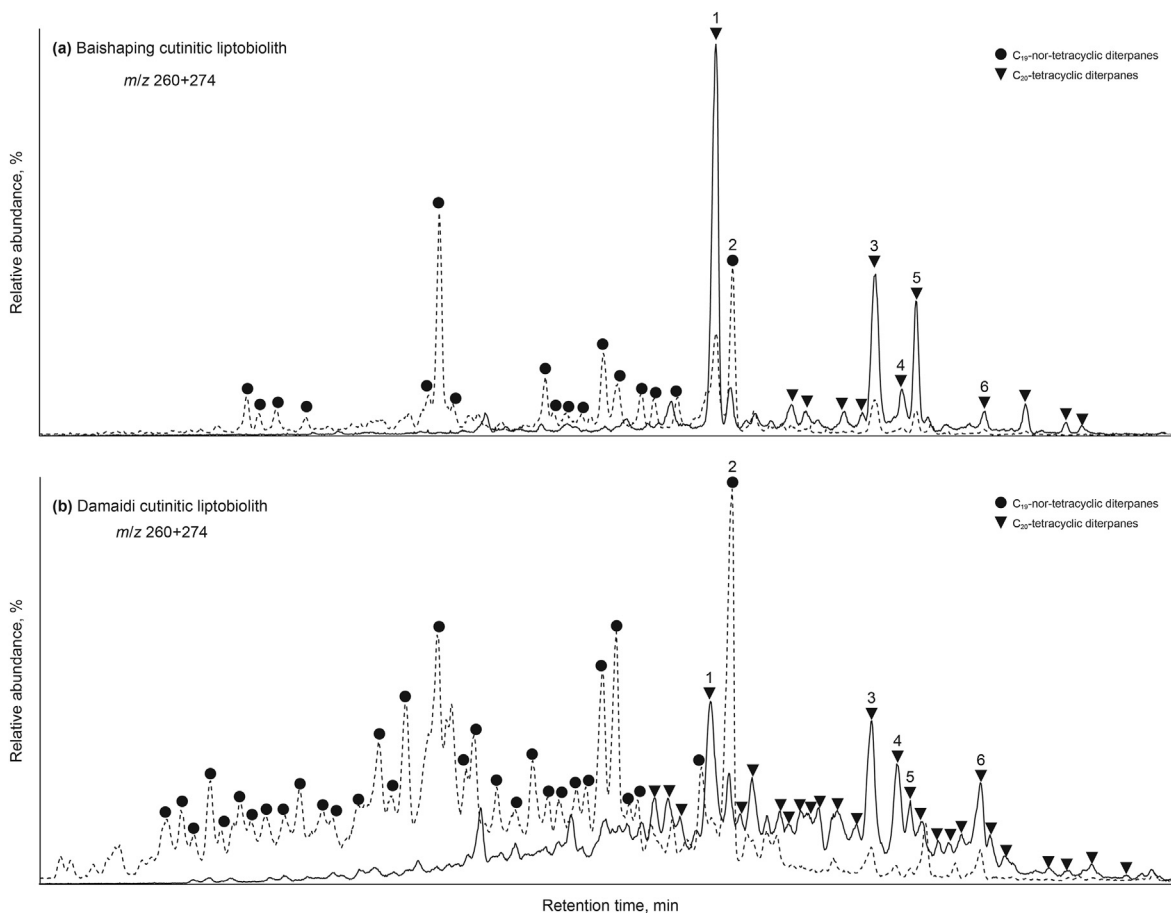


Fig. 8. Representative saturate fraction m/z 260 and 274 chromatograms showing the C_{19} – C_{20} tetracyclic diterpene distribution in the Baishaping and Damaidi cutinitic liptobioliths.

diterpenoids are characterized not only by their high abundance but also by their numerous homologues (Fig. 10). Aromatic diterpenoids may originate by aromatization from tetracyclic diterpanes during diagenesis and catagenesis. The relatively higher maturity of the Damaidi liptobioliths may have resulted in the higher abundance and increased homologues of aromatic diterpenoids.

In the NSO fraction, only a small amount of C_{16} – and C_{18} –monocarboxylic acids was detected. They likely originate from the cutin of plant cuticles.

5. Discussion

5.1. Hydrocarbon generation potential

Coals are generally regarded as gas-prone source rocks, whereas some of them also has the potential to generate oils (Tissot and Welte, 1984). The hydrocarbon generation potential of coals depends on several factors, such as maceral type, depositional environment, microbial activity and maturity (Snowdon, 1995; Wan Hasiyah, 2003). TOC is an indicator for the amounts of organic matter, and is always combined with the S_2 value in order to allow assumptions about the hydrocarbon generation potential. Peters and Cassa (1994) suggested that hydrocarbon generation potential is classified as excellent, very good, good, fair, and poor based on TOC contents and S_2 values. The TOC contents and S_2 values in the analyzed liptobioliths are 40.54%–60.36% and 135.44–362.96 mg/g, respectively, suggesting an excellent hydrocarbon generative potential (Fig. 11a). The nature of hydrocarbon can be obtained from the HI values of the samples. Peters and Cassa (1994) proposed the

following three-fold classification of kerogen: oil-prone (HI > 300), gas and oil-prone (HI = 200–300), and gas-prone (HI = 50–200). The analyzed samples have HI values in the range of 323.65–624.29 mg/g, indicating that the coals are expected to generate commercial liquid hydrocarbons. The conclusion is also supported by the S_2/S_3 vs. TOC diagram (Fig. 11b). Comparatively, the higher TOC contents and S_2 and HI values in the Baishaping liptobioliths indicate a better potential of oil generation relative to that of the Damaidi coals. It has been shown that the Baishaping and Damaidi liptobioliths are of oil-prone Type I-II kerogen (Fig. 3). It is most apparent that the oil-prone nature of the analyzed coals is predominantly attributed to the accumulation of cutinite. A minimum of 15%–20% liptinite content (by volume) of total macerals in sediments is considered as important criteria for a rock to be characterized as a potential oil source rock (Thompson et al., 1985; Hunt, 1991). In the studied samples, the content of cutinite is 56.3%–89.7%, which suggest an excellent potential to generate liquid hydrocarbons of waxy nature.

Thermal maturity not only controls the organic matter residual hydrocarbon generation potential but also determines their products (Peters and Cassa, 1994). The measured R_o values of the Baishaping and Damaidi coals are 0.44%–0.50% and 0.62%–0.69%, respectively. However, the vitrinite reflectance of the cutinitic liptobioliths is suppressed due to the accumulation of cutinites. The T_{max} values for the Baishaping and Damaidi coals range from 434 °C to 442 °C, corresponding to an early to peak oil-window maturity (Peters and Cassa, 1994). This agrees with the presence of the exsudatinite which represents the liquid hydrocarbons, suggesting that oil generation has begun (Pickel et al., 2017).

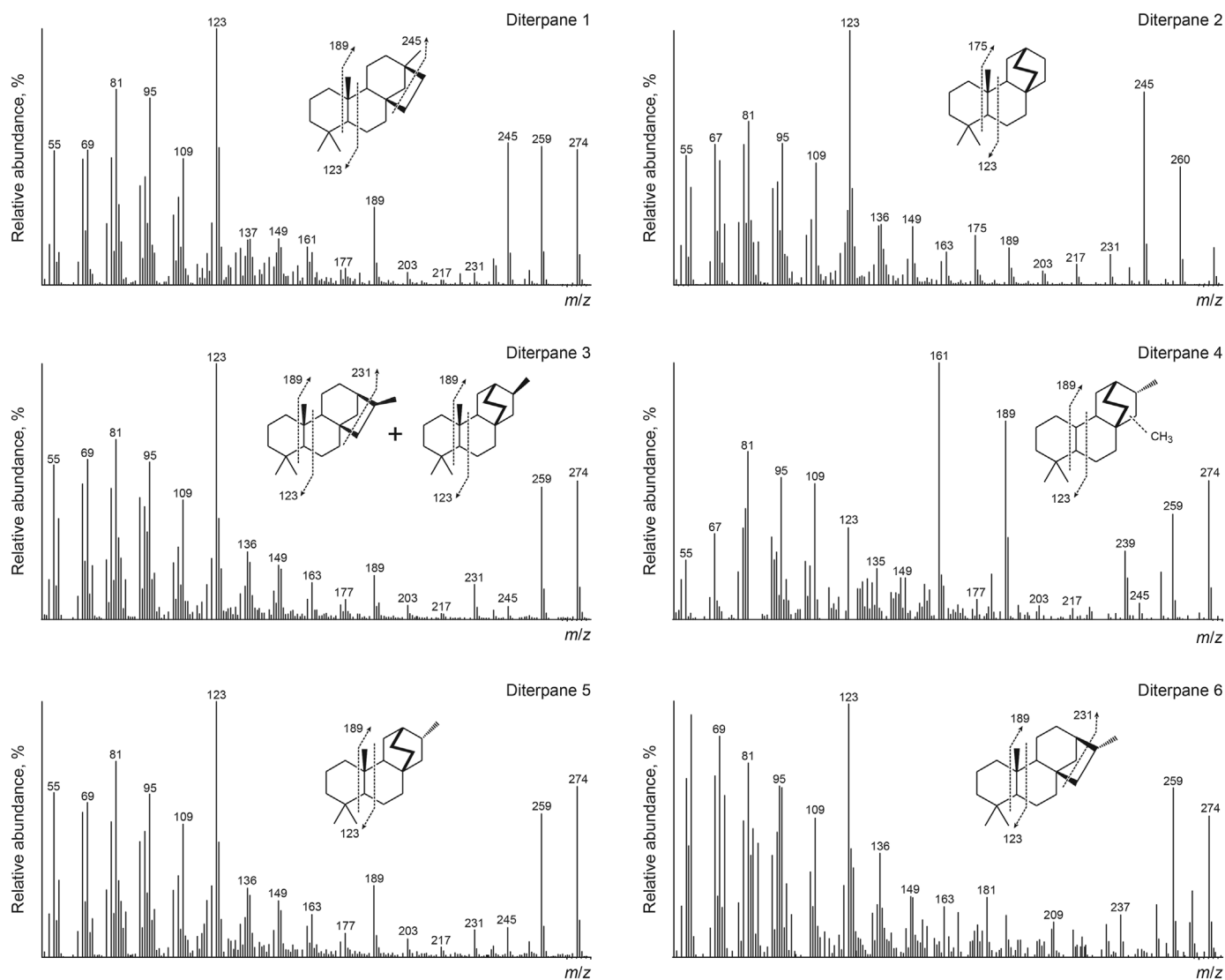


Fig. 9. Mass spectra for the diterpanes 1–6 labelled in Fig. 8.

5.2. Coal formation

The different petrological characteristics between the Baishaping and Damaidi cutinitic liptobioliths indicate a structural variation in the coal-forming plant cuticles and different coal-forming conditions. The thickness and morphology of plant cuticles vary widely among plants, organs and growth stages, as well as the plant growth environment (Heredia, 2003; Jeffree, 2006; Riederer, 2006). Plants grown in a dry and sunny areas usually have thick cuticles, whereas those grew in damp and dark conditions commonly have thin cuticles (Jenks and Ashworth, 1999; Frost-Christensen et al., 2003). As discussed in above, the Baishaping area was closer to the ancient land and at a relatively higher elevation during the Middle Devonian, receiving good sunlight. Plants grown in this area usually have well-developed thick cuticles, which were preserved as thick-walled cutinites in coals. In comparison, the Damaidi area was in a low-lying region, wherein early vascular plants were semiaquatic or submerged in water periodically. These plants usually develop thin cuticles, which were preserved as thin-walled types in sediments (Wang and Han, 1998).

Baishaping area, in the shallow water, may had have a stronger water current. Except for cutinite, the majority of the other unstable

macerals are removed by the water current and only small amounts of them were left and mainly dispersed in the mineral layers. In comparison, the low-lying Damaidi area was likely a still or weak water current environment. Plant tissues accumulated in the stable condition and underwent a severe gelification process, forming a microscopic structure in which collotelinites were bordered by thin-walled cutinites. However, the Damaidi area was also stuck in periodic flows. When these flows came, massive inorganic matter was brought into the peat bog and macerals were broken into pieces, producing a microstructure of maceral fragments dispersed in minerals.

5.3. Composition of early land plant cuticles

Cutinite originates from plant cuticles, which cover nearly all the aboveground parts of terrestrial plants and forms the interface between plant and environment (Riederer, 2006). Plant cuticle is basically composed of cutin and waxes, which are insoluble and soluble, respectively, in organic solvents (Holloway, 1982, 1986; Jeffree, 2006; Goodwin and Jenks, 2005). These waxes, deposited on the surface (epicuticular waxes) or embedded in the cutin matrix (intracuticular waxes), are complex mixtures of homologue

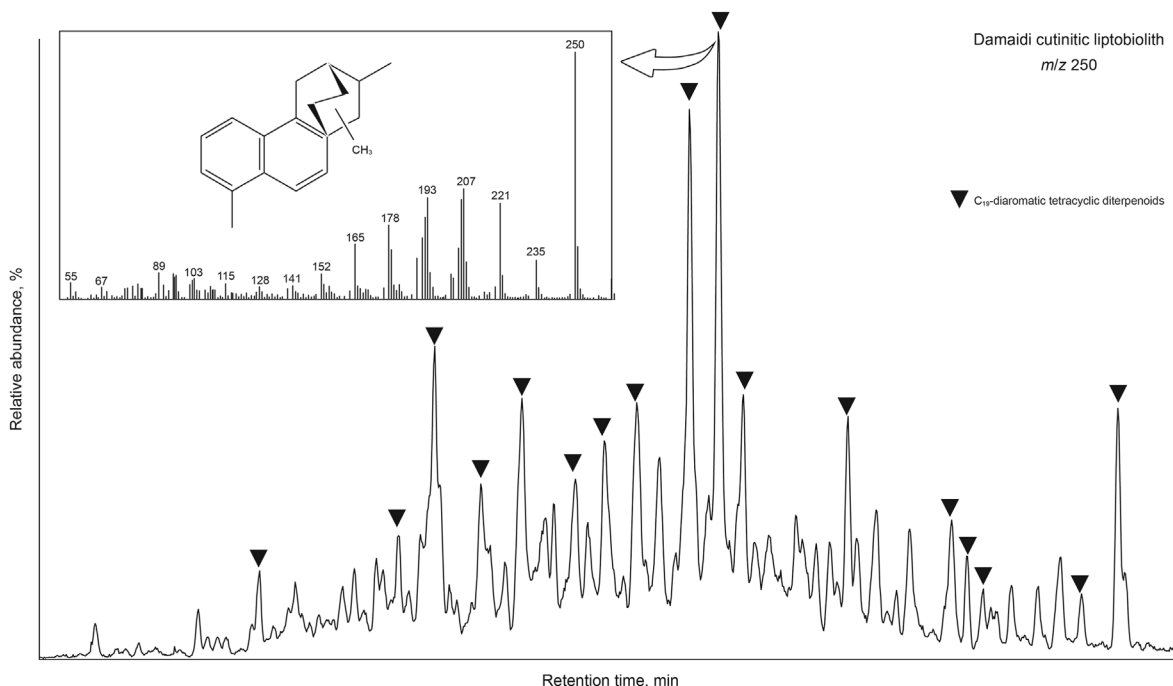


Fig. 10. Representative aromatic fraction m/z 250 chromatograms showing the diaromatic tetracyclic diterpenoid distribution in the Damaidi cutinitic liptobiolith.

series of long-chain aliphatics, such as alkanes, alcohols, aldehydes, fatty acids and esters (Kolattukudy, 1976; Baker, 1982; Holloway, 1984; Bianchi, 1995; Riederer and Markstädter, 1996; Jeffrey, 2006). Cutin is a cross-linked polyester derived from families of C_{16} and C_{18} hydroxy-carboxylic acids (Walton, 1990). The membrane may also contain more chemically resistant, insoluble, high molecular mass material, cutan (Nip et al., 1986; Tegelaar et al., 1989; McKinney et al., 1996), usually in minor amounts. The cutinites usually yield a highly aliphatic signature upon pyrolysis, such that coals containing them would be oil prone (Collinson et al., 1994).

Abundant n -alkanes in source rocks with significant input of land-plant organic matter originate from epicuticular waxes and either are synthesized directly by higher plants or are defunctionalized acids, alcohols, or esters (Tissot and Welte 1984; Peters et al., 2005). n -Alkanes are the predominant constituents of source rock extracts and non-biodegraded oils. Surprisingly, these compounds were only present in small amounts in the Devonian cutinitic

liptobioliths, in which the content of cutinite was >56.3%. The lack of n -alkanes might indicate an undeveloped wax in the early land-plant cuticles. Cuticular waxes coat the outer surfaces of leaves and protect the plant from a variety of environmental pressures (Thompson, 1993), and may directly or indirectly affect the survival and productivity of a plant. The waxes have many functions including reduction of water loss (Schönherr, 1976; Ristic and Jenks, 2002), providing defense against pathogens, diffracting excess light, and increasing resistance to frost damage (Rosenvist and Laaks, 1991). A lack of wax in the cuticles of early land plants is unfavorable for plant survival. An increase in cuticle thickness may be the result of land plant attempting to overcome this disadvantage (Givnish, 1988; Jenks and Ashworth, 1999).

Diterpenoids are abundant in the higher plants. Tetracyclic diterpenoids, i.e., phyllocladanes and kauranes, have been recognized as biomarkers of gymnosperms and their occurrence in Upper Carboniferous coals is attributed to the appearance of the first conifers (Hanson, 1972; Simoneit, 1977; Schulze and Michaelis,

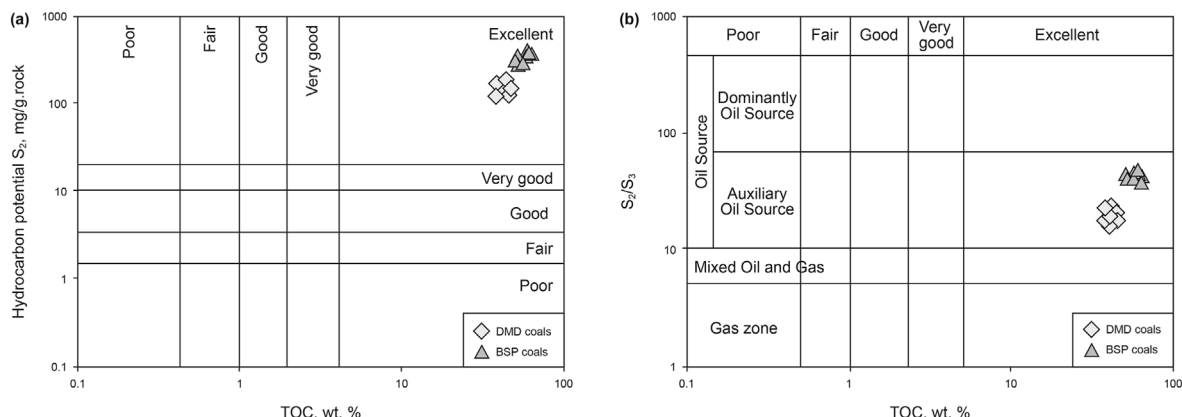


Fig. 11. Plots of TOC versus S_2 (a) and TOC versus S_2/S_3 (b) for the studied samples (modified after Peters and Cassa, 1994).

1990). Sedimentary organic matter derived from higher plant sources often contains low concentrations of diterpenoids, since the Upper Carboniferous (Barrick and Hedges, 1981; Snowdon and Powell, 1982; Philp et al., 1983; Livesy et al., 1984). However, the massive accumulation of tetracyclic diterpanes in the Devonian coals was unexpected because there were no gymnosperms during that time. In fact, abundant tetracyclic diterpenoids were not only present in our samples but also occurred in all the reported Devonian cutinitic liptobioliths, including those from the Luquan and Xinjiang areas (Sheng et al., 1991, 1992; Song et al., 2017), and in the Barzas Basin of Siberia (Kashirtsev et al., 2010). Tetracyclic diterpenoids are assumed to be the dominant soluble parts of Devonian land plant cuticles (Song et al., 2017). The occurrence of massive tetracyclic diterpenoids indicates a distinct composition of the early land plant cuticles, which is markedly different from that of well-known typical land-plant cuticles. The transition from a marine to a terrigenous environment for plant required many molecular adaptations (Waters, 2003). Tetracyclic diterpenoids in the cuticle may be one of the most important molecular adaptations. They might have played an important role in land-plant radiation during the Middle Devonian.

6. Conclusion

The Baishaping and Damaidi Devonian coals are typical cutinitic liptobioliths, with an unusually high cutinite content (>50%) and a distinct papery texture. The coals are characterized by an extremely high yield of volatile matter and high hydrogen content. They are bituminous coals and have a suppressed vitrinite reflectance. Rock-Eval pyrolysis and elemental analysis results indicate that the Devonian cutinitic liptobioliths are dominated by type I-II kerogens within the early to peak oil-window maturity range, and have an excellent potential to generate liquid hydrocarbons. The Baishaping cutinitic liptobioliths are mainly composed of thick-walled cutinites, whereas the Damaidi coals are mainly composed of thin-walled type. The different cutinite types might indicate a structural variation in the coal-forming plant cuticles. Petrological characteristics also suggest two distinct coal-forming conditions for the Baishaping and Damaidi liptobioliths. The molecular biomarkers of the Baishaping and Damaidi cutinitic liptobioliths are dominated by tetracyclic diterpenoids, with a small amount of *n*-alkanes. The molecular compositions of the Devonian cutinitic liptobioliths indicate a distinct composition of early land-plant cuticles, which is significantly different from that of well-known typical land-plant cuticles. Moreover, tetracyclic diterpenoids might be the dominant soluble part of early land-plant cuticles and probably played an important role in land-plant radiation during the Middle Devonian.

Different maturities and intense of secondary alteration also resulted in some geochemical differences between the Baishaping and Damaidi liptobioliths. For example, the tetracyclic diterpenoids in the Damaidi liptobioliths are mainly composed of C₁₈–C₁₉-nor homologues, whereas those in the Baishaping Devonian coals are dominated by their C₂₀ counterparts. Furthermore, relative to the Baishaping Devonian coals, the Damaidi liptobioliths have a higher content of aromatic tetracyclic diterpenoids, a lower hydrogen content and HI index, and weaker fluorescence.

Acknowledgement

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