

Molecular composition and indigenuity of organic matter in Late Neoproterozoic sedimentary rocks from the Yangtze region, South China*

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Abstract Diamicrites from Late Neoproterozoic Nantuo tillites (~600 Ma), and dolomites from the overlying Dousantuo and Dengying formations in the Yangtze region, southern China, were analyzed for solvent extractable hydrocarbons. Even though all these samples have low contents of TOC and have undergone overmature thermal evolution, there has been still preserved quite a large amount of hydrocarbons. Analysis of the extracts by gas chromatography-mass spectrometry (GC-MS) revealed the presence of *n*-alkanes, regular acyclic isoprenoids, tricyclic terpanes, hopanes, gammacerane, steranes, and polyaromatic hydrocarbons. Strict experimental measurements were performed in the analytical procedure to prevent any potential contaminants from being introduced. All these bitumens have molecular markers of Precambrian characteristics and no external organics derived from current contamination events or migrated hydrocarbons from younger strata. The maturity parameters for bitumens indicate that the hydrocarbons are of over-maturity, which is consistent with the thermal maturity of the host rocks. Consequently, it is concluded that the Late Neoproterozoic bitumens in the Yangtze region, South China, are indigenous to their host rocks, which provides the basis for our organic geochemical research on “Snowball Earth” and “Cambrian Explosion.”

Key words indigenuity; contamination; molecular marker; Late Neoproterozoic; Yangtze region

1 Introduction

As a linkage between the biosphere and the geosphere, organic geochemistry, especially molecular markers, has become a powerful tool for investigating important geological events and the evolutionary history of ancient life on Earth (Kvenvolden and Curiale, 1998). The “Cambrian Explosion”—all major taxa appeared simultaneously and very suddenly during the Early Cambrian at about 540 million years ago, is one of the most important life evolutionary events and has become a subject of great concern in

recent years (Gould, 1993; Ridley, 1993; Chen Junyuan et al., 1996). The Late Neoproterozoic global glaciation, which is now commonly interpreted by a “Snowball Earth” hypothesis, has been considered one of the main constraints on the “Cambrian Explosion” (Hoffman et al., 1998; Hoffman and Schrag, 2002; Wang Tieguan et al., 2003). Previous studies reported the composition of biomarkers from the Upper Neoproterozoic rocks sampled from 12 stratigraphic sections in the Yangtze Region, South China (Wang Tieguan et al., 2003). The molecular markers provided essential evidence for the palaeoceanographic environment of “Snowball Earth” age in the Yangtze region, South China.

A common problem encountered in Precambrian molecular marker research is the contamination to rock extracts (Brocks et al., 2003; Peng Ping'an et al.,

1998). Because the concentrations of individual molecules are quite low owing to a low content of organic matter (OM) and its high thermal maturity in Precambrian rocks, especially for diamictites from the Nantuo tillites in this study. They are very easy to be contaminated by external organics either in the field or in laboratory procedures. Moreover, a long geological history may lead to the introduction of allochthonous organic compounds into the samples. Thus, the indiginity will be the basis for our published works and further interpretation in other publications of this study.

2 Geological setting and samples

The Yangtze region is geographically located in South China and is tectonically called the Yangtze Block or the South China Block (Fig. 1). The Yangtze region is characterized stratigraphically by well-developed successions of Upper Neoproterozoic to Lower Cambrian marine strata. The Upper Neoproterozoic strata consist principally of diamictites of the Jiangkou and Nantuo Tillites, Si-, P-, Fe-, Mn-containing rocks of the Datangpo Formation and dolomites of the Doushantuo and Dengying formations (Table 1).

The Late Neoproterozoic glacial units, the Nantuo Tillites, dated at ~600 Ma relevant to the Marinoan ice-ages (Zhang Qirui et al., 2002, Yan Ming et al., 1995), are overlaid with a 1–2 m thick layer of cap dolomite. A total of 27 typical Upper Neoproterozoic sedimentary rock samples were collected from 7 stratigraphic sections, which are distributed respectively in West Hubei, Northwest Hunan, East Chongqing, and South Guizhou, in the Yangtze region, South China (Fig. 1). The lithologies of rock samples are described in Table 1. Of those rock samples, 10

samples were collected from the Nantuo diamictites and 2 from the cap dolomite associated with the Nantuo tillites.

3 Experimental

3.1 Clean laboratory conditions

In order to prevent these samples from being contaminated by external organic matter during laboratory procedures, the following strict measurements have been performed.

3.1.1 Sample preparation

Any potential pollutants on the surface of rock samples were eliminated by means of a grinder, and then, the surface of the remaining rocks was cleaned out with distilled water and dichloromethane in turn in order to ensure all the rock samples against the introduction of organics.

3.1.2 Cleaning of glassware

Both glassware and aluminum foil to be used were successively washed with chromic acid mixture, distilled water and dimethylchloride. After dried, the glassware was baked in an electric furnace at 450°C for 6 hours to keep the glassware under a clean condition.

3.1.3 Purification of solvents, chemicals and other laboratory reagents

Dichloromethane, petroleum ether, methanol and toluene were double distilled. Silica gel, alumina, absorbent cotton, filter paper and copper turnings

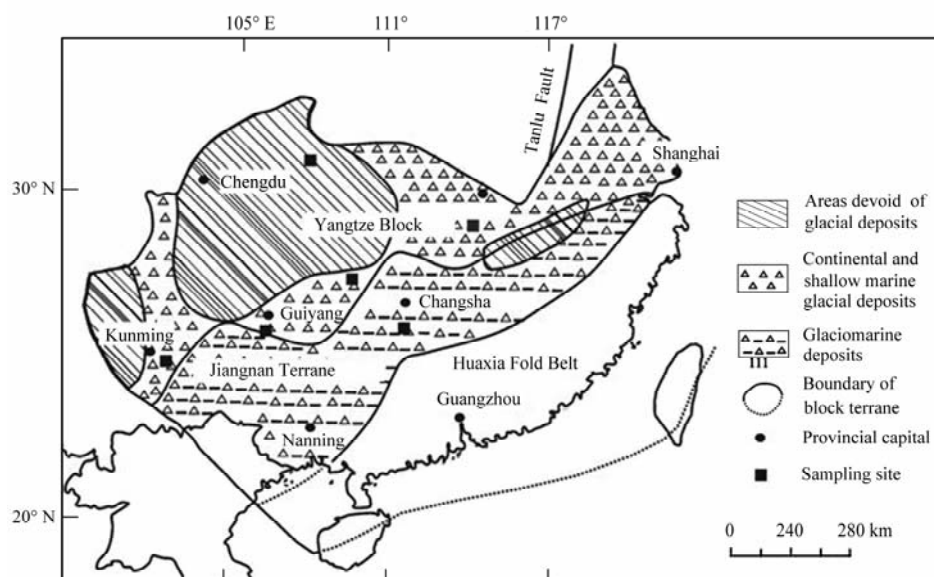


Fig. 1. Distribution of Late Neoproterozoic glacial deposits in the Yangtze region, South China (after Zhang Qirui and Piper, 1997) and the sampling sites in this study.

were Soxhlet extracted with dichloromethane prior to use to make all the solvents and chemicals pure and clean enough.

3.2 Soxhlet extraction and fractionation

Each of the clean and dry rock samples was completely ground into fine powder (<100 mesh). 300 g were Soxhlet extracted with 500 mL of dichloromethane:methanol (83:17 v/v) at 50°C for 72 hours as one run, and low-organic level samples (such as diamictites) had to be multiply run. After desulfurating with copper turnings and deasphalting with petroleum ether, the extract was quantitatively separated into aliphatic, aromatic and N-, S-, O-compound fractions by routine column chromatography on a

silica gel plus alumina (9:1 v/v) column.

3.3 R_o measurement and TOC analysis

All these rock samples were prepared into polished sections. The marine vitrinite (also called “vitrinite-like maceral”) reflectance, $R_{o\text{mv}}$, was measured on each polished section using a Leica Model MPV-SP microscopic photometer, and then the measured $R_{o\text{mv}}$ was converted to the equivalent vitrinite reflectance value (R_o) (Buchardt and Lewan, 1990; Zhong Ningning and Qin Yong, 1995), so that the thermal maturity of OM in the rock samples could be worked out.

The total organic content (TOC) of each rock sample was measured on a WR-112 carbon analyzer

Table 1. Bulk characteristics and extract yields

Sample	Lithology	Mass (g) ^①	TOC (%) ^②	“A” ($\times 10^{-6}$) ^③
Dengying Fr.				
Sandouping, Hubei				
No. 18	Blackish lamellose dolomite	1360	0.42	11.4
No. 17	Black recrystallized dolomite	1370	0.26	8.0
No. 16	Dark gray laminal dolomite	1348	0.12	11.4
No. 15	Blackish argillaceous dolomite	1400	9.37	40.6
Dousantuo Fr.				
Jijiawan, Hubei				
No. 14	Black argillaceous dolomite	837	1.82	19.0
No. 13	Blackish-gray carbonaceous	990	3.63	12.5
No. 12	Gray laminal dolomite	2150	0.08	8.8
No. 6	Cap domolite	1660	0.13	6.7
Weng'an, Guizhou				
w9	Cap domolite	1350	0.23	9.4
w10	Phosphoric & argillaceous silt-crystal-like mudstone & molite	1220	0.18	10.5
Nantuo Fr.				
Jijiawan, Hubei				
No. 5	Diamictite/tillite	2530	0.10	15.3
Tianping, Hunan				
No.28	Diamictite/tillite	388	0.05	16.9
No. 27	Diamictite/tillite	769	0.02	14.8
No. 26	Diamictite/tillite	436	0.07	15.0
Liuchapo, Hunan				
No. 29	Diamictite/tillite	435	0.06	13.0
No. 30	Diamictite/tillite	247	0.06	16.1
Anhua, Hunan				
w3	Gravelly sandy mudstone /tillite	1630	0.11	17.3
w4	Gravelly sandy mudstone/tillite	1330	0.09	9.1
w5	Sandy mudstone/tillite	1093	0.13	8.4
w6	Gravelly sandy mudstone/tillite	944	0.13	3.5
Datangpo Fr.				
Xiushan, Chongqing				
w7	Siliceous & phosphoric ferromanganese rocks	866	0.18	5.7
w8	Siliceous & phosphoric ferromanganese rocks	800	2.51	20.0
w1	Rhodochrosite	700	5.41	7.3
w2	Rhodochrosite	680	3.10	6.4

Note: ① Mass of solvent-extracted rock powder; ② total organic carbon; ③ the yield of Soxhlet extraction.

to determine the OM abundance in all rock samples.

3.4 Gas chromatography (GC)

Gas chromatography (GC) was performed using an Agilent 6890 gas chromatograph with an SE-54 fused silica capillary column (30 m×0.25 mm in inner diameter, 0.25 μm in film thickness). Helium was used as the carrier gas. The oven temperature was initially set at 100°C and programmed to 300°C at 4°C/min, with a final hold at 300°C for 30 minutes. The internal standard—deuterium-substituted tetracosane (C₂₄H₅₀) was co-injected into the gas chromatograph for getting the absolute contents of individual compounds.

3.5 Gas chromatography-mass spectrometry (GC-MS)

Full-scan GC-MS was performed on a Finnigan Model SSQ-710 spectrometer interfaced to a gas chromatograph equipped with a 60-m fused silica capillary column (HP-5MS, 0.32 mm in inner diameter, 0.25 μm in film thickness). Helium was used as the carrier gas. The oven temperature was initially set at 80°C, and programmed to 250°C at 3.5°C/min, then to 310°C at 2°C/min with a final hold of 20 minutes. A scan speed of 1.4 s/scan from 50 to 500 amu was used in the mass spectrometric analysis. Electron ionization was employed (70 eV).

4. Results and discussion

4.1 Bulk characteristics and extract yields

The analyzed samples are significantly different in lithologic character and organic matter, ranging from organic matter-poor diamictites (less than 0.2%) to argillaceous dolomite with up to 9.37% TOC (Table 1). The yields of bitumen obtained by Soxhlet extraction are generally low (Table 1). Even though all these Neoproterozoic sedimentary rocks have undergone a super-mature thermal evolution, there have been still well preserved large amounts of hydrocarbons. The concentrations of saturated and aromatic hydrocarbons vary from 0.51×10^{-6} to 19.29×10^{-6} .

4.2 Bitumen composition

4.2.1 Normal alkanes and regular isoprenoids

A complete homologous series of C₁₁ to C₃₅ *n*-alkanes has been detected from the aliphatic fraction in all the samples analyzed. The distribution of *n*-alkane series shows a bimodal pattern with the 1st major peak appearing at *n*C₁₇. All the samples but No. 5 Nantuo tillite sample have no odd to even

carbon-number predominance with a CPI value lower than 1.25 and OEP value lower than 1.2. Sample No. 5, however, has relatively higher CPI and OEP values (1.41 and 1.31, respectively).

The acyclic isoprenoids pristane (Pr) and phytane (Ph) are very abundant in all bitumens. Pr/Ph ratios are generally lower than 1.0 except those in five samples are slightly higher than 1.0. Both Pr/*n*C₁₇ and Ph/*n*C₁₈ ratios are lower (generally less than 0.6 and 1.0, respectively) except for No. 5 Nantuo tillite sample.

4.2.2 Tricyclic terpanes

m/z=191 mass-chromatograms show that the C₁₉ to C₂₅ tricyclic terpanes are present in all the samples and have a high abundance relative to hopane series (Fig. 2). The distribution patterns, however, are different. C₂₃ is the most abundant homologue in all bitumens from the Nantuo tillite, with C₂₁/C₂₃ ratios being generally lower than 1.0. While all other samples including rocks from the Dengying, Dousantuo and Datangpo formations have the highest concentrations of C₂₁ and C₂₀ homologues and have C₂₁/C₂₃ ratios higher than 1.0.

4.2.3 Hopanes, gammacerane and oleanane

Complete C₂₇ to C₃₅-17α(H), 21β(H)-hopane series have been detected in all the samples (Fig. 2). Regular 17α(H), 21β(H)-hopane (C₃₀-αβ) is the most abundant pentacyclic terpane in all bitumens. C₂₉-αβ/C₃₀-αβ ratios generally vary from 0.45 to 0.55. C₂₇-hopane-related parameter—Ts/(Ts+Tm) ratio is generally from 0.45 to 0.55. The diagenetic rearrangement product 18α(H), 21β(H)-30-norneohopane (C₂₉ Ts) has also been detected in concentrations 1/3 of the C₂₉-αβ hopane. The No. 5 Nantuo tillite sample, however, is quite exceptional with these ratios being 0.15, 0.35 and 1/5, respectively.

Gammacerane has been detected in all the samples with concentration about 1/5 of the C₃₀-αβ hopane. The oleanane, a diagnostic marker for higher plants is absent in all the samples.

4.2.4 Steranes

Steranes, including regular steranes and diasteranes, have been detected in all the samples. Ethyl-cholestane (C₂₉) comprises 30% to 47% of the total C₂₇ to C₂₉-regular steranes; the methyl-cholestane (C₂₈), 17% to 29%; and the cholestane (C₂₇), 28% to 40% (Table 2). Diasteranes derived from diagenetic rearrangement of functionalized steroid precursors (Sieskind et al., 1981) generally increase in abundance relative to regular steranes (Dia/Reg) with increasing clay contents and

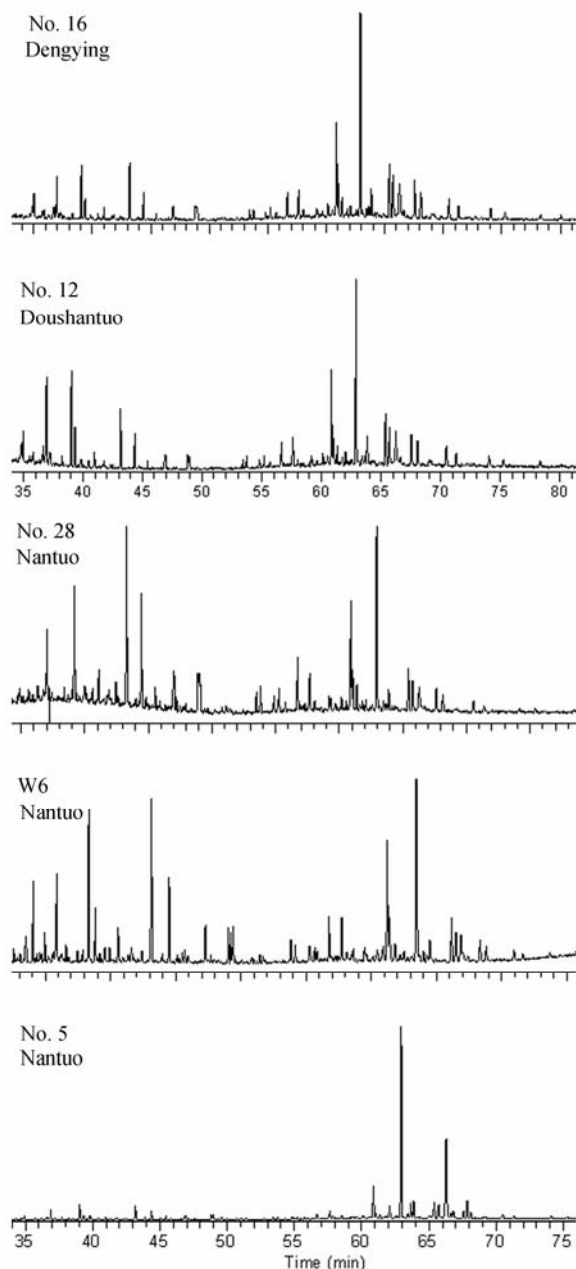


Fig. 2. Distributions of tricyclic terpanes, hopanes and other pentacyclic terpanes in the saturated fraction.

decreasing kerogen contents of the source rock. Dia/Reg might also increase with thermal maturity (Goodarzi et al., 1989). All the samples in this study have relatively low concentrations of diasteranes with C_{27} Dia/Reg ratios varying from 0.15 to 0.48 except for an unusual low value of 0.05 in the No.5 Nantuo tillite sample. The observed values are generally consistent with the clay-poor nature of the dolomite and diamictite lithologies of these samples.

4.2.5 Aromatics

All these samples contain abundant polyaromatic

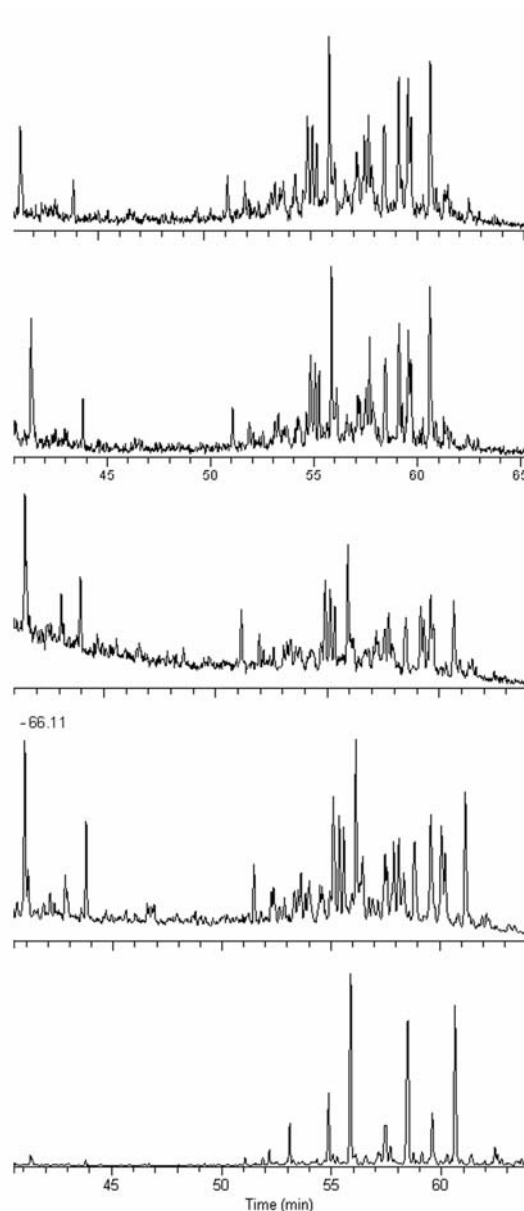


Fig. 3. Distribution of steranes in the saturated fraction.

hydrocarbons (PAH). Mono- to tricyclic aromatics including naphthalene, phenanthrene, dibenzothio-*phene*, dibenzofuran, and fluorene series are relatively high in concentrations, and many related parameters can be calculated (Table 3).

4.3 Possible contamination sources and arguments for indigency

4.3.1 Possible contaminating in the sampling process

Even though the rocks were collected from 7 sections in 4 provinces several hundred kilometers apart during several field trips by different workers, all these samples have molecular markers with

apparent Precambrian characteristics. If the hydrocarbons detected in these samples were introduced during the sampling process including outcrop handling, packing, transport and storage in different field trips, they could not have so consistent characteristics. Furthermore, any potential pollutants on the surface of rock samples were cut off by a grinder machine, and then, the surface of remaining rocks was cleaned out with distilled water and dichloromethane in turn. Thus, contamination in the sampling process can be ruled out.

4.3.2 Organic compounds introduced by subsurface biologic activity or circulating water

Subsurface biologic activity or circulating water might have introduced organic compounds in to ancient Neoproterozoic rocks. The hydrocarbons extracted from these samples, however apparently have a thermally mature hydrocarbon signature. As an typical exception, the Nantuo tillite No. 5 sample clearly have immature saturated hydrocarbon characteristics, which might be derived from immature biolipids. Thus, most part of the extracted hydrocarbons were not contaminated by organic compounds introduced by subsurface biologic activity or circulating water.

4.3.3 Contaminations in laboratory and strict laboratory procedure

Table 2. Molecular parameters calculated based on saturated hydrocarbons

	Hopanes ^①					Steranes ^②					
	C ₂₉ /C ₃₀	C ₂₉ Ts/C ₂₉	Ts/(Ts+Tm)	C ₃₁ S/(S+R)	C ₂₁ /C ₂₃	C ₂₉ ββ/(ββ+αα)	C ₂₉ S/(S+R)	Reg C ₂₇ (%)	Reg C ₂₈ (%)	Reg C ₂₉ (%)	C ₂₇ Dia/Reg
Dengying Fr.											
Sandouping, Hubei											
No.18	0.41	0.41	0.46	0.54	1.86	0.39	0.43	37	17	46	0.15
No.17	0.40	0.32	0.48	0.53	1.51	0.34	0.42	39	23	38	0.18
No.16	0.44	0.33	0.49	0.57	0.91	0.39	0.42	35	20	45	0.25
No.15	0.45	0.32	0.45	0.57	1.45	0.42	0.47	32	29	38	0.24
Dousantuo Fr.											
Jijiawan, Hubei											
No.14	0.45	0.38	0.46	0.56	2.22	0.41	0.28	36	22	41	0.26
No.13	0.47	0.32	0.44	0.56	1.56	0.38	0.45	37	23	40	0.18
No.12	0.44	0.31	0.43	0.57	1.44	0.38	0.39	34	21	45	0.23
No.6	0.49	0.41	0.47	0.57	1.60	0.37	0.47	39	20	42	0.27
Weng'an, Guizhou											
w9	0.58	0.34	0.49	0.60	1.09	0.42	0.51	35	28	37	0.25
w10	0.58	0.34	0.52	0.59	1.79	0.42	0.47	38	26	36	0.32
Nantuo Fr.											
Jijiawan, Hubei											
No.5	0.15	0.20	0.35	0.57	0.91	0.26	0.07	34	35	31	0.05
Tianping, Hunan											
No.28	0.50	0.36	0.53	0.56	0.92	0.41	0.43	36	24	40	0.41
No.27	0.49	0.38	0.51	0.56	0.66	0.42	0.44	35	25	40	0.39
No.26	0.54	0.38	0.55	0.57	0.68	0.42	0.45	40	24	36	0.40
Liuchapo, Hunan											
No.29	0.53	0.37	0.54	0.70	0.71	0.40	0.44	43	24	33	0.48
No.30	0.50	0.39	0.52	0.57	0.48	0.44	0.47	37	25	38	0.44
Anhua, Hunan											
w3	0.47	0.31	0.51	0.59	1.01	0.40	0.48	31	25	44	0.19
w4	0.57	0.35	0.51	0.61	1.02	0.41	0.47	40	23	37	0.28
w5	0.57	0.35	0.50	0.62	0.85	0.40	0.50	36	26	38	0.20
w6	0.55	0.34	0.52	0.59	0.85	0.41	0.48	37	25	39	0.24
Xiangmeng Fr.											
Xiushan, Chongqing											
w7	0.45	0.40	0.54	0.60	1.09	0.37	0.44	29	27	44	0.18
w8	0.51	0.32	0.50	0.61	1.51	0.39	0.48	32	25	43	0.29
w1	0.49	0.34	0.50	0.63	1.78	0.41	0.51	31	27	42	0.20
w2	0.47	0.37	0.53	0.60	1.31	0.41	0.52	28	25	47	0.22

Note: ① The definition of hopane biomarker ratios: C₂₉/C₃₀=C₂₉-αβ/C₃₀-αβ; C₂₉-Ts/C₂₉=C₂₉-Ts/C₂₉-αβ; C₃₁S/(S+R)=C₃₁-αβ-22S/(C₃₁-αβ-22S+C₃₁-αβ-22R); C₂₁/C₂₃=C₂₁-13β(H), 14α(H)-tricyclic terpane/C₂₃-13β(H), 14α(H) tricyclic terpane; ② the definition of sterane biomarker ratios: C₂₉ββ/(ββ+αα)=C₂₉-αββ/(C₂₉-αββ+C₂₉-ααα); C₂₉S/(S+R)=C₂₉-ααα-20S/(C₂₉-ααα-20S+C₂₉-ααα-20R); RegC₂₇(%)=(C₂₇ααα-20[S+R] and αββ-20[S+R])/(Σ C₂₇ to C₂₉ααα-20[S+R] and αββ-20[S+R]) [RegC₂₈(%) and RegC₂₉(%) are defined according to RegC₂₇(%)]; C₂₇Dia/Reg=C₂₇βα-diasteranes/(C₂₇-ααα and αββ-steranes).

Table 3. Molecular geochemical parameters calculated based on aromatic hydrocarbons^①

	MPR	MPI-1	MPDF	Phen/MP	MNR	DNR-1	TNR-1	TNR-2	MDR	DMDR-1	DMDR-2
Dengying Fr.											
Sandouping, Hubei											
No.18	2.20	0.20	0.67	4.76	0.90	4.78	1.17	0.92	20.46	5.83	2.68
No.17	1.98	0.36	0.64	2.28	1.57	3.13	1.64	1.10	15.40	4.48	2.26
No.16	1.31	0.23	0.58	3.35	1.97	3.53	1.39	1.00	10.00	3.04	1.61
No.15	1.46	0.71	0.70	1.18	2.97	17.04	1.43	0.80	10.28	2.96	1.62
Dousantuo Fr.											
Jijiawan, Hubei											
No.14	2.19	0.18	0.66	5.24	1.27	3.82	1.07	0.87	17.94	3.81	2.24
No.13	2.84	0.25	0.70	3.92	1.11	5.06	1.01	0.86	43.30	5.14	2.94
No.12	1.61	0.21	0.61	3.94	1.01	3.46	1.17	0.92	5.65	1.65	1.05
No.6	2.00	0.17	0.64	5.22	1.51	2.66	0.88	0.77	6.08	2.30	1.25
Weng'an, Guizhou											
w9	0.57	0.44	0.37	0.62	3.59	12.37	1.86	0.93	19.21	7.62	1.78
w10	1.72	0.33	0.61	2.38	1.82	5.99	3.02	1.35	20.05	5.69	3.01
Nantuo Fr.											
Jijiawan, Hubei											
No.5	1.49	0.19	0.60	4.44	1.11	4.33	0.92	0.79	5.85	2.97	1.34
Tianping, Hunan											
No.28	1.70	0.47	0.61	1.54	1.85	2.41	1.89	1.07	3.86	2.34	1.30
No.27	1.68	0.30	0.60	2.58	2.55	*	2.26	1.29	4.41	2.50	1.37
No.26	1.65	0.32	0.59	2.40	2.38	*	*	*	3.95	2.12	1.30
Liuchapo, Hunan											
No.29	1.65	0.42	0.48	2.77	1.65	10.27	3.27	1.57	3.79	2.20	1.33
No.30	1.59	0.58	0.59	2.52	2.22	10.13	4.05	1.74	4.42	2.33	1.27
Anhua, Hunan											
w3	0.74	0.32	0.62	2.77	1.49	10.58	1.28	1.02	4.66	2.29	1.19
w4	0.67	0.33	0.61	1.78	1.65	8.84	1.36	1.03	4.17	2.94	1.11
w5	0.61	0.28	0.60	1.16	1.81	5.43	1.30	0.97	3.85	1.95	1.07
w6	0.66	0.33	0.46	1.61	1.54	6.31	1.46	0.96	3.70	2.17	1.14
Xiangmeng Fr.											
Xiushan, Chongqing											
w7	1.20	0.37	0.49	1.46	1.17	6.03	1.27	1.00	3.12	1.31	1.11
w8	0.87	0.29	0.43	1.67	1.64	3.37	1.02	0.77	1.85	*	*
w1	3.41	0.93	0.71	0.87	1.39	5.26	14.28	2.31	8.14	3.34	1.70
w2	0.88	0.23	0.49	2.76	1.50	5.30	0.80	0.71	1.92	*	*

Note: ① Compound abbreviations: Naph. naphthalene; MN. methylnaphthalene; DMN. dimethylnaphthalene; TMN. trimethylnaphthalene; Phen. phenanthrene; MP. methylphenanthrene; DMT. dibenzothiophene; and MDBT. methyl dibenzothiophene. Aromatic parameters are defined as follows: $MPR=2\text{-MP}/1\text{-MP}$; $MPI-1=1.5 \times (2\text{-MP}+3\text{-MP})/(Phen+1\text{-MP}+9\text{-MP})$; $MPDF=(\text{methylphenanthrene distribution factor})=(3\text{-MP}+2\text{-MP})/(3\text{-MP}+2\text{-MP}+9\text{-MP}+1\text{-MP})$; $Phen/MP=\text{phenanthrene}/(2\text{-MP}+3\text{-MP}+9\text{-MP}+1\text{-MP})$; $MNR=2\text{-MN}/1\text{-MN}$; $DNR-1=(2, 6\text{-DMN}+2, 7\text{-DMN})/(1, 5\text{-DMN})$; $TNR-1=2, 3, 6\text{-TMN}/(1, 3, 5\text{-TMN}+1, 4, 6\text{-TMN})$; $TNR-2=(1, 3, 7\text{-TMN}+2, 3, 6\text{-TMN})/(1, 3, 5\text{-TMN}+1, 3, 6\text{-TMN}+1, 4, 6\text{-TMN})$; $MDR=4\text{-MDBT}/1\text{-MDBT}$; $DMDR-1=(4, 6\text{-DMDBT})/(1, 4\text{-DMDBT})$; $DMDR-2=(2, 4\text{-DMDBT})/(1, 4\text{-DMDBT})$. * Not measured or not detectable.

Another main source of contaminants are derived from laboratory. In this study, all glassware and aluminum foil used were successively washed by chromic acid mixtures, distilled water and dimethylchloride and then baked in an electric furnace at 450°C for 6 hours. All solvents, chemicals and other laboratory materials were Soxhlet extracted with dichloromethane prior to use. The strict laboratory procedure can effectively prevent these rocks and bitumens from organic contamination during analysis.

4.3.4 Migrated hydrocarbons from younger formations and comparison of bitumen maturity and thermal history of the host rocks

Hydrocarbons expelled from a younger Lower Cambrian source might have migrated into the Dengying, Dousantuo and Nantuo formations. In comparison, 12 Lower Cambrian rocks are also analyzed in our study, which have clearly different organic geochemical signature, for example, relatively lower thermal maturity, higher absolute Pr plus Ph concentrations and higher Pr/Ph ratios (unpublished

Table 4. Aromatic maturity parameters, measured and calculated vitrinite reflectance for part samples

	MPR ^①	MPI-1	MPDF	Phen/MP	R_{0MV} (%) ^②	R_0 (%) ^③	$Rc1$ (%) ^④	$Rc2$ (%) ^⑤
No. 18	2.20	0.20	0.67	4.76	2.33	2.13	2.89	2.18
No. 17	1.98	0.36	0.64	2.28	2.64	2.42	2.80	2.08
No. 16	1.31	0.23	0.58	3.35	2.61	2.39	2.87	2.16
No. 14	2.19	0.18	0.66	5.24	2.91	2.66	2.90	2.19
No. 13	2.84	0.25	0.70	3.92	2.94	2.70	2.86	2.15
No. 12	1.61	0.21	0.61	3.94	2.11	1.93	2.88	2.17
No. 6	2.00	0.17	0.64	5.22	2.40	2.20	2.91	2.20
No. 5	1.49	0.19	0.60	4.44	2.66	2.44	2.90	2.19
No. 27	1.68	0.30	0.60	2.58	2.25	2.06	2.83	2.12
No. 26	1.65	0.32	0.59	2.40	2.73	2.50	2.83	2.11
W8	0.87	0.29	0.43	1.67	2.37	2.17	2.84	2.13
W1	3.41	0.93	0.71	0.87	2.32	2.12	2.49	1.74
Beibuwan Basin Tertiary ^⑥							$Rc3$ (%) ^⑦	
M1	0.96	0.62	0.46	0.56		oil window	0.77	
Fc1	0.97	0.68	0.45	0.43		oil window	0.81	
M2	0.98	0.63	0.46	0.56		oil window	0.78	

Note: ① Aromatic parameters are defined in Table 2; ② R_{0mv} = measured marine vitrinite reflectance; ③ equivalent R_0 value $R_{0mv}=1.082 \times R_{0mv} + 0.025$ ($2\% < R_0 < 5\%$) (Buchardt and Lewan 1990; Zhong Ningning and Qin Yong, 1995); ④ calculated vitrinite reflectance equivalent $Rc1(\%) = -0.55 \times (MPI-1) + 3.0$ (Eqn. 5 in Boreham et al., 1988, for $Rm > 1.35\%$); ⑤ calculated vitrinite reflectance equivalent $Rc2(\%) = -0.60 \times (MPI-1) + 2.3$ (Radke and Welte, 1983, for $Rm > 1.35\%$); ⑥ Tertiary lacustrine mudstone sourced oils in Beibuhai Basin, South China Sea; ⑦ calculated vitrinite reflectance equivalent $Rc3(\%) = 0.6 \times MPI-1 + 0.4$ (Radke and Welte, 1983, for $0.65\% < Rm < 1.35\%$).

data). Therefore, hydrocarbon in Neoproterozoic migrating from overlying Lower Cambrian is unlikely.

Peters and Moldowan (1993) provided four principal tests to judge the indiginity of bitumen. Here we compare the thermal maturity of the bitumen with the level of thermal maturity of the host rock to certificate the indiginity of the bitumens.

Sterane and Hopane ratios are conventionally used to assess thermal maturity apparently reach their end-values within the oil-generation window and therefore cannot be used to evaluate overmature bitumens in this study. However, they can be used to assess contaminations from less mature organic matter. For example, the Nantuo tillite No.5 sample have much lower C_{29} -sterane isomer ratios $20S/(20S+20R)$ and $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ of 0.07 and 0.26, respectively. These two isomer ratios have reported thermal equilibrium values of ~ 0.55 and ~ 0.70 respectively, which can reached close to the peak of oil generation (Peters and Moldowan, 1993). Both $20S/(20S+20R)$ and $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ ratios in Neoproterozoic rocks from Yangtze region did not get to the equilibrium value (Table 2), which are not apparently consistent

the overmature signature of these bitumens. Similar phenomenon was discovered by other authors in Precambrian research, for example, Brocks et al. (2003) in the molecular fossils study of 2.78 to 2.45 billion-year-old rocks. Furthermore, inversion of $20S/(20S+20R)$ and $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ to lower values was observed in pyrolysis experiments at temperature above 300°C (Peters et al., 1990).

The epimer ratio $22S/(22S+22R)$ for $\alpha\beta$ -homohopane have all got to the thermodynamic end point value of 0.55 to 0.60 including the Nantuo tillite No. 5 sample. The epimer ratios $22S/(22S+22R)$ for extended $\alpha\beta$ -homohopanes reach equilibrium at the early oil-generative stage (Peters and Moldowan, 1993). Quite abundant C_{29} and C_{30} moretanes which are generally present in much higher concentration in immature and low mature bitumens also occurred in Nantuo tillite No. 5 sample (Fig. 2).

The CPI and OEP values of n -alkanes in most of the samples are lower than 1.20, which indicate mature thermal maturity. The Nantuo tillite No. 5 sample, however, have much higher values, which imply less thermal maturity.

Ratios of aromatics and dibenzothiophenes are frequently used to assess petroleum maturity. But the behavior of aromatic isomer ratios in overmature source rocks is poorly understood. At very high maturities, some ratios have been shown to reverse trends (Radke et al., 1982a). So using aromatics to evaluate the bitumen maturity is limited. However, the assemblage of some ratios, for example methylphenanthrene index (MPI-1), the Methylphenanthrene Distribution Factor (MPDF) and the unsubstituted to monomethylated phenanthrenes (Phen/MP) might be used to indicating overmature bitumen.

MPI-1($1.5 \times [2\text{-MP} + 3\text{-MP}] / [\text{Phen} + 1\text{-MP} + 9\text{-MP}]$) apparently reaches its maximum value at a vitrinite reflectance equivalent to $R_o \approx 1.7\%$ and then decrease with higher maturities (Boreham et al., 1988; Radke et al., 1982b). This trend "reversal" is related to demethylation of methylphenanthrene to phenanthrene. So low MPI-1 values can be indicative of immature or highly mature bitumen, but a revised MPI-1 can be recognized by high Phenanthrene/Methylphenanthrene ratios. The MPI-1 of all these bitumens are much lower, ranging from 0.17 to 0.47 except higher than 0.50 in three samples. The MPDF, however, is generally higher than 0.60 and the Phen/MP is much higher than 1.0. Similar results were also discovered by Brocks et al. (2003) in the study of Archean bitumens. As comparison, corresponding parameters of three oils sourced from Tertiary lacustrine mudstone in Beibuwan Basin, South China Sea and generated within the oil-generation window, are also listed in Table 4. All these three oils have relatively higher MPI-1 (0.62 to 0.68), but the MPDF is as lower as 0.46, and the Phen/MP ratio is especially lower (0.43 to 0.56).

The marine vitrinite reflectance ($R_{o, mv}$) of part samples and the equivalent vitrinite reflectance R_o values calculated on the basis of empirical formula (Burchardt and Lewan, 1990; Zhong Ningning and Qin Yong, 1995) are listed in Table 4. These rocks have a R_o value of 1.93 to 2.70, corresponding to wet gas phase. The calculated vitrinite reflectance equivalent R_{c1} based on the formula of Boreham et al. (1988) and the calculated vitrinite reflectance equivalent R_{c2} based on Radke and Welte (1983) are also listed for comparison. Considering $\pm 0.20\%$ measurement error, the maturity of the bitumen are generally consistent with that of the host rocks.

4.3.5 Comparison with Precambrian research by other authors

Since contamination in Precambrian rock extracts is a common phenomenon, the indiginity tests would have to be conducted in any organic geochemical research on Precambrian rocks. In order to prevent

these Precambrian rocks from external organic compounds contaminating, strict clean laboratory measurements have been carried out in analytical procedure (e.g. Brocks et al., 2003, Li Chao et al., 2003, Peng Ping'an et al., 1998). In this study, the analytical procedure we designed was referred to above literatures and others, even stricter in some aspects. The extracts generally have signatures of Precambrian molecular markers.

4.3.6 The unusual composition of Nantuo tillite sample No. 5

The sample No. 5 of Nantuo tillite has unusual molecular markers. The maturity parameters indicate the hydrocarbons have only undergone immature thermal evolution. Thus this sample is contaminated by external organic compounds and the extracts were not generated by the host rock. Therefore, this sample should be eliminated in study.

5 Conclusions

All possible contamination sources for Upper Neoproterozoic sedimentary rocks from Yangtze region in analytical procedure are discussed. The strict clean laboratory conditions can prevent any potential contaminations in extractable hydrocarbons. The characteristics of molecular markers indicate that the bitumens were not contaminated by current contamination.

The maturity parameters of bitumen indicate that the hydrocarbons have overmaturity, which is consistent with the thermal maturity of the host rocks. Consequently, it is concluded that the bitumens of Late Neoproterozoic in Yangtze region, Southern China is indigenous to their host rocks, which forms the basis for our molecular organic geochemical research on "Snowball Earth" and "Cambrian Explosion".

Acknowledgements We thank Professor Chen Junyun, Zhu Maoyan (Nanjing Institute of Geology & Paleontology, CAS), Zhang Qirui, Chu Xuelei (Institute of Geology & Geophysics, CAS) for providing rock samples, fieldwork supports and constructive comments. We acknowledge Zhu Lei and Shi Quan for their laboratory work.

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