SPECIAL REPORT

Initial organic geochemical investigation on Late Neoproterozoic-Early Cambrian sediments in the Yangtze region, China*

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Abstract Totally 19 samples of typical Upper Proterozoic-Lower Cambrian sedimentary rocks were collected and analyzed for an organic geochemical investigation. Almost all these rocks have high TOCs, super-maturities and similar biomarker distribution. As an exception, however, the Sinian Nantuo Tillite shows much lower TOCs and little phytane and pristane in comparison with those in other strata, which implies a very faint photosynthetic process, and a restricted euphotic zone and quite limited sunlight within the sedimentary water column during the Sinian glaciation age in the western Yangtze region providing an evidence for palaeo-oceanic environment of the Neoproterozoic Snowball Earth age.

Keywords: Late Neoproterozoic, Early Cambrian, molecular organic geochemistry, euphotic zone, Snowball Earth, Yangtze region.

Cambrian bioradiation was a revolutionary event during the bio-history[1]. The palaeo-oceanic environmental conditions of Late Neoproterozoic global glaciation or snowball earth age[2,3] may be one of the important constraints on the bioradiation and also on bio-history. As an initial result of the Sino-German Cooperative Program, "From Snowball Earth to the Cambrian Bioradiation", the authors would like to report some significant information on the source input, palaeo-oceanic environment, maturity of sedimentary organic matter for the bioradiation event and the Neoproterozoic snowball earth on the basis of a molecular organic geochemical study.

1 Samples and experimental

Totally 19 samples of typical Late Neoproterozic-Early Cambrian sediments, which include drill cores and outcrop rocks, were collected from the western Yangtze region, south China (Fig. 1 and Table 1). These rock samples were investigated by geochemical and petrological techniques. All these samples were measured for marine vitrinite (i. e. also called as vitrinite-like macerals) reflection R_{omv} under a microscopic photometer[4], and also, analyzed by TOC analyzer, gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) after sample preparation of organic solvent extraction and fraction separation.

In order to prevent these samples from external organic matter contaminating, all solvents must be double-distilled, rock samples be cleanned up by distilled water and dimethylchloride, and also, glasswares be washed by chromic acid mixture, distilled water and dimethylchloride in turn, and then baked at 450 ℃ before the extraction was performmed.

2 Results and discussion

Based on the measurement of marine vitrinite reflectance R_{omv}[4~6], the equivalent vitrinite reflectance R_o values were caculated[6], which refer these Upper Neoproterozoic-Lower Cambrian sedimentary rocks to a super-mature phase, with R_o values from 2.00% ~ 3.50% (Table 1)[6], in the western Yangtze region. In comparison, the Early Cambrian sedimentary organic matter shows a relatively low maturity with R_o values 2.00% ~ 2.31% in Chengjiang (Yunnan) and Ningqiang (Shanxi),

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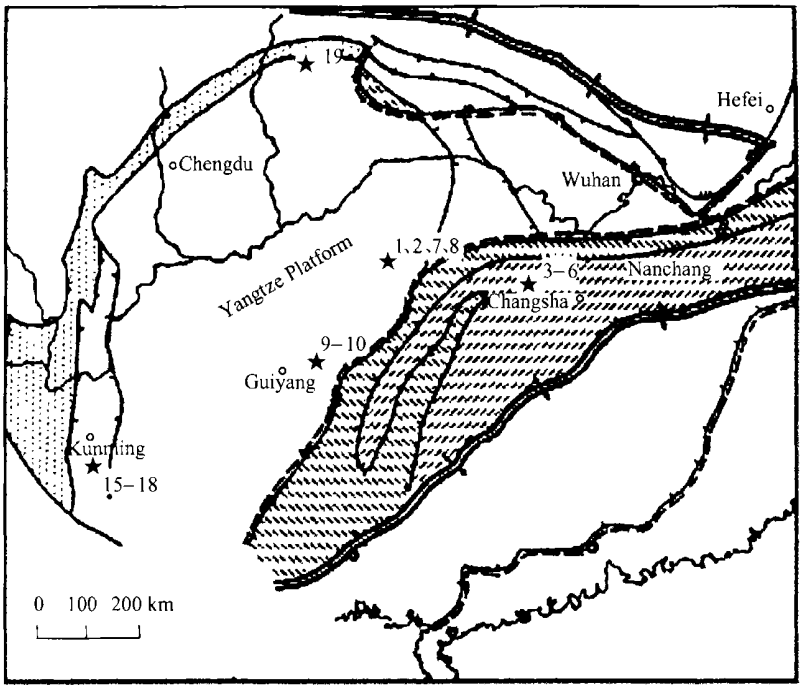

Fig. 1. Tectonic framework and sampling sites in the western Yangtze region. Stars indicate the sampling sites and sample Nos. 1 ~ 19 are the same as in Table 1.

Table 1. Typical Pt_{3-1} sedimentary rock samples, TOC and Ro data

Stratigraphy			Sample No.	Lithology[a)]	Location	TOC (%)	Ro_{mv}[b)] (%)	Ro[d)] (%)
Series	Formation							
Cambrian	1ya Yuanshan		16 ~ 18	Silty ferromanganese rocks	Chengjiang, Yunnan	1.03 ~ 3.08	2.48 (21)[c)]	2.31
	1ms Meishucun		19	Phosphoric limestone	Ningqiang, Shanxi	0.40	2.14 (4)	2.00
Sinian	Z_{ds} Doushantuo		9 ~ 10	Phosphoric & pelitic silt-crystal-like mud-stone & dolomite	Wengan, Guizhou	0.18 ~ 0.23	3.07 (17)	2.86
	Pt_{3nt} Nantuo Tillite		3 ~ 6	Gravelly sandy mudstone (tillite)	Anhua, Hunan	0.09 ~ 0.13	2.55(3) ~ 3.76 (23)	2.38 ~ 3.50
Nanhua	Pt_{3xm} Xiangmeng	Up	7 ~ 8	Siliceous phosphoric ferromanganese rocks	Xiushan, Chongqing	0.18 ~ 2.51	2.37 (10)	2.21
		Mid	1	Rhodochrosite	Xiushan, Chongqing	5.41	2.32 (24)	2.17
		Low	2	Rhodochrosite	Xiushan, Chongqing	3.10	3.12 (40)	2.86

a) Based on polarizing microscopic examination combined with energy spectrometry and X-ray diffractiometry; b) marine vitrinite reflectance in average; c) the numerals in brackets are the numbers of measured points for Ro_{mv} values; d) the equivalent vitrinite reflectance Ro is calculated based on the following empirical formula: $Ro_{mv} = 1.082 \times Ro + 0.025$, $2.00\% < Ro < 5.00\%$[6].

whereas the Late Neoproterozoic sediments in Weng'an (Guizhou), Anhua (Hunan) and Xiushan (Chongqing) have Ro values up to 2.17% ~ 3.50%, all of which are corresponding to the maturity phase of anthracite or dry gas and unfavorable for biomarker preservation.

These typical Upper Neoproterozoic-Lower Cambrian sedimentary rocks generally show high total carbon contents (TOCs) commonly up to 1% ~ 5% (Table 1). As the outwash in postglacial age, the phosphoric and pelitic mudstones of Doushantuo Formation show just 0.18% ~ 0.23% in TOCs in Wengan (Guizhou), while the phosphoric ferromanganese rocks and rhodochrosites of the Xiangmeng Formation, as inter-tillite deposits, have much higher TOCs

up to 5.41% in Xiushan (Chongqing). However, only the Sinian Nantuo Tillite in Anhua (Hunan) has much lower TOCs from 0.09% to 0.13%, just one order of magnitude less than most rocks in other strata (Table 1), which indicates obvious lack of aquatic organisms in the sedimentary water column of palaeo-oceanic environment during the age of snowball earth.

Even though these Upper Neoproterozoic-Lower Cambrian sedimentary rocks are in such a high maturity, however, some biomarker information can still be preserved. According to GC analytical results, both complete series of $C_{13} \sim C_{35}$ *n*-alkanes and $iC_{16} \sim iC_{20}$ (no iC_{17}) regular isoprenoid hydrocarbons (e.g. phytane and pristane) have been detected (Fig. 2). The *n*-alkane series shows a major peak at C_{17} or C_{16} with the C_{21}^{-}/C_{22}^{+} ratios from 1 to 34, which indicates a microbial source input, while the isoprenoid series includes iC_{20} phytane (Ph), iC_{19} pristane (Pr) and their $iC_{18} \sim iC_{16}$ pseudohomologues with a Pr/Ph ratio of 0.72 ~ 1.15. The principle precursors for phytane and its pseudohomologues are known as chlorophyll-a and dibiphytanylglyceryl ether (Fig. 3)[7,8]. Chlorophyll-a can be found in higher plants, most algae, cyanobacteria and photosynthetic bacteria as a major member of chlorophylls in these photosynthetic organisms[8], whereas dibiphytanylglyceryl ether is the important membrane composition in archaebacteria[9]. As primitive organisms, archaebacteria include halophiles, thermoacidophiles, methanogens, and even photosytnthetics, which appear only in "extreme" niches[10], but not common in the normal palaeo-ocean for the Upper Neoproterozoic-Lower Cambrian strata. In this case, therefore, the major precursor of phytane and its pseudohomologues should be chlorophyll-a, instead of dibiphytanyl- glyceryl ether, during the Late Neoproterozoic age in the Yangtze region.

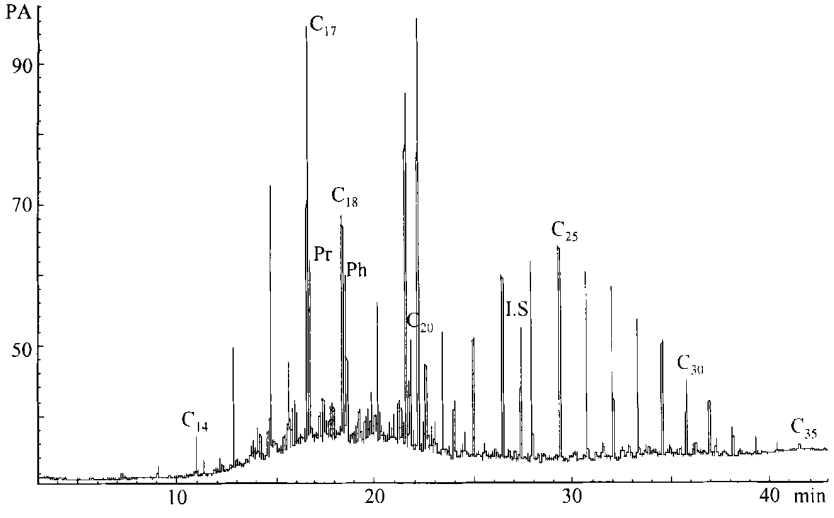

Fig. 2. Gas chromatogram of the gravelly sandy mudstone in the Sinian Nantuo Tillite. Ph, phytane; Pr, pristine; Ci, *n*-alkane (i is carbon number); I.S, internal standard.

Generally the detection of phytane and its pseudohomologues from the sedimentary rocks in the western Yangtze region should be indicative of an obvious photosynthetic process within the palaeo-oceanic water column during the Late Neoproterozoic-Early Cambrian ages. Compared with other Upper Neoproterozoic-Lower Cambrian strata, however, both TOCs and absolute contents of phytane and pristane are in the lowest level, with phytane and pristine contents of 7 ~ 16 ng/g rock respectively, in the Nantuo Tillite (Table 1 and Fig. 4), which should imply a very faint photosynthetic process during diagenesis, and reveal a restricted euphotic zone and quite limited sunlight within the water column during the Sinian glaciation age in the western Yangtze region, and hence providing a case evidence for palaeo-oceanic environment of the Neoproterozoic Snowball Earth age.

Moreover, according to the GC-MS analytical results, the Upper Heoproterozoic-Lower Cambrian sedimentary rocks show almost similar composition and distribution of both triterpane and $C_{27} \sim C_{29}$ sterane series (Figs. 5 and 6).

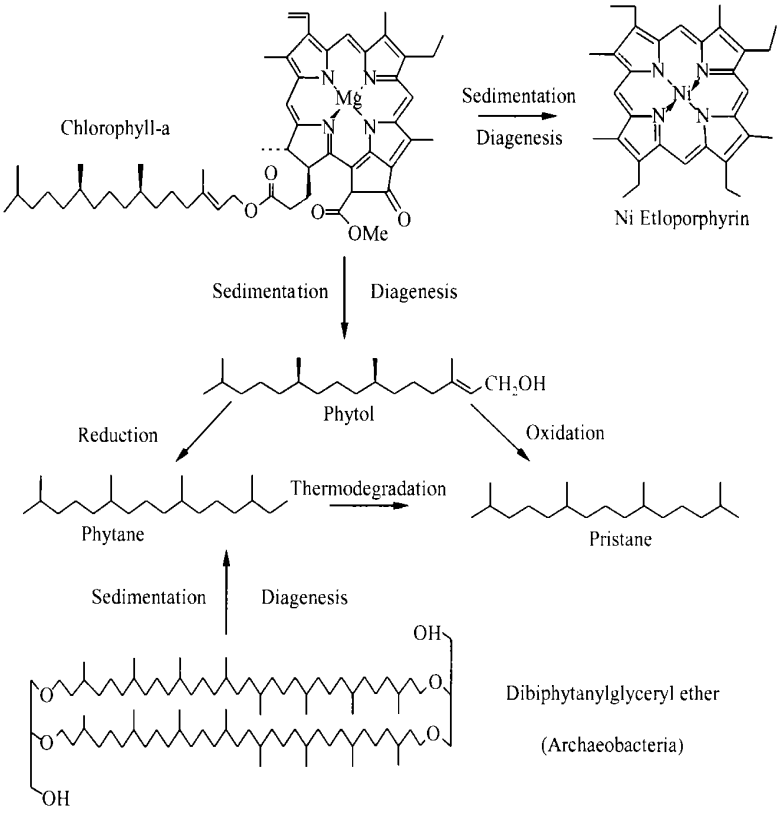

Fig. 3. The source input and genesis of phytane and its pseudohomologues.

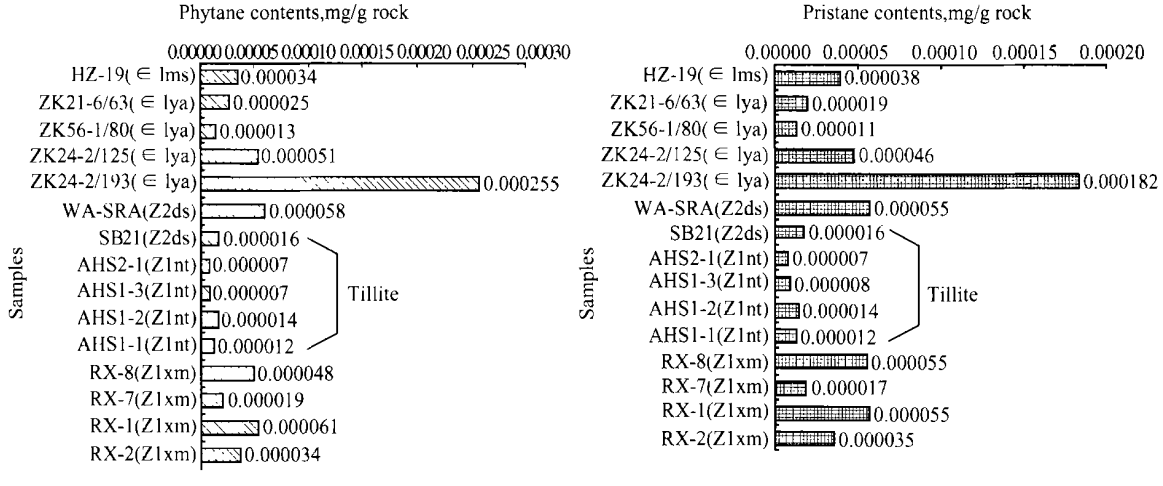

Fig. 4. The absolute contents of phytane and pristane in the Upper Neoproterozoic-Lower Cambrian sedimentary rocks in the western Yangtze region.

Among the triterpane series, $C_{27} \sim C_{35}$ (no C_{28}) hopanes, $C_{29} \sim C_{34}$ moretanes, C_{27} and C_{29} neohopanes and C_{30} diahopane are attributed to a bacterial (Prokaryote) origin[8], C_{30} gammacerane is believed to be a biomarker of *Tetrahymena phriforis* (Ciliate, Protozoa)[11]; while the precursors of $C_{27} \sim C_{29}$ sterane series are derived from algae (Eukaryote)[8].

Since the Late Neoproterozoic-Early Cambrian sedimentary organic matter in the western Yangtze region seems to have a similar biomarker assemblage with various microbial source inputs, and no biomarker indicative of "extreme" niches was detected, the sedimentary environments for these organic matter should be principally referred to a normal palaeo-

ocean, which is also a circumstantial evidence to attribute the majority of phytane and its pseudohomologues to a chlorophyll-a origin. However, there still is a certain unusual molecular composition in need of further study.

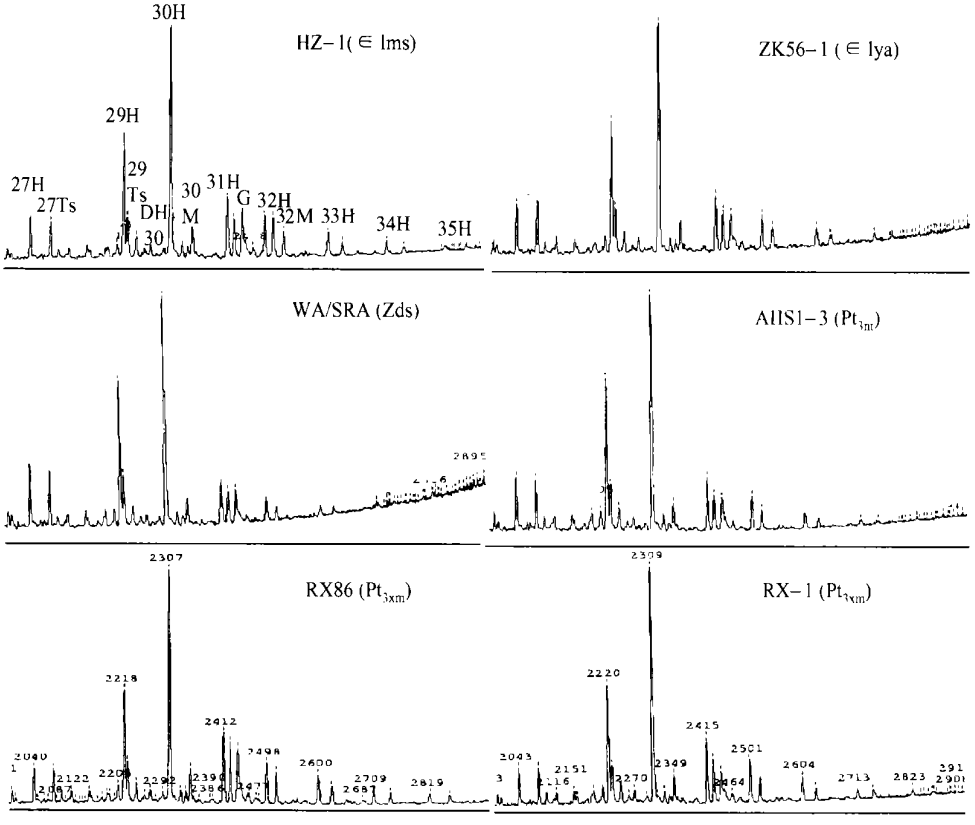

Fig. 5. Composition and distribution of triterpenoids in the Upper Neoproterozoic-Lower Cambrian sedimentary rocks in the western Yangtze region. H, C_{27}~C_{35}(no C_{28}) hopane series; M, C_{29}~C_{32} moretane series; Ts, C_{27}, C_{29} neohopane series; DH, C_{30} diahopane; G, gammacerane. Numerals indicate the carbon numbers.

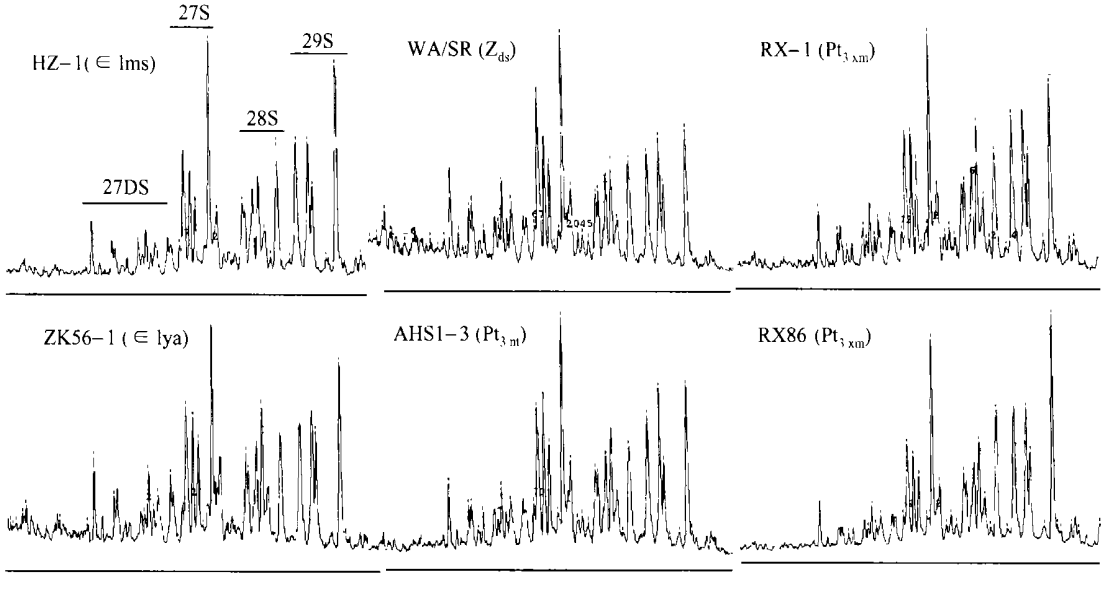

Fig. 6. Composition and distribution of steranes in the Upper Neoproterozoic-Lower Cambrian sedimentary rocks in the western Yangtze region. DS, diasteranes; S, steranes. Numerals indicate the carbon numbers.

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