Molecular Organic Geochemical Records of the ANT28-D5-06 Sediment Core in the Weddell Sea of West Antarctica and their Petroleum Geology Significance*

Han Xibin, Zhao Jun, Chu Fengyou, Pan Jianming, Tang Linggang, Bian Yeping, Ge Qian
Key Laboratory of Submarine Geosciences, Second Institute of Oceanography, SOA
Second Institute of Oceanography, SOA
Hangzhou, China
hanxibin@sio.org.cn

***Abstract*—the chromatography - mass spectrometry of soluble extracts from organic sediment source ANT28-D5-06 in the Weddell Sea of West Antarctica allows investigations on molecular biomarkers (n-alkanes, isoprenoid, serroid terpane), organic carbon and isotope, forming environment, organic maturity, hydrocarbon-generation potential and hydrocarbon migration of this core sediment. The results show that, n-alkanes show a unimodal distribution, with peak carbons of nC_{16}, nC_{17} and nC_{18}, and weak high-carbon peak group; the organic matter type is sapropel, with ($\sum C_{21}^{-}/\sum C_{22}^{+}$) and ($C_{21}+C_{22})/(C_{28}+C_{29}$) ratios greater than 1.0, indicative of the derivation of organic matter chiefly from a marine environment; the organic sediment is abundant with tricyclic terpanes and pentacyclic triterpane, with a high content of gammacerane and a distribution dominance of C_{29} sterol and C_{27} sterol, further suggesting the organic matter is dominated by input of lower organisms; isotopes of organic carbon ($\delta^{13}C$) lie between -25.30‰ and -25.91‰, implying a characteristic of marine aquatic organisms; Pr/Ph ratios range from 0.41 to 0.97, indicating a strong reducing environment; organic carbon in 2cm-11cm of the site ANT28-D5-06 is greater than 1.5; $C_{29}\alpha\alpha\alpha 20S/C_{29}\alpha\alpha\alpha(20S+20R)$ ratios are mostly between 0.32 and 0.48; $C_{29}\alpha\beta\beta/C_{29}(\alpha\alpha\alpha+\alpha\beta\beta)$ ratios lie in a range of 0.31-0.54; $C_{32}22S/C_{32}(22S+22R)$ ratios range from 0.56 to 0.62; Ts/(Tm+Ts) ratios lie between 0.33 and 0.51; all these indices for discrimination of mature oil illustrate that, the organic sediment ANT28-D5-06 has an overall high maturity, close to high-quality organic sediment source, possessing favorable hydrocarbon-generation conditions, and some organic sediment source horizons have reached hydrocarbon-generation peak, which indicate a great prospecting potential for the Weddell basin.

Keywords—***Weddell basin; surface sediment; biomarker; organic matter source; sedimentary environment; hydrocarbon generation***

Chinese Polar Environment Comprehensive Investigation & Assessment Programmes (CHINARE2012-01-02, CHINARE2013-01-02, CHINARE2014-01-02, CHINARE2015-01-02, CHINARE2013-04-01, CHINARE2014-04-01, CHINARE2015-04-01), National Natural Science Foundation of China (41306202 and 41376193), and Fund of Global Change and Air-Sea Interaction (No. GASI-04-01-02)

I. INTRODUCTION

Oil and gas resources are an important strategic resource. As the world's energy consumption is gradually increasing, countries have begun to turn their attention to the South Pole, which will be the last region in search for new oil and gas resources. A comprehensive evaluation of the potential oil and gas resources in the Antarctic region is of significant importance from the prospective of national strategy. However, the harsh natural environments have limited scientific investigations, resulting in inadequate petroleum prospecting achievements and no great breakthrough in the South Pole.

Reservoir formation involves a series of complex processes: hydrocarbon generation, migration and accumulation. Marine sediments are abundant with organic residues, which are derived from plankton (such as algae) and bacteria. When these organic detritus sank to seafloor along with silt and sand, fine-grained organic-rich sediments varied in chemical features under hypoxic conditions. Therefore, hydrocarbon accumulation is intimately associated with organic matter of organic matter source, and thence, organic matter and paleo-sedimentary environments have attracted much attention among petroleum geologists. Effective organic sediments are those could generate and expulse hydrocarbon, and further to form industrial reservoirs[1-2], which act as a premise for reservoir formation. Organic sediment distribution and petroleum source are two general closely-related issues, which directly affects petroleum resource prediction, prospecting direction and strategy. Identification techniques of (high-quality) organic sediments have been capturing much interest.

Molecular organic geochemistry, a rapidly developing branch discipline since the 1970s, investigates the evolution of sedimentary organic matter and sedimentary deposits (especially oil and gas) through chemical composition and structure of biomarkers. Biomarkers, like paleo-fossils, can help to discuss organic geochemical history of hydrocarbon in a molecular level, and provide information on organic sources,

978-0-933957-43-5 ©2015 MTS

sedimentary environments, maturity, hydrocarbon migration and biodegradation for hydrocarbon prospecting[3-4]. N-alkanes, isoprenoids, steranes and terpenes are such a kind of typical molecular-level biomarkers, whose variations of structures or types can reflect the early diagenesis and un-diagenesis, and are fundamental in search for high-quality organic sediments and reservoirs. However, little attention has been paid to these biomarkers to investigate marine organic sediments finely, especially in high-latitude polar seas.

This study applies molecular organic geochemical methods to explore the biomarker composition, source of organic matter, maturity and organic geochemical features of the organic sediments in the north Weddell Sea of the South Pole, aiming to illuminate the formation, development degree of high-quality organic sediments and their hydrocarbon-generation potential.

II. Regional Geography and Geological Review

The Weddell Sea, the largest marginal sea in Antarctica, is situated between Antarctic Peninsula and Coats Land. It is bounded by frontal barriers of the Filchner and Ronne ice shelves on the south, South Sandwich Islands and the South Orkney Islands on the north, and connects with the South Atlantic in the northeast. Affected by the high pressure in the Antarctic, its southern ocean current becomes east drift as controlled by east wind all year round, while the northern ocean current becomes west drift (Fig. 1). These cold and dense shelf waters sank to become Antarctic bottom water, acting as a major source for the world’s oceanic deep water, whose salinity is about 34.7‰. Their low temperature and great density allow it to be at the bottom of the ocean stably, and their density differences make it to scatter horizontally in varying depths.

Previous studies suggest that, the Weddell Sea was formed in the Gondwana breakup period, and the oceanic crust in the southern margin changed to continental crust, which is interpreted to be the preliminary results of continental margin rifting or oblique rifting in the middle Jurassic or later[5-6]. Results from the voyage ODP113 also validate it[7]. In combination with regional studies from Storey et al.[8], it is inferred that, the initial opening of the Weddell Sea began in the middle Jurassic (180 Ma). Paleomagnetic data indicate that, the East Weddell Sea moved to its current location at 122 Ma [9]. Sedimentary rocks below the Weddell Sea’s continental shelf can reach thicker than 10 km [10], which can be a potential prospecting area for oil and gas reservoirs in West Antarctica due to its favorable conditions for hydrocarbon generation, storage and migration[10].

III. Sample Collections and Analysis

A. Sample collection

On 29th, January, 2012, the Chinese 28th Antarctic scientific expedition took the “Xuelong” icebreaker to collect the core sediment ANT28-D5-06 in the south of South Orkney Islands north of Weddell Sea, east of the Antarctic Peninsula (44°40.709’W, 61°47.878’S, with a water depth of 385 m) (shown in Fig.1). This core sediment was obtained through tube sampler box, with a column length of 17 cm. It is chiefly composed of livid silty clay and clay, and was separated with an interval of 1 cm in laboratory for analysis of organic carbon isotopes and molecular markers.

B. Analysis of ^{210}Pb

This sediment was lyophilized, and was taken about 10 g to ground to 100 mesh. After being screened by a 100-mesh sieve, the sample was loaded to a plastic container with the same specifications to the standard source, and sealed for a month to ensure ^{226}Ra and ^{210}Pb in a permanent equilibrium system. It was then tested for the content of radionuclide ^{210}Pb in the Second Institute of Oceanography, State Oceanic Administration, with a high-purity germanium detector (GWL-120-^{15}N), a digital spectrometer and multi-channel analysis system produced by the U.S. EG & GORTEC company. Every samples were measured for 1-3 days, and their peak area at energy of 46.5keV (^{210}Pb) is used to calculate specific activity of ^{210}Pb, energy of 295.6keV (^{214}Pb, ^{226}Ra’s daughter) for calculation of specific activity for background ^{210}Pb, and their difference is the specific activity of excess ^{210}Pb. Energy resolution (FWHM) of ^{60}Co at energy of 1.33 MeV is ≤2.4Kev, and that of ^{57}Co at energy of 122 keV is ≤1.4 Kev, with a relative detection efficiency of 62%, showing a good stability. The standard samples of ^{210}Pb and ^{226}Ra are provided by the China Institute of Atomic Energy.

C. Particle size analysis

A combined method of sieve analysis and laser particle size analyzer was performed on the samples due to their partly coarse granilarity. For samples with grain size less than 2 mm, laser particle size analyszer were adopted; for samples with grain size greater than 2 mm, an integrated method of both was utilized. Particle size analysis was conducted based on technical specification of marine sediment survey, i.e., Marine Geological Survey Specification-Part 8: Marine Geological and Geophysical Survey GB/T 12763.8-2007. An appropriate amount of wet samples were placed in glass, and 5 cm^3 of 0.5 mol/L sodium hexametaphosphate ($[NaPO_3]_6$) was added in.

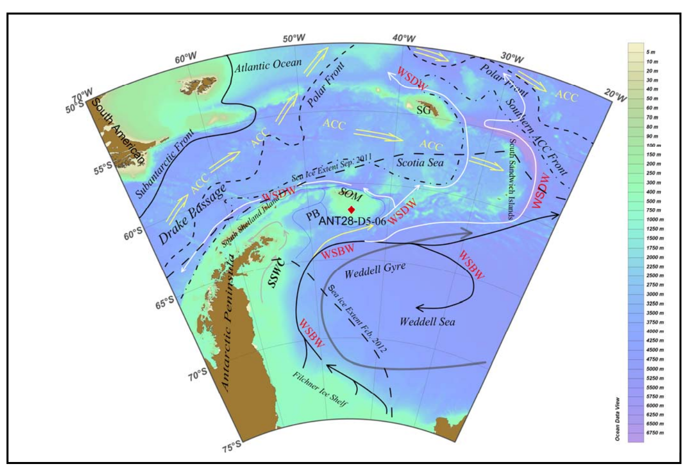


Fig. 1. Example of a figure caption Map showing schematic circulation pattern and core sample position in the west of Antarctica Peninsula (Schematic circulation pattern from Hernández-Molina et al.[12], ACC-Antarctic Circumpolar Current, WSBW-Weddell Sea Bottom Water, WSDW-Weddell Sea Deep Water, SOM-South Orkney Islands, PB- Powell Basin, SSWC-Shelf Surface Water Circulation)

The samples were then soaked for 24 h, and were gently stirred every 8 h to ensure its fully dispersion. These soaked samples were poured into a laser sample slot, adding ultrasonic vibration and high-speed centrifugation to be fully dispersed. Then the samples were send to the Second Institute of Oceanography, State Oceanic Administration for analysis using a UK Malvern 2000 laser particle size analyzer, whose measuring range is 0.02-2000μm, with a relative error of less than 2%. The grain size criteria for the classification uses the Youden - Windward's geometric system Ø median particle standard.

D. Analysis of organic carbon, nitrogen, and C-N isotopes

Organic carbon and isotopic tests were conducted in the Stable Isotopic Laboratory at the Second Institute of Oceanography, State Oceanic Administration. We took certain sediment samples, and added 4 mol/dm^3 excess HCl to react for 24 h. Deionized water was used to wash acid to be netural, and the samples were placed in a drying oven at 60℃. After being dried, the samples were weighted and ground to powder, passing through a 60-mesh sieve. Tin cups (4mm×6mm) were used to pack 10 mg decarbonatized samples, which were then tested for TOC, TON, $\delta^{13}C$ and $\delta^{15}N$ values through an element analyzer-stable isotopic mass spectrometer (No. Flash EA 1112 HT- Delta V Advantages, from the Thermo Company). Carrying gas He has a flow rate of 90 mL/min; the temperature for reaction tube is 960℃; and the column temperature is 50℃.

To control the quality of the test data, a duplicate sample is inserted every 17 samples for core sediment ANT28-D5-06, and a duplicate sample is inserted every 15 samples for core sediment . The STD for total organic carbon (TOC) is <0.25‰ (5); STD for total organic nitrogen is <0.2‰ (5); STD for organic carbon isotope ($\delta^{13}C$) is <0.2‰ (5); STD for organic nitrogen (δ15NTON) is < 0.2‰ (5).

E. Analysis of molecular biomarkers

Organic matter of the sample was extracted through conventional organic geochemical methods, and was tested in the Petroleum Geological Test Center, Geological Scientific Research Institute, Shengli Oilfield, Sinopec. The sediment samples were lyophilized, crushed to 80 mesh, and extracted for 78 h. Petroleum ether was utilized to precipitate asphaltene; silica gel and alumina chromatographic column were used to separate aromatic component; and n-hexane, methylene chloride and chloroform / ethanol mixed solvent were used as an eluent for saturated hydrocarbons, aromatic hydrocarbons and non-hydrocarbons.

The operation conditions were: gasification chamber temperature of 310 ℃, transmission line temperature of 310 ℃ ; temperature programs: initial column temperature of 100 ℃, with a heating rate of 4 ℃ / min, final column temperature of 3154 ℃ , thermostat for 22 min; column of DB5-MS 60m×0.25mm×0.25um; pre-column pressure of 170 kPa, split ratio of 20:1; carrier gas of helium; wire speed of 27cm/s; collection of circle scan (SCAN)/multi-ion monitoring (SIM); ion source temperature of 250 ℃, scan rate of 0.46 scan/s; ionization method of electron impact (EI).

IV. Results and Discussions

A. Organic carbon and isotopes, chloroform bitumen "A" and maturity

Organic sediments, acting as a basis for hydrocarbon accumulation, can be divided into varying classification based on their hydrocarbon-generation capacity, and high-quality organic sediments are a good type. Table 1 shows that, organic sediments between 2cm and 11cm of the core sediment ANT28-D5-06 in the Weddell Sea basin have an organic carbon content of >1.5%, belonging to good organic sediments, and organic sediments in 12 cm, 13 cm and 14 cm have organic carbon content of 1.24%, 0.95% and 1.43%, respectively, belonging to fairly good ones.

The soluble organic matter in the sample ANT28-D5-06 is highly variable, and the content of chloroform bitumen "A" lies between 0.0111% and 0.0867% (Table 1). The low content of chloroform bitumen "A" and total hydrocarbon reflect their high maturity. It is also suggested that, the content of chloroform bitumen "A" in ANT28-D5-06 does not correspond well with that of organic carbon. The increasing evolutional degree may attribute to it, especially for highly evolved organic sediment layers. Organic sediments may generate some hydrocarbon in different evolutional stages, and the content of chloroform bitumen "A" may represent remained hydrocarbon-generation quantity. If there are no expulsed hydrocarbons, the hydrocarbon quantity reflects the total hydrocarbon-generation amount, which has a positive relationship with the TOC content. Otherwise, if hydrocarbon was expulsed, it may represent the remained hydrocarbon content after hydrocarbon expulsion[13].

TABLE I. CHLOROFORM BITUMEN "A" AND ORGANIC CARBON CONTENT, CONVERSION RATE AND ISOTOPIC RATIOS OF ORGANIC CARBON FOR THE ORGANIC SEDIMENT ANT28-D5-06

Depth (cm)	**Chloroform bitumen "A"(W %)**	**TOC (%)**	**Conversion rate "A"/C**	**$^{13}C_{V\text{-}PDB}$ (‰)**	**$^{15}N_{V\text{-}AirN2}$ (‰)**
1	0.0867	1.17	0.074	-25.58	2.81
2	0.0254	1.77	0.014	-25.86	2.81
3	0.0308	1.57	0.020	-25.54	2.82
4	0.0111	1.60	0.007	-25.91	2.78
5	0.0244	1.63	0.015	-25.54	2.82
6	0.0229	1.95	0.015	-25.72	2.90
7	0.0255	1.63	0.016	-25.59	2.60
8	0.0232	1.64	0.014	-25.86	1.41
9	0.0220	1.66	0.013	-25.42	2.66
10	0.0298	1.40	0.021	-25.70	2.96
11	0.0228	1.58	0.014	-25.83	2.90
12	0.0254	1.43	0.018	-25.44	2.95
13	0.0232	0.95	0.024	-25.59	3.11
14	0.0177	1.24	0.014	-25.37	2.82
15	0.0159	0.87	0.018	-25.39	3.33
16	0.0239	0.59	0.041	-25.36	3.64
17	0.0149	0.44	0.034	-25.30	3.60

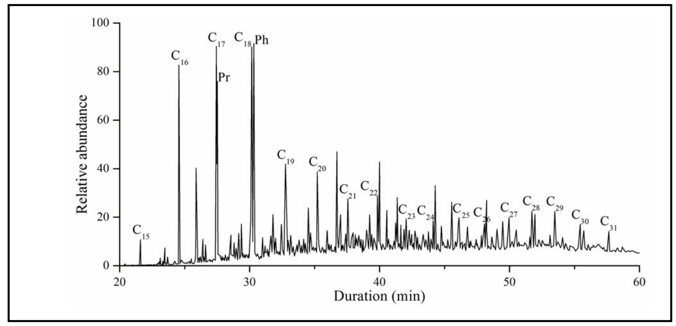
Organic carbon isotope ($\delta^{13}C$ org) and organic nitrogen isotopes ($\delta^{15}N$ org) can also be used to determine their derivation from terrestrial plants or algae. $\delta^{13}C$ primarily reflects photosynthesis, carbon assimilation and carbon isotopic composition. $\delta^{13}C$ of sedimentary organic matter is intimately associated with source and sedimentary environment of primary organic matter, and thermal maturation does not significantly change the carbon isotopic composition. Hence, carbon isotopic composition of organic matter is representative of, in most cases, primary organic matrix. As shown in Table 1, $\delta^{13}C$ values of the organic sediment ANT28-D5-06 range between -25.30‰ and -25.91‰, indicative of their derivation mostly from marine lower algae and bacteria, mixed with a small amount of terrestrial plants. There is also a hypoxic environment which may seriously affect the original isotopic equilibrium of $\delta^{13}C$. When the ambient hypoxic conditions predominate, $\delta^{13}C$ tends to be lighter[14].

B. N-alkanes, isoprenoid hydrocarbons and organic matter and hydrocarbon-generation environment

A large amount of primary organic matter is a prerequisite for good organic sediments, and organic matter may contain different types, such as marine algae, bacteria and higher plants. Under different depositional environments, different biomarker assemblages may occur. For marine sediments surrounding the Antarctic, organic matter produced by aquatic organisms themselves, i.e., productivity of the ocean itself, is highly significant.

N-alkanes of sedimentary organic matter are one of the important organic compounds, and their molecular composition can reflect characteristics of parent source. Composition of n-alkanes in low-middle thermal evolutional stages, especially, can be indicative of source assemblage features, and those in mature stage also have indication to source assemblages[15-16]. As illustrated in Table 2, carbon numbers of the sediment ANT28-D5-06 range from C_{13} to C_{34} (or C_{30}, C_{31}), exhibiting a single peak of low carbon numbers, and the peak carbon number is C_{18} (C_{16} for the surface) (Fig. 2). Parameters of $\sum C_{21-}/\sum C_{22+}$ and $(C_{21}+C_{22})$ / $(C_{28}+C_{29})$ are commonly utilized in petroleum geochemistry to discriminate marine or continental biogenic genesis. These two parameters for ANT28-D5-06 are mostly greater than 1, showing a high number of low carbons and implying derivation from marine algae and bacteria, mixed with a very small amount of terrestrial higher plants. This is in agreement with that sea water is rich in salts, with densely concentrated plankton and whales.Long-chain n-alkanes will crack to short-chain alkanes with the evolving maturity of organic matter, resulting in a small range of carbon numbers. Before entering hydrocarbon-generation threshold, CPI {[(C25+C27+C29+C31+C33) / $(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})$ + $(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})$ / $(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})$/2]} and OEP $((C_{23}+6\times C_{25}+C_{27})$ / $4\times(C_{24}+C_{26}))$ values of saturated hydrocarbons for organic sediments are principally affected by organic sediment derivation and sedimentary environments, with a significant odd-even or even-odd predominance. After entering hydrocarbon-generation threshold, hydrocarbons generated from kerogen have an odd-even or even-odd predominance,

Fig. 2. Chromatography – mass spectrometry of n-alkanes from the core sediment ANT28-D5-06 in north Weddell Sea



with their CPI and OEP close to 1. When CPI and OEP range from 0.8 to 1.2, the odd-even or even-odd predominance is considered to disappear. It is seen from Table 2 that, the CPI values for the sediment ANT28-D5-06 north of the Weddell Sea lies between 0.93 and 1.22, and OEP values locate in a range of 0.65-1.37. Except for 0.65 in 5cm to 6 cm and 1.37 in 2 cm to 3 cm, most OEP values are in a range of 0.8-1.2, close to 1, implying that the organic matter has undergone high-degree degradation, with no clear odd-even predominance. Therefore, most organic sediment horizons of ANT28-D5-06 have entered a mature stage.

Storage conditions exert a critical control on formation of marine high-quality organic sediments[17]. For a sedimentary basin, determination ofpaleo-sedimentary environments can provide evidence for relationship between hydrocarbon reservoirs and organic matter and thus for searching hydrocarbon reservoirs. In a heterogeneous series of regular isoprenoids, pristine (Pr) and phytane (Ph) are important components. In the early stages of diagenesis, phytyl side-chain of chlorophyll forms phytol under action of microorganisms. Under oxidizing environments, side chain of

TABLE II. GEOCHEMICAL PARAMETERS OF N-ALKANES FROM THE CORE SEDIMENT ANT28-D5-06 IN THE NORTH WEDDELL SEA, WEST ANTARCTICA

Layer (cm)	Ranges of carbon numbers	Peak carbon	$\sum C_{21}^{-}/\sum C_{22}^{+}$	$C_{21}+C_{22}/C_{28}+C_{29}$	C_{23}/C_{17}	CPI	OEP	Pr/Ph	Pr/nC_{17}	Ph/nC_{18}
0-1	nC13-nC31	nC16	2.47	1.99	0.19	1.22	0.89	0.97	0.63	0.84
1-2	nC13-nC34	nC18	0.87	0.73	0.54	1.18	1.12	0.75	1.17	0.76
2-3	nC13-nC30	nC18	1.68	0.97	0.54	1.46	1.37	0.82	2.11	0.81
3-4	nC13-nC34	nC18	1.53	1.28	0.30	1.10	1.16	0.61	1.03	1.41
4-5	nC13-nC31	nC18	1.39	1.53	0.42	1.04	0.99	0.60	0.65	0.77
5-6	nC13-nC34	nC18	1.04	0.67	0.25	1.01	0.65	0.67	0.68	0.80
6-7	nC13-nC31	nC18	1.49	1.23	0.52	0.99	0.83	0.93	1.79	0.76
7-8	nC13-nC31	nC18	1.16	0.73	0.32	0.93	1.02	0.69	0.96	0.88
8-9	nC13-nC31	nC18	1.65	1.18	0.43	1.13	1.18	0.64	1.08	0.92
9-10	nC13-nC34	nC18	0.54	1.53	1.53	1.06	1.02	0.53	0.78	0.76
10-11	nC13-nC31	nC18	1.82	2.03	0.39	1.10	1.08	0.68	0.84	0.86
11-12	nC13-nC31	nC18	2.15	1.82	0.50	1.07	1.13	0.60	1.03	0.83
12-13	nC13-nC30	nC18	3.10	3.58	0.29	1.15	1.37	0.74	0.85	0.75
13-14	nC13-nC34	nC18	0.44	0.32	0.44	1.10	1.03	0.75	0.84	0.74
14-15	nC13-nC31	nC18	3.00	1.71	0.22	0.87	1.15	0.78	0.80	0.90
15-16	nC13-nC30	nC18	1.51	0.73	0.27	0.90	1.19	0.78	0.81	0.75
16-17	nC13-nC31	nC18	1.56	1.62	0.86	1.10	0.84	0.41	0.68	0.83

Note: CPI={ $(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})$ / $(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})$ + $(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})$ / $(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})$ }/2; OEP= $(C_{23}+6\times C_{25}+C_{27})$ /$4\times(C_{24}+C_{26})$.

phytol cracks, being oxidized to phytanic acid; phytanic acid underwent decarboxylation and hydrogenation to form pristine. In contrast, under reducing environments, side chain of phytol will be reduced to dihydrogen phytol, which underwent dehydration and hydrogenation to form phytane[18]. Pristine, phytane and Pr/Ph are common indicators for discrimination of redox conditions of sedimentary environments and salinity of medium. Pr/Ph ratios <1 are indicative of a weak redox environment, while rations close to 1 are suggestive of alternate oxidizing and reducing environments. Integrating with their adjacent n-alkanes of C_{17}, C_{18} and Pr/C_{17}, Ph/C_{18}, it is considered that, lower values of Pr/C_{17} suggest a large contribution from algae, while higher values of Ph/C_{18} indicate a strong reducing environment [19]. Previous studies have suggested that, organic matter derived from algae under anaerobic environments is the best-quality parent material for oil generation. The Pr/Ph values of organic sediments from the sediment ANT28-D5-06 are between 0.41-0.97 (Table 2), mostly 0.60-0.97, with few horizons of 0.41 and 0.53. This suggests a relatively lower content of pristine than phytane, indicative of a weak redox environment. Pr/C_{17} ratios range from 0.63 to 2.11 and Ph/C_{18} ratios range between 0.74 and 1.41, implying a strong reducing environment. High biological productivity and anoxic environments are necessary for the formation of high-quality organic sediments, and superstition of both conditions can form particularly enriched zone of organic matter [20]. Therefore, there are favorable hydrocarbon generation conditions for organic sediments in the north of the Weddell Sea.

C. *Distribution of steranes and terpanes and organic sediment source*

Biomarker composition of sterane and terpane correlates strongly with sedimentary environments of organic sediments, organic matter source and thermal evolution. Both biomarkers occurring stably in geological bodies maintain specific object types and distribution patterns during their transformation from organisms to geological bodies, exhibiting a good genetic nature, and can provide fingerprint information for organic matter source and accurate information for thermal maturity of organic matter.

Table 3 and Fig. 3 illustrate that, sterane compounds in the sediment ANT28-D5-06 are dominated by regular steranes, accounting for 71.09%-85.64% of the total steranes; 4-methyl sterane occupies 4.88%-8.95%; pregnanes account for 3.35%-10.47%; rearranged steranes account for 3.87%-9.06%. Values of 5α-C_{27}20R/5α-C_{29}20R for primary steranes (except that in 15cm-16cm as 35.4%, and 7cm-8cm as 44.08%) in the sediment ANT28-D5-06 range from 68.21% to 101.46%, and 5α-C_{28}20R/5α-C_{29}20R values (except 13cm-14cm as 45.65%) lie between 67.48% and 87.94%. Varying horizons exhibit dissimilarities in sterane series distribution for the sediment ANT28-D5-06. Steroid compounds are chiefly C_{29} and C_{27}, followed by C_{28}. Different distribution types of C_{27}, C_{28} and C_{29} steroids in different organisms and in variable stages under the same sedimentary environment reflect undoubtedly the ecological environment, and can be used as an indicator of paleo-ecological environment and community succession. In a common sense, C_{27} steranes mainly derive from marine planktonic animals[21]; C_{28} steranes originate from phytoplankton [22]; C_{29} steranes principally derive from terrestrial higher plants[23]. However, C_{29} steranes in sediments of the Antarctic waters more tend to be from marine authigenic algae than from terrestrial higher plant. High-quality organic sediments are mainly from burial of marine biological framework, and those in the West Antarctic are dominated by a biological genesis (such as hydrocarbon-rich organisms, benthos and fungi hydrocarbon-forming organisms). Hydrocarbon-generation marine organisms are fundamental for the formation of high-quality organic sediments, and horizons abundant of these organisms are often the major organic sediment layers. Marine high-quality organic sediments are commonly featured by multiple parent materials, i.e., every horizon exhibits a combined source from phytoplankton and benthic photosynthetic bacteria, which shows disparity of sedimentary environments. Abundant tricyclic terpanes and pentacyclic triterpenoids series were detected in the sediment ANT28-D5-06, including C_{27}-C_{35} hopane series and gammacerane. This indicates the dominance of tricyclic terpanes, and it is generally believed that tricyclic terpenes and steroids are originated from microorganisms and steroids[24] . There were no detected oleanane originated from higher plants, indicative of their derivation from low aquatic organisms. Table 3 and Fig. 4 list the distribution and composition of terpene biomarkers. It is seen that, C_{29} hopane /C_{30} hopane ranges from 35.80 to 53.04; C_{31} homohopane /C_{30} hopane lies between 47.55 and 57.02; gammacerane / C_{30} hopane ranges between 9 and 28.33 (except 46.85 for 9-10 cm layer); and Σ tricylic terpanes / Σ pentacyclic triterpane lies from 0.113 to 0.288. Gammacerane is a triterpenoid marker of non-hopane series, which comes from dehydration and hydrogenenation of tetrahymena alcohol and varies greatly in content under different conditions of organic sediment maturity [25]. It is present in most crude oil and chloroform extracts. A large amount of gammacerane is indicative of a strongly reducing hypersaline environment during organic sediment deposition, and is related to water delamination[26]. The organic sediment ANT28-D5-06 contains a high content of gammacerane, and gammacerane / C_{30} hopane can reach up to 46.58, mostly 9.0-28.33.

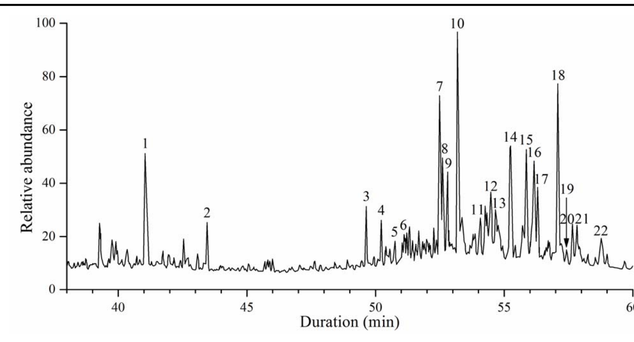


Fig. 3. sediment ANT28-D5-06 in north Weddell Sea Chromatography–mass spectrometry of m/z217 from the core

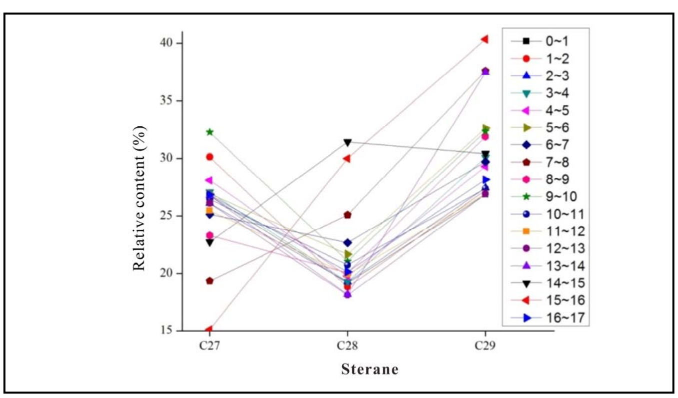
TABLE III. COMPOSITION OF STEROID AND TERPANE BIOMARKERS FROM THE SOURCE ROCK D5-6 IN THE NORTH WEDDELL SEA

Layer (cm)	Composition of sterols/%				Relative composition of native steranes		Relative composition of regular steranes/%			Composition of terpane compounds			
	Regular sterols	*4-methyl sterols*	*Progesterol*	*Diasteranes*	*5α-C_{27}20R/ 5α-C_{29}20R*	*5α-C_{28}20R/ 5α-C_{29}20R*	C_{27}	C_{28}	C_{29}	*C_{29} hopane /C_{30} hopane*	*C_{31} hopane/ C_{30} hopane*	*gammacerane /C_{30} hopane*	*Σ Tricyclic terpanes/ Σpentacyclic triterpenoids*
0-1	72.76	7.70	9.29	7.27	0.92	0.76	26.76	19.15	26.85	0.47	0.57	0.18	0.25
1-2	76.14	5.99	6.75	9.06	1.01	0.72	30.12	18.80	27.22	0.36	0.55	0.14	0.16
2-3	72.79	7.91	8.47	7.31	0.92	0.72	26.11	19.24	27.43	0.53	0.51	0.22	0.27
3-4	76.41	8.15	6.15	6.95	0.81	0.73	27.04	19.28	30.09	0.50	0.49	0.23	0.23
4-5	77.15	8.12	5.88	6.28	0.84	0.76	28.08	19.77	29.29	0.44	0.49	0.17	0.22
5-6	81.20	8.95	3.57	4.86	0.79	0.67	26.92	21.66	32.62	0.48	0.51	0.22	0.17
6-7	77.52	7.18	5.44	6.87	0.79	0.87	25.15	22.65	29.71	0.52	0.51	0.22	0.23
7-8	82.02	5.50	5.91	4.66	0.44	0.78	19.33	25.08	37.60	0.50	0.47	0.18	0.22
8-9	75.22	7.46	7.83	6.27	0.68	0.70	23.29	20.05	31.88	0.44	0.48	0.20	0.25
9-10	85.64	8.57	1.21	3.87	0.98	0.73	32.26	21.06	32.33	0.40	0.55	0.47	0.13
10-11	74.56	7.57	8.40	6.36	0.88	0.73	26.45	20.74	27.37	0.45	0.49	0.18	0.25
11-12	72.29	7.39	9.40	6.84	0.80	0.76	25.47	19.92	26.90	0.44	0.48	0.18	0.28
12-13	71.09	7.72	10.47	7.18	0.94	0.74	26.11	18.10	26.89	0.50	0.49	0.18	0.29
13-14	82.39	5.08	4.56	6.32	0.80	0.46	26.75	18.16	37.48	0.43	0.49	0.09	0.11
14-15	84.52	4.88	4.76	4.31	0.88	0.87	22.72	31.40	30.41	0.50	0.50	0.28	0.23
15-16	85.45	4.60	4.48	4.19	0.35	0.88	15.11	29.99	40.35	0.53	0.48	0.22	0.21
16-17	75.13	8.36	7.92	6.63	0.92	0.79	26.82	20.16	28.14	0.49	0.48	0.17	0.22

D. Sterane and terpane distribution and organic sediment maturity, and hydrocarbon features

Sterane is a common compound for oil-gas correlations [27]. A detailed biomarker analysis can lead to an accurate determination of thermal evolution of organic sediments. There is a good correlation between different isomers distribution and organic sediment maturity for regular steranes. Generally, isomers of 5α, 14α, 17α and 20R can be observed in living organisms, while other isomers only exist in geological bodies. Thus, different isomers can be utilized to determine maturity. Ratios of C_{29}αα20S / (20S+20R) and C_{29}αββ / (αββ+ααα) of regular steranes are two commonly utilized indicators to determine maturity, and the higher the maturity is, the larger the ratios are. Ratios of C_{29}ααα20S / (20S+20R) smaller than 0.25 are characteristic of immature organic matter; values of 0.25-0.43 are for low-maturity organic matter, 0.43-0.50 formature organic matter; and ratios greater than 0.5 are indicative of high-maturity organic matter. Ratios of C_{29}αββ/ (αββ+ααα) smaller than 0.25 are indicative of immature organic matter, while 0.25-0.38 for low maturity, 0.38-0.46 for mature organic matter, and ratios greater than 0.46 are high-maturity organic matter. The isomer of αββ sterane is more abundant than ααα isomer in the core sediment ANT28-D5-06 of the Weddell basin, and the abundance of geological isomer (20S) is also high. As listed in Table 4, C_{29}ααα20S/ (20S+20R) ratios for ANT28-D5-06 range between 0.34 and 0.48, and ratios of C_{29}αββ / (αββ+ααα) lie between 0.33 and 0.54. It is thus inferred that, this organic sediment has entered into a mature to high-mature stage, especially some layers (3-4cm, 5-6cm, 13-14cm and 14-15cm) whose biomarker parameters ≥0.4, has entered into hydrocarbon-generation threshold acting as high-quality organic sediments. This coincides with maturity inferred from carbon number predominance of n-alkanes.

Fig. 4. Content of sterane C27, C28 and C29 for the core sediment ANT28-D5-06 in north Weddell Sea



A high abundance of pregnanes (C_{21}) and homopregnanes (C_{22}) was detected in ANT28-D5-06, and ratios of (C_{21}+C_{22}) pregnanes / regular steranes lie between 0.055 and 0.147. Pregnanes may come from progesterone, and also may be main and side-chain cracking products of normal steranes. For geological bodies, 80%-85% pregnanes are originated from cracking of regular steranes, with small input of primary sediments. A comprehensive study of organic carbon content and other effective parameters suggests that, pregnane content

Fig. 5. Chromatography–mass spectrometry of m/z191 from the sediment core ANT28-D5-06 in north Weddell Sea

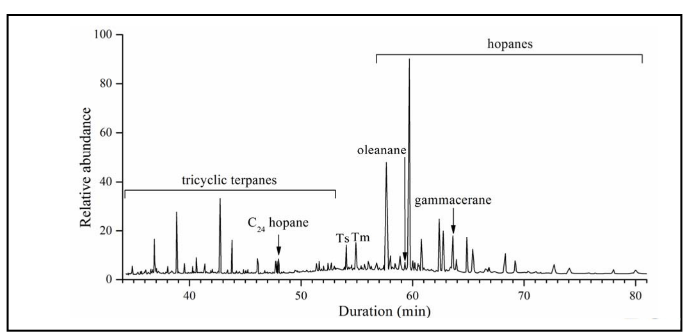


TABLE IV. MATURITY PARAMETERS OF STEROID AND TERPANE BIOMARKERS FROM THE ORGANIC SEDIMENT ANT28-D5-06 IN NORTH WEDDELL SEA

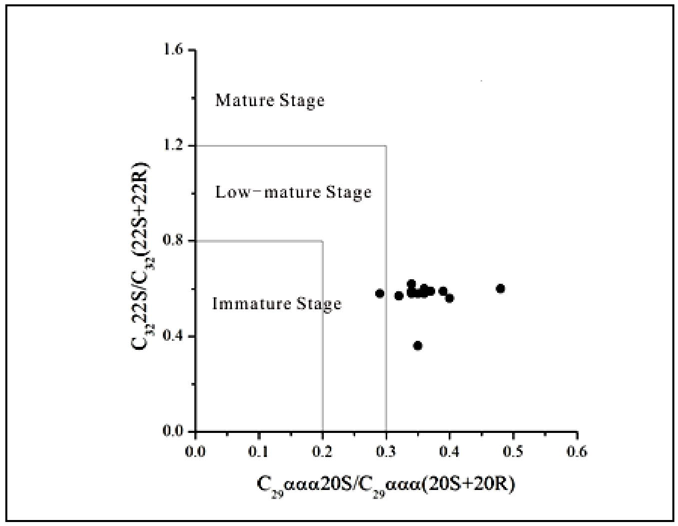
Layer (cm)	$C_{29}\alpha\alpha\alpha20S/C_{29}\alpha\alpha\alpha(20S+20R)$	$C_{29}\alpha\beta\beta/C_{29}(\alpha\alpha\alpha+\alpha\beta\beta)$	$C_{31}22S/C_{31}(22S+22R)$	$C_{32}22S/C_{32}(22S+22R)$	Ts/(Tm+Ts)
0-1	0.34	0.38	0.55	0.62	0.45
1-2	0.34	0.41	0.55	0.59	0.51
2-3	0.36	0.37	0.55	0.59	0.45
3-4	0.40	0.40	0.53	0.56	0.46
4-5	0.35	0.36	0.54	0.36	0.40
5-6	0.39	0.41	0.56	0.59	0.40
6-7	0.36	0.33	0.56	0.58	0.42
7-8	0.29	0.28	0.54	0.58	0.40
8-9	0.34	0.38	0.54	0.58	0.41
9-10	0.32	0.31	0.56	0.57	0.38
10-11	0.35	0.39	0.53	0.58	0.45
11-12	0.36	0.39	0.55	0.58	0.43
12-13	0.36	0.37	0.54	0.58	0.42
13-14	0.39	0.54	0.56	0.59	0.36
14-15	0.48	0.44	0.52	0.60	0.33
15-16	0.37	0.34	0.55	0.59	0.40
16-17	0.36	0.36	0.54	0.60	0.40

in sedimentary strata is linked to organic matter maturity to some extent, i.e., the higher the maturity is, the higher the content of pregnanes is. The abundance of pregnanes also indicates the organic sediment ANT28-D5-06 has reached a mature stage.

Ts/(Ts+Tm) is a common indicator for determination of maturity (Ts-trisnorneohopane, Tm- trisnorhopane). Thermal stability of Tm [$C_{27}17\alpha$(H)- Trisnorhopane] is poor than Ts [$C_{27}18\alpha$(H)- Trisnorhopane], and higher maturity may lead to greater Ts/(Tm+Ts) values. This trend will continue to higher-maturity stage, and Ts/(Tm+Ts) values will reach up to 0.5 in the late stage of hydrocarbon-generation stage (Ro values of 1.4%)[3]. Ts/(Tm+Ts) ratios of ANT28-D5-06 range mostly from 0.4 to 0.51, with a thermal equilibrium, indicative of a higher maturity [28] and a favorable hydrocarbon-generation potential. These values also suggest a strongly reducing environment, corresponding well with those implied by Pr/Ph<1. 22S / C_{31}(22S+22R) and C_{32}22S/C_{32}(22S+22R) values are considered to be the best parameters for determining hydrocarbon-generation threshold [29], which vary from 0 to 0.6, and reach about 0.6 in a mature stage. 22S/C_{31}(22S+22R) values for the organic sediment ANT28-D5-06 range from 0.52 to 0.56, and 22S/C_{32}(22S+22R) ratios range from 0.56 to 0.62 (except the 4-5 mm layer), averaging 0.59, with a thermal equilibrium, indicating a thermal maturity stage. Once reaching hydrocarbon-generation threshold, a thermal equilibrium will be reached (ratios of 0.57 to 0.6), which is also indicative of micro seepage (Table 4 and Fig. 5).

It is thus inferred that, the organic sediment ANT28-D5-06 has high organic matter abundance, good parent material types, and their reducing-strong reducing environments are favorable to

Fig. 6. Diagram of C_{32}22S/C_{32}(22S+22R)-$C_{29}\alpha\alpha\alpha$20S/$C_{29}\alpha\alpha\alpha$(20S+20R) for hopanes from the sediment core ANT28-D5-06 in north Weddell Sea



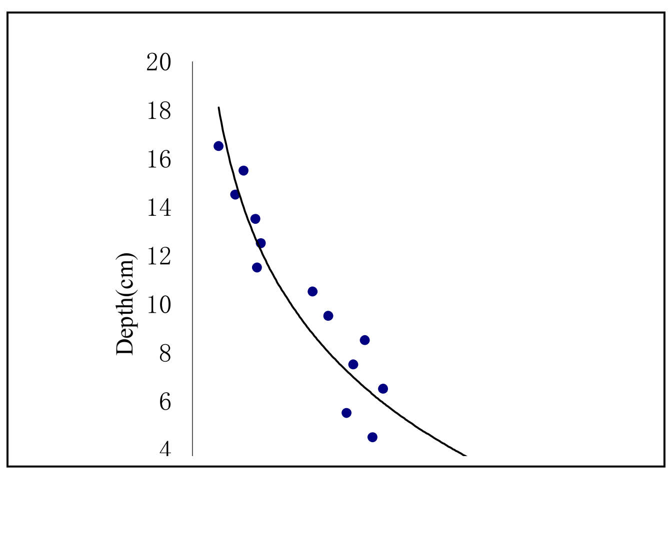
organic matter storage. It is in a high-maturity stage, with a great hydrocarbon-generation potential.

E. Hydrocarbon features and migration of ANT28-D5-06

Vertical distribution of ^{210}Pbex for the core sediment ANT28-D5-06 is variable in the lower and upper sediment, but no significant segmentation. As illustrated in Fig. 7, ^{210}Pbex decreases with sediment depth exponentially. Through decay curve fitting of ^{210}Pbex with sediment depth, we calculated the depositional rate (S) as S=0.19cm/a, and the correlative coefficient (R) is 0.96 (n=17), showing a good fitting degree. The core sediment ANT28-D5-06 formed from 1922 to 2011, indicative of modern marine sediment. However, petroleum generation requires extra-high temperature and pressure, and also long geological periods.

The core sediment ANT28-D5-06 contains 4.27%-37.87% sand (averaging 16.77%), 51.55%-80.36% silt (averaging 69.13%) and 10.58%-17.33% clay (averaging 14.10%) from the top to bottom. The average particle size is 4.77-6.35φ, averaging 5.73φ; the sorting coefficient lies from 1.59 to 2.42φ,

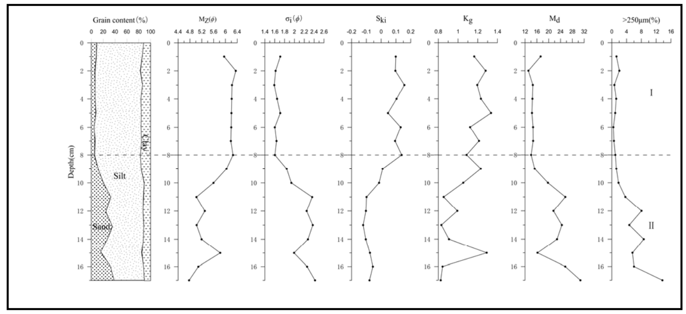
Fig. 7. Variations of ^{210}Pbex with depth for the core sediment ANT28-D5-06



averaging 1.93φ, showing a poor sorting feature; the skewness ranges from -0.12 to 0.16, averaging 0.01, showing a positive bias; and kurtosis is 0.92 to 1.34, averaging 1.09, displaying flat to sharp peaks. Fig.8 demonstrates two layers of the sediment based on particle parameters from the bottom to top: layer II and layer I. The layer II (8-17 cm), with coarse particles, is greatly variable in grain size and content, and contains 25.85% sand, 61.48% silt and 12.67% clay, corresponding to sandy silt (ST), clayey silt (YT) and silt (T). Its average grain size is 4.77φ, and median particle size is 13.13μm. The layer I (0-8cm) has fine grains, and is composed of 6.25% sand, 77.89% silt and 15.87% clay (Fig.7). Hydrocarbon can not be generated in shallow depth, as faults communicating deep hydrocarbon are needed, and hydrocarbon can be traced when it migrates from the deep to shallow. Migration direction and distance of hydrocarbon depends on permeable formations largely, and the sandy and silty formations of ANT28-D5-06 show a favorable hydrocarbon migration condition.

Chromatographic effect leads to variations of physical and polar features of hydrocarbon, which can be generally observed in ANT28-D5-06. Hydrocarbon will first migrate with deep water under a certain pressure system in a basin, and accumulate in a certain position. Hydrocarbon migration is a complex theoretical and practical issue, and biomarkers can provide reliable information for it. Selective absorption of minerals in strata, especially clay minerals, to organic compounds results in retard of some composition and biomarkers, making enriched of components easy to migrate. For example, long-chain tricyclic terpenes are easier to migrate than 17α (H)-hopanes; αββ component in steranes is easier to migrate than ααα component; and monoaromatic steranes are easier to migrate than triaromatic steranes. Biomarker combination will undergo changes with the increasing migration distance. A famous organic chemist of Seifert inferred from laboratory chromatography analysis that, 5α14β17β component in sterols migrates more quickly than 5α14α17α component, and diagrams of C_{29}ααα20S/20R and αββ20R/ααα20S are utilized. In the maturity-migration diagram, dashed curves on the right side of the diagram represent migration distance. Integrated with 5α-C_{27}20R/5α-C_{29}20R ratios and relative smaller molecular mass of C_{27} steranes than C_{29} steranes, it is thus indicated that C_{27} steranes are easier to migrate, resulting in high C_{27} steranes / C29 steranes, and 5α-C_{27}20R/5α-C_{29}20R ratios mostly range from 0.68 to 1.01 (Table 3). It is also indicative of input of exogenous organic matter. Hydrocarbon migration fractionation of αββ20R/ααα20S is strong, thus acting as a migration tracer. Plate tectonics provides a basis for revealing environments of hydrocarbon generation, and great thickness of sedimentary rocks under the continental shelf of the Weddell Sea may be a promising area for hydrocarbon reservoirs in the South Antarctic. This sea basin contains important conditions for hydrocarbon generation, migration and accumulation, including: (1) a large area; (2) great thickness of sedimentary strata; (3) strata spanning a wide range of ages and varying sedimentary facies of buried deltas, rivers and evaporates; and (4) large positive structures, local folds, unconformities and faults which tend to form various traps.

Fig. 8. Variations of grain size parameters with depth for the core sediment ANT28-D5-06



V. CONCLUSIONS

Hydrocarbon source, generation, maturity and oil-generation potential were explored using biomarker tracer technique in combination with carbon number ranges, peak carbon, $\sum C_{21-}/\sum C_{22+}$, $C_{21}+C_{22}/C_{28}+C_{29}$, Pr/Ph, Pr/n$C_{17}$, Ph/n$C_{18}$, CPI, OEP, sterol C_{27}, C_{28} and C_{29} distribution. The result shows that, organic matter of the organic sediment ANT28-D5-06 is mainly derived from lower aquatic organisms, and input of bacteria and algae is critical for hydrocarbon generation. This organic sediment has a good type of organic matter, with most layers in a high-maturity stage. The organic matter deposited in reducing-strong reducing, and high-salinity anaerobic environments.

Integrated with maturity indicators of [C_{29}ααα20S/C_{29}ααα(20S+20R), C_{29}αββ/C_{29}(ααα+αββ), C_{31}22S/C_{31}(22S+22R), C_{32}22S/C32(22S+22R) and Ts/(Tm+Ts)], it is suggested that, the organic sediment ANT28-D5-06 is excellent, forming in strong-reducing environments. It has favorable hydrocarbon-generation conditions, and some organic sediment layers have entered hydrocarbon generation peak, which implies the Weddell basin to be a promising hydrocarbon exploration area.

Biomarker parameters of rearranged steranes / steranes, tricyclic terpanes / pentacyclic terpane and sterane / hopane can be used to determine maturity of organic matter, but it cannot be traced migration of crude oil. However, hydrocarbon migration fractionation of αββ20R/ααα20S is strong, which can act as a tracer of migration.

ACKNOWLEDGMENT

We give our heartfelt thanks to all expedition staff and crew who attended the China's 28th Scientific Expedition to Antarctica, and thank research fellow Lu Bing from the Second Institute of Oceanography, State Oceanic Administration for her kind help during thesis writing.

REFERENCES

[1] Z.H.Chen, M. Zha, and Q. Jin, "Determining the expelling hydrocarbon threshold of organic sediment of Well Niu 38". NAT. Gas Indus., vol. 25,pp. 7-9, 2005 (in Chinese with English abstract).

[2] G. Gao, G. D. Liu, and J. H. Fu, "A new method for determining lower limit of organic matter abundance for effective organic sediments-A case study of organic sediments from the upper Triassic Yanchang

[3] Formation lacustrine shale in the Longdong area of Ordos Basin". J. Xi'an Shiyou Uni. (Natural Science Edition), vol.2, 2012, pp.22-26 (In Chinese).

[4] S. C. Brassell, G. Eglinton, and V. J. Howell, "alaeoenvironmental assessment for marine organic-rich sediments using molecular organic geochemistry". In Marine Petroleum Organic sediments, J. Brooks and A. J. Fleet, Geological Society Special Publication No.26, Blackwell, Oxford, 1987, pp.79-98.

[5] Q. J. Wang, J. Y. Chen. "Petroleum geochemistry". Wuhan: China University of Geosciences Press, 1988.

[6] K.Hinz , W. Krause, "The continental margin of Queen Maud Land/Antarctica: Seismic sequences, structural elements, and geo–logical development". Geol. Jahrb., 1982, vol. E23, pp.17–41.

[7] Kristoffersen and Haugland. "Geophysical evidence for the East Antarctic plate boundary in the Weddell Sea". Nature, 1986, vol.322, pp.538-541.

[8] P. F.Barker , J. P. Kennett. "Proceedings of the ODP, Initial Reports, Leg 113 (Ocean Drilling Program, College Station, TX)", 1988.

[9] B. C. Storey, M. J. Hole, and R. J. Pankhurst, "Middle Jurassic within-plate granites in west Antarctica and their bearing on the break-up of Gondwanaland". J. Geol. Soc. (London), 1988,vol.145, pp. 999-1007.

[10] A.M.Grunow, D. V. Kent and I.W.D. Dalziel, "Mesozoic evolution of West Antarctica and the Weddell Sea Basin: New paleomagnetic constraints." Earth Planet SS Lett, 1987, vol. 86, pp. 16-26.

[11] I. N. Kadmina, R. G. Kurinin, and V. N. Mosolov, "Antaectic crustal structure from geophysical evidence: a review", In : R L. Oliver,P R James, and J. B. Jago(eds): Antarctic Earth Science. Canberra（Austral.Acad.Sci.）, 1983, pp.498-502.

[12] V. L. Ivanov, "Prediction of the oil and gas potential of Antarctica on the basis of geological conditions," Polar Geo., 1985, vol. 9,pp.116-131.

[13] F. J. Hernández-Molina, R. D. Larter, and M. Rebesco, "Miocene reversal of bottom water flow along the Pacific Margin of the Antarctic Peninsula: Stratigraphic evidence from a contourite sedimentary tail". Mar. Geo.,2006,vol.228, pp. 93-116.

[14] Z. Z. Ma, X. Q. Pang, and J. K. Sun, J. Southwest Petrol. Uni. (Sci. & Tech. Edi.), 2009,vol.3,pp.14-20.

[15] G. Kleemann, K. Proalla, G.and Englert. "Tetrahymanol from the phototrophic bacterium Rhodopseudomonaspalustris:first report of a gammaceranetriterpene from a prokaryote", J. General Microbiol., 1990,vol.136, pp. 2551-2553.

[16] L. Y. Zhang, Y. T. Song, and G. L. Wang, "Chemical composition of organic matter from the lacustrine organic sediments in Jiyang depression and its petroleum geological significance," Chinese Sci. Bull., 2005, vol.50, pp. 2392-2402. (in Chinese).

[17] W. B. Chen, Z. L. Liao, and J. Q. Liu, "Biomarker characteristics of the middle-upper Jurassic organic sediments in the Zharen area of Qiangtang basin," Petrol. Geol. & Recovery Efficiency, 2008, vol. 15, pp.17-19 (in Chinese with English abstract).

[18] G. J. Demaison and G. T.Moore, "Anoxic environments and oil source bed genesis," AAPG Bull.,1980,vol. 64,pp.1179-1209.

[19] T. G. Wang, "Geochemical researches on biomarkers," Wuhan: China University of Geosciences Press, 1990, pp.55-73 (in Chinese).

[20] K. E. Peters, and J. M. Muldowan, "The biomarker guide: interpreting molecular fossils in petroleum and ancient sediments," Englewood Cliffts , NJ Prentice Hall,1993.

[21] Q. Jin, "Importance and research about effective hydrocarbon organic sediments," Petrol. Geol. Recovery efficiency, 2001, vol.8, pp.1-4(in Chinese with English abstract).

[22] J. K. Volkman, J. W. Farrington, and R. B. Gagosian, "Marine and terrigenous lipids in coastal sediments from the Peru upwelling region at 15°S: sterols and triterpene alcohols," Org. Geochem, 1987, vol.11, pp.463-477.

[23] J. K. Volkman, "A review of sterol markers for marme and temgenous matter," Org. Geochem, 1986, vol.9, pp.83-99.

[24] L. J. Goad, and T. W. Goodwin, "The biosynthesis of plant sterols. Progr," Phytochemi., 1972, vol.3, pp.113-198.

[25] F. R. Aquino, J. M. Trendel, and A. Restle, "Occucrence and formation of tricychc and tetracyclic terpanes in sediments and PETROLEUMS," In: Advances in Organic Geochemistry, New York:Wiley and Sons, 1983, pp.659-676.

[26] Q. J. Wang, and J. Y. Chen, "Petroleum geochemistry," Wuhan: China University of Geosciences Press, 1988.

[27] J. M. Moldowan, W. K. Seifert, and E. J. Gallegos, "Relationship between petroleum composition and depositional environment of petroleum sourcerocks," AAPG Bull., 1985,vol. 69, pp.1255-1268.

[28] K. M. Cheng, T. G. Wang, and N. N. Zhon, "Geochemistry of organic sediments". Beijing: Petroleum Industry Press, 1997.

[29] K. E. Peters, and J. M. Moldowan, "The Biomarker Guide," Englewood Cliffs, NJ, Prentice Hall, 1993, pp.363.

K. E. Peters, C. C. Walters, and J. M. Moldowan, "The biomarker guide (second edition)II: Biomarkers and isotopes in petroleum exploration and earth history," London: Cambridge University Press, 2005.